4-1-2021

Plasmonic Heat Generation in Arrays of Au Nanoantennas Using Quantum Dots as Markers

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Plasmonic Heat Generation in Arrays of Au Nanoantennas Using Quantum Dots as Markers

by

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An Honors Capstone

submitted in partial fulfillment of the requirements

for the Honors Diploma

to

The Honors College

of

The University of Alabama in Huntsville

3/03/2021

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Abstract

The objective of this experiment was to excite localized surface plasmon resonances in a gold metallic nanostructure array and measure the heat generation using colloidal semiconductor nanocrystals (quantum dots) as markers. This was done by attempting to excite a plasmon in the metallic nanostructure using a laser (at 980 nm) that is resonant with the array's surface lattice resonance (SLR). This laser does not excite the quantum dots (QDs). There is another laser that weakly excites the QDs so that they emit. The heat of the nanoantenna array was expected to cause a redshift in the QDs due to the temperature dependent band gap shrinkage of their emission energy. This redshift in the peak emission is the marker for generation of heat. The outcomes of this study would have determined the dependence of heat generation in gold nanoantenna arrays on the incident light polarization and demonstrate the extent of heat distribution, but the results are inconclusive as the sample tested did not display the expected redshift.

Introduction

Nanophotonics and Experiment Importance

Nanophotonics is the study of the interaction of light with nanometer scale objects. Colloidal semiconductor nanocrystals, also known as Quantum Dots (QDs), are building blocks for contemporary research for optoelectronic devices such as lasers, LEDs, and solar panels due to their narrow, bright, and size dependent emission spectrum, and their broad absorption spectrum among other properties.[3] The development of these applications can be furthered by a deeper understanding of the interactions between QDs and other nanoscale building blocks such as metallic nanostructures.

Plasmonics

Broadly speaking, plasmonics is the study of the collective motion of conduction electrons in metal. A localized surface plasmon resonance (LSPR) is a specific type of resonance which occurs in metallic nanostructure when the free electrons around the nanostructure oscillate coherently with the electric field of incident light. This oscillation of the free electrons causes an enhancement of the electric field around the nanostructure, which is called plasmonic field enhancement. The enhancement of the electric field produces an associated increase in the quantum yield of the QDs by increasing the probability of radiative decay of the excitations. Plasmonic field enhancement competes with energy transfer from the quantum dots to the metallic nanostructures through effects such as Föster resonant energy transfer, the results of which depend on the distance between the array and the QDs. Another specific effect of

the excitation of a plasmon is the generation of heat around the nanostructure. This heat generation occurs because the nanostructure has a good absorption coefficient at the plasmonic peak but is not a good emitter.[1]

Plasmonic Coupling

Plasmons can be coupled in two different ways, near field and far field. Near field coupling occurs when the metallic nanostructures are relatively densely packed, and the electric fields of the particles are able to interact. This can lead to spectral shifts of the resonances, among other effects.[2] Far field coupling occurs when the scattered light corresponding to the diffraction of the incident light in the plane of the array is in phase with the plasmonic resonance of the metallic nanoantenna, thereby reinforcing the plasmons of the other nanoparticles.[2] The diffractively coupled localized surface plasmon resonance is called a plasmonic surface lattice resonance (SLR). SLRs depend on the size and shape of the particles in the array, as well as the spacing between the particles in the array.[2]

Research Context

There have already been studies performed which show that the peak emission wavelength of CdSe QDs emission redshifts in the presence of heat due to the temperature-dependent band gap shrinkage of the CdSe.[3] Still other studies, such as *Abrupt Plasmonic Activation of Photoionization Rates in Quantum Dot Solids* by A. Nejat and S. Sadeghi have seen this in work about the interactions between quantum dots and metallic nanostructures and have noted the change. In this study, the QDs and the metal were excited using the same laser.[1]

Experimental Goal

The goal of this study is to specifically examine the heat generation of metallic nanostructures by exciting the plasmon separately from the excitation of the QDs. This heat generation will be measured by the change in the peak emission wavelength of the quantum dots. This causal relationship will be further displayed using the polarization dependence of the heat generation due to the polarization dependence of the absorption of the array.

Experimental Method

Optical Setup

For the excitation of the QDs and the nanoantenna array to be independent, the nanoantenna array needs to be excited by a laser with a wavelength that is not absorbed by the QDs. The two excitation lasers also have to hit the sample at the same spot so that the interaction occurs. Figure 1 is a labeled picture of the optical setup and Figure 2 is a diagram of the setup.

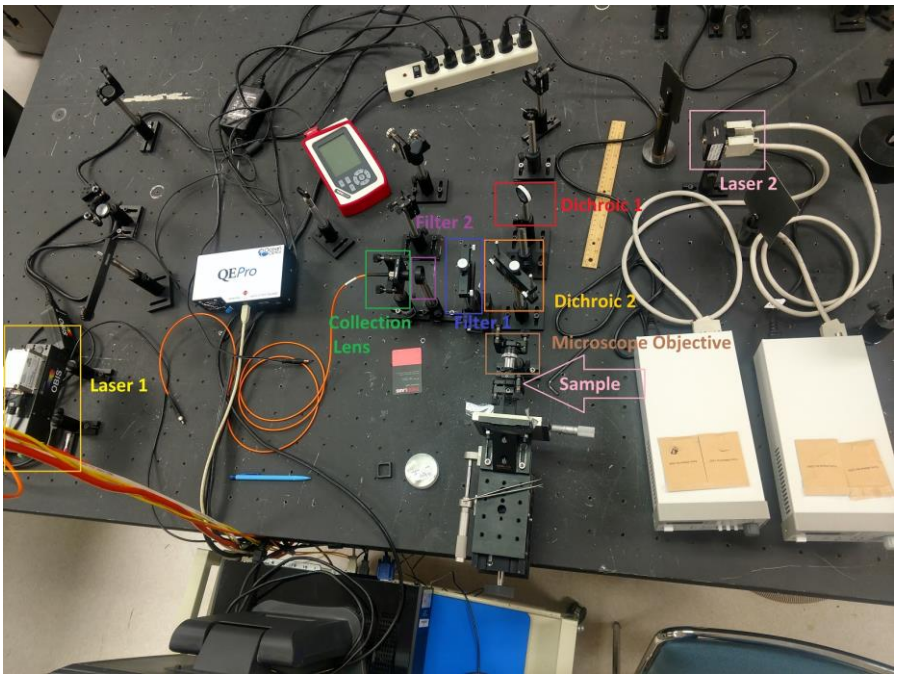


Figure 1: Optical Setup

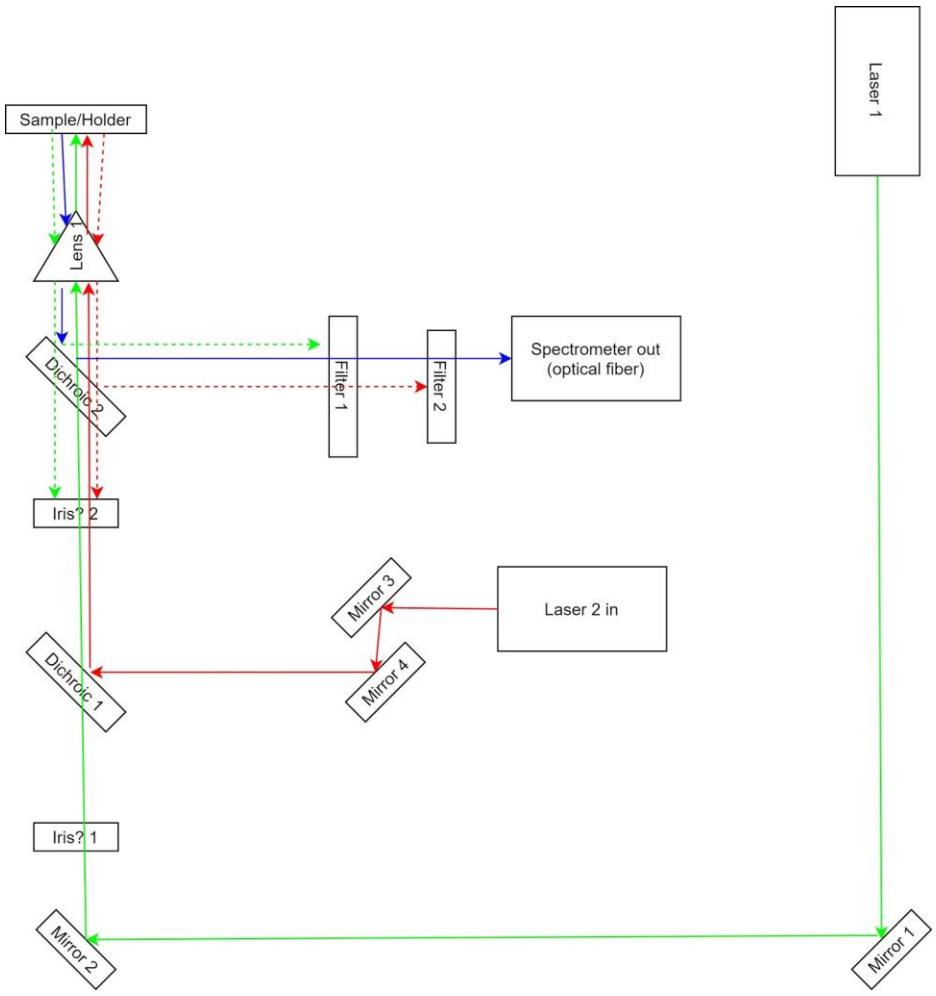


Figure 2: Diagram of Optical Setup

The different colored paths in Figure 2 represent the paths of light through the system: Green = 552 nm laser, Red = 980 nm laser, Blue = emitted light. Laser 2, the 980 nm laser, is the more powerful laser, rated to output 200 mW of optical power. A more powerful laser was selected for this because it is the one intended to excite the metal to generate heat, while the 552 nm laser lightly excites the QDs. As can be seen in the light paths, the first dichroic is necessary to ensure two lasers travel along the same path and enter the objective and reach the sample at the same point. The second dichroic is necessary so that the emission of the QDs can be collected. The losses of

laser power when passing through or reflecting off of the dichroics constitute a majority of the power loss for the system.

Sample Details

The sample (labeled DS2a) has 6 regions, labeled A through F as shown in Figure 3. Each of these regions is an array of gold nanorods shown in Figure 4. On top of the arrays there is a thin layer of QDs spin coated onto the sample. For the spin coat, the spread time was 15 seconds at 300 RPM and the spin time was 30 seconds at 1000 RPM. It is also important to note that the metal is off center toward one side of the sample, on the edge of the region spin coated QDs. This means that, because the edge of a spin coat is not uniform, the regions of the sample are not uniformly coated with QDs.

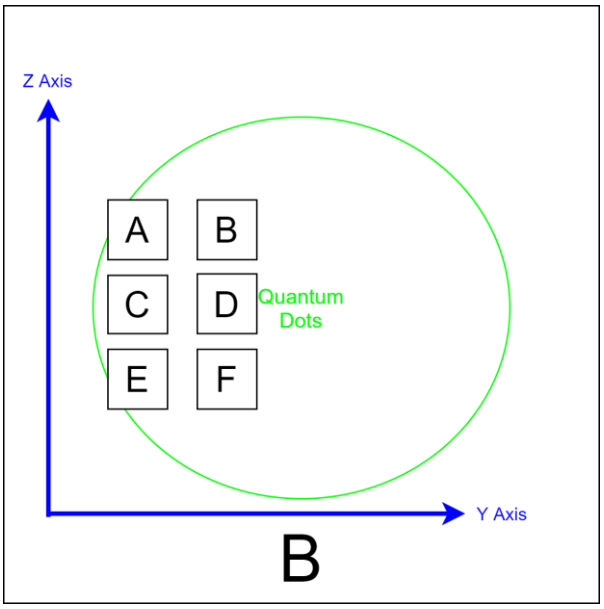


Figure 3: Diagram of Sample

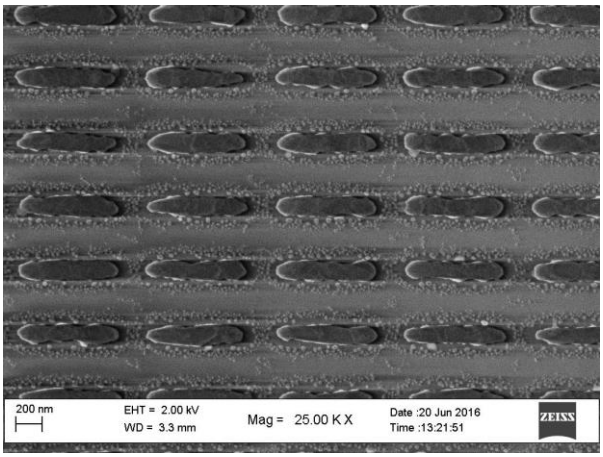


Figure 4: SEM Image of Metallic Nanoantenna Array on Sample

There is also a defined pair of axes, Y and Z, which are along the axes of symmetry for the nanorod array. Figure 5 displays the extinction spectra for each polarization on each region of the sample.

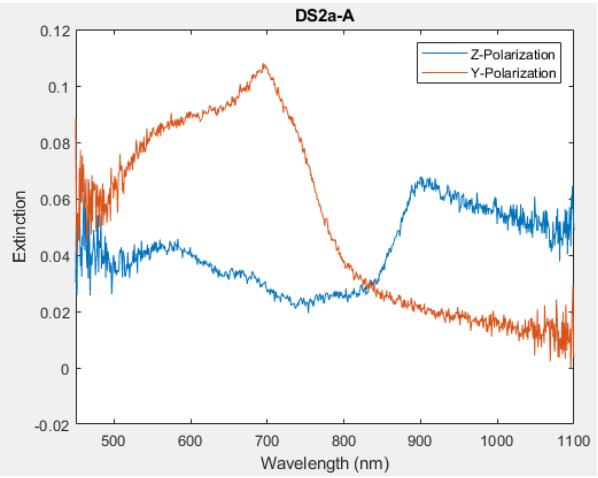
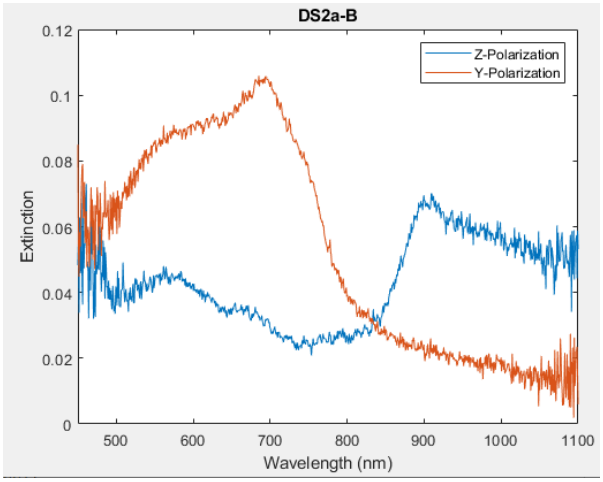


Figure 5a



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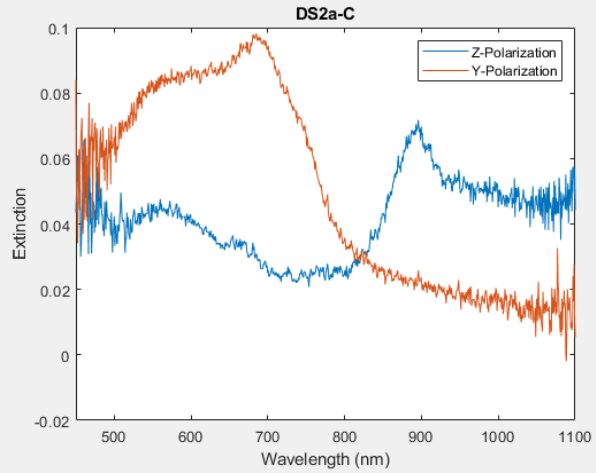

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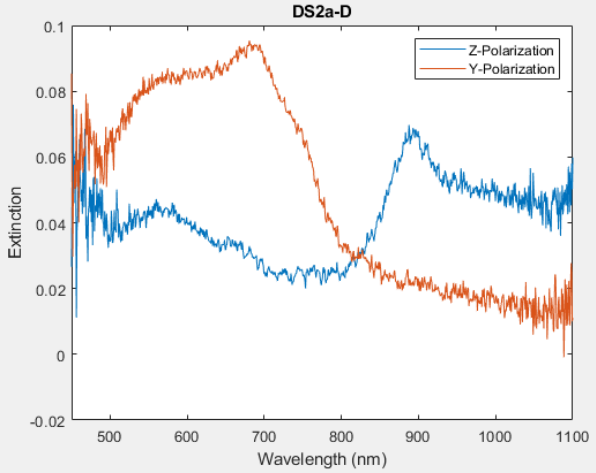

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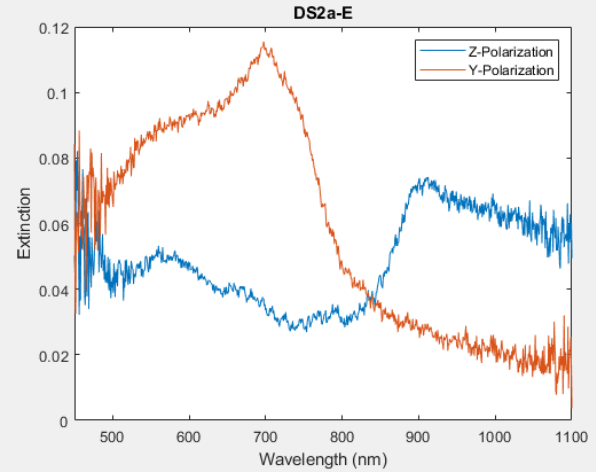

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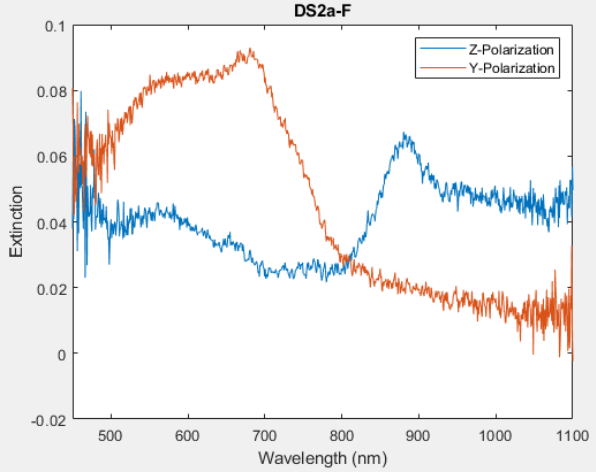


Figure 5f

Figure 5: Extinction Spectra

As can be seen in Figure 5, the sample has the desired extinction peak at 980 nanometers in the Z polarization, and a minimum for the same spot in the Y polarization. This is important because part of the goal of this project is to show that the heating effect only occurs when the second excitation laser is absorbed by the metal.

Results

Observations

The emission spectra of the sample was measured four times per region. It was measured for both Y and Z polarization, and each polarization was measured with only the 552 nm laser running and both the 552 and 980 nm lasers running. After taking the measurements, no difference in the emission peak wavelength was observed, as can be seen in Figure 6.

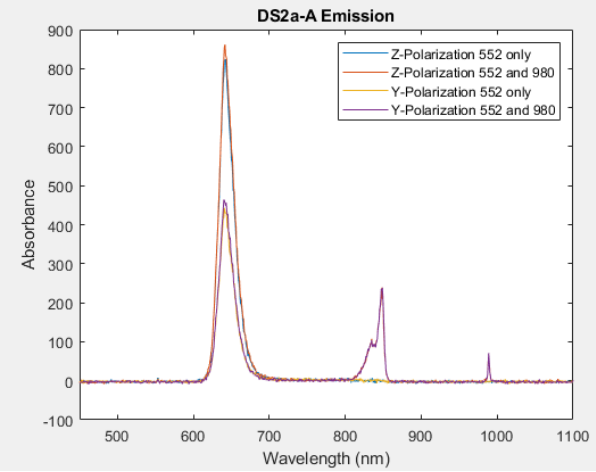
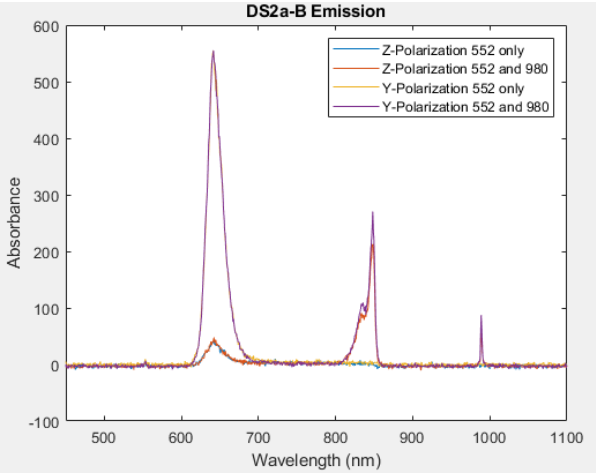


Figure 6a



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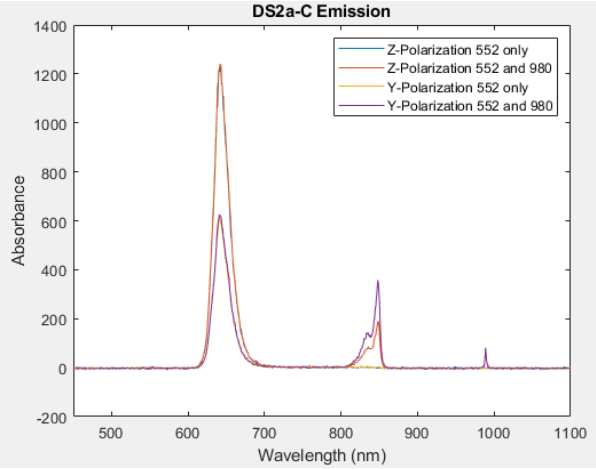

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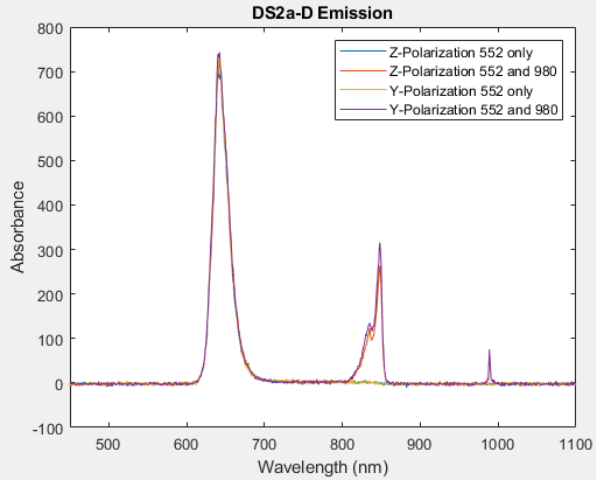

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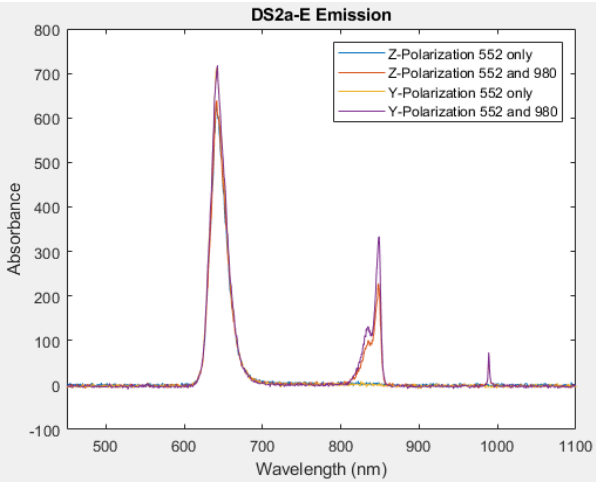

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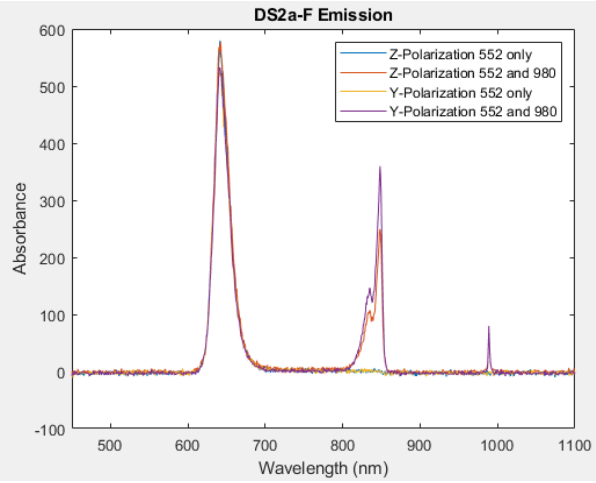

Figure 6f

Figure 6: Emission Spectra, Varying Polarization And Lasers

The primary difference between the spectra with only the 552 nm laser on and the spectra with both the 552 nm and 980 nm laser on is the presence of a peak that ends abruptly at 850 and a smaller peak that ends abruptly at 990 with a tail in the opposite direction in only the spectra with the 980nm laser on. The secondary difference, which only occurs in spectra A, B, and C, is that the intensities of the peak emission for the sample are different for the two polarizations. Other effects of the presence of the array include a sharp increase in the intensity of the quantum dot emission, shown in Figure 7.

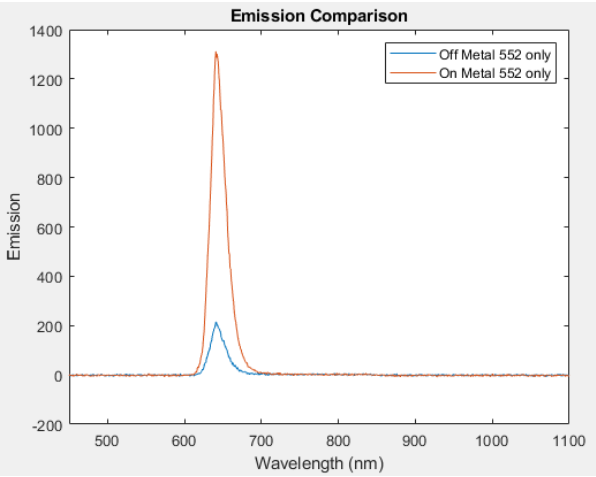

Figure 7a

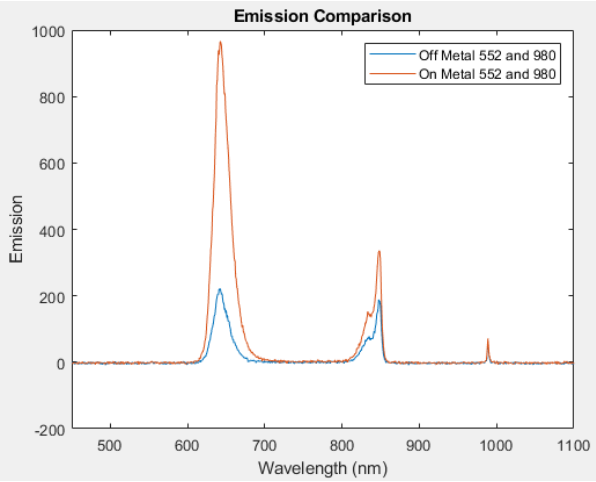

Figure 7b

Figure 7: Emission Spectra, Varying Lasers and Location Relative to Array

Conclusions

The results of the experiment are inconclusive, with both unexpected effects and a lack of the expected effects. The effects noted in the results section can be explained by various properties of the sample. The presence of the strangely shaped peaks at 850 and 990 nm is likely due to the filter blocking the 980nm laser from entering the spectrometer filters to those points, and it is the relatively minor edges of the same peak. The differences in the emission intensity for the two polarizations for regions A though C are likely due to the uneven coating of the regions, as well as the fact that when changing between polarizations the lasers had to be moved onto the sample again, so the measurements may not have been taken from the same spot on the metal. This would explain why it is those regions in that corner of the sample, and why one polarization does not have a greater yield than the other in all cases. Also, the most probable reason for the lack of the expected change in peak emission wavelength is that the peak in the extinction spectra for the Z polarization around 980 nm was caused by scattering and not by absorbance. This would make sense, recognizing that the Y

polarization peak was much sharper and the Z polarization has another bump around 550 nm which could be the LSPR peak. The increase in the intensity of the emission of the QDs when on the metal when compared to just off the metal was likely caused by the effect of plasmonic enhancement being greater than the effect of the energy transfer from the QDs to the metal, as mentioned in the introduction. These interactions make sense due to the peak around 552 nm in the extinction spectra along the Y polarization axes shown in Figure 6.

Possible Improvements and Future Work

There are several improvements possible for this experiment, and other implications for future work. The first set of improvements all relate to the aspects of the sample noted in the conclusion. First, a sample with arrays more specifically designed for this application is necessary for a conclusive result. This is because this experiment requires a sample with a strong lattice resonance at 980 nm on only one of the two polarization axes, so the sample effectively absorbs the 980 nm laser light. Also, the metal being centered on the sample slide so that the spin coated QDs would be centered on the metal would be a significant improvement. Furthermore, testing on a sample which does not have an extinction peak at the wavelength of the excitation laser for the QDs would be better, because if that were the case,the only laser which could generate heat in the nanoantenna array would be the desired one. Another improvement regarding the optical setup would be the ability to change the polarization of the 980 nm laser rather than moving the sample to change the polarization axis of the sample being excited. One way to change the polarization of the 980 nm laser traveling to the sample is with a half-wave plate, a crystal with fast and slow propagation axes.

Finally, more precisely designed dichroics with higher transmission and reflection coefficients could make the system much more efficient, which is important to the higher power laser in order to excite the nanoantenna array. Possible future work could include further analysis of the effect of heat on other properties of the QDs, such as the quantum yield, excitation lifetime, strength of the effects of plasmonic enhancement, and more.

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