

Plasmonic enhancement of photobrightening in CdSe quantum dots

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Abstract. Quantum dots are becoming more recognized as a tool to use in varying photonic and sensing technologies. When quantum dots are illuminated, they can emit light; by altering the quantum dot characteristics, the wavelength of the emitted light can be finely tuned. The emitted light of quantum dots may gradually increase in intensity when continuously illuminated, a behavior of quantum dots called photobrightening. We focus on this brightening behavior and explore different factors that contribute to quantum dot photobrightening. Increased excitation of the quantum dots results in increased rate of photobrightening, shown in this work by exciting quantum dot samples with different laser intensities. By adding plasmonic nanostructures, the excitation light to the quantum dots is enhanced, which also increases the rate of photobrightening. By combining gold nanoparticles with cadmium selenide quantum dots, we determined that gold nanoparticles enhance QD photobrightening by a significant factor, potentially leading to more efficient quantum dot technologies. © 2021 Society of Photo-Optical Instrumentation Engineers (SPIE) [DOI: [10.1117/1.JNP.15.046005](https://doi.org/10.1117/1.JNP.15.046005)]

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1 Introduction

Quantum dots have shown a variety of applications and are being used in medical imaging,¹ sensors,² solar technology,³ and TV displays.⁴ By studying the behavior of quantum dots, we can improve these technologies. In this study, we focus on quantum dots and their behavior regarding emitting light by studying the wavelength and intensity of the emitted light. Quantum dots emit a different wavelength of light based on their size, shape, and composition.⁵ By exciting a sample of quantum dots with a laser, we can measure the emission spectrum and determine the wavelength of emitted light for our sample of quantum dots, and by increasing the incoming light, we can increase the intensity of the emitted light.

In this work, we combine plasmonic nanostructures⁶ with quantum dots to observe the effect of plasmonic enhancement on quantum dot photobrightening at longer time scales, on the order of hundreds of seconds. When quantum dots are excited by incoming energy, an electron is excited into a higher energy level. When that electron returns to its original state, the quantum dot emits light. When a quantum dot is subject to constant excitation energy, the emitted light may gradually increase over long times (hundreds of seconds), a behavior of quantum dots known as photobrightening.⁷ Previous work has investigated photobrightening dependence on pulsed laser excitation intensity⁸ and the surrounding environment.⁹ At short (nanosecond) time-scales, quantum dots show photodarkening when using a pulsed excitation laser.¹⁰ Studies have also investigated the effects of the environment surrounding the quantum dots and photobrightening.⁷ Previous studies have investigated the plasmonic effects on photobrightening, and some have concluded that combining plasmonic nanostructures and quantum dots dampens out all

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quantum dot photobrightening due to the quenching of the photoluminescence effect through energy transfer.¹¹

In this study, it is shown that the photobrightening is not only not quenched, but it is actually increased with the addition of plasmonic nanostructures. The mechanism of photobrightening is not completely understood, but likely due to photoinduced passivation, caused by a permanent chemical change in the nanoparticle that creates charge-carrier traps.^{7,12}

The emission spectrum of quantum dots is known to be highly tunable-based on size, material, and structure of the quantum dots.¹³ This ability to manipulate the emission spectrum and the idea that the intensity of the emitted light can be changed by changing the temperature,^{14,15} size,¹⁶ and intensity of incoming light¹⁷ make quantum dots ideal for uses including sensing,¹⁸ biomedical imaging,¹⁹ light-emitting diodes,²⁰ and solar cells.²¹

2 Methods

The quantum dots used in this study are semiconductor nanostructures that are 7 nm in diameter, with a 3-nm cadmium selenide sphere core, and a 2-nm cadmium sulfide outer shell, suspended in hexane at a molarity of 3.64×10^{-6} .²² The quantum dots were synthesized by the process outlined in Ref. 3. This process includes adding octadecylamine and trioctylphosphine oxide ligands to the QDs.

This work measures two different types of samples. First, we study the baseline photobrightening behavior in QD ensembles (without the presence of plasmonic nanostructures). Next, we study a sample that has both QDs and plasmonic nanostructures, as shown in Fig. 1, to see the interaction between the two types of nanostructures. The plasmonic structures in this work are gold nanospheres (AuNPs) with a 100-nm diameter and a polyvinylpyrrolidone surface, suspended in deionized water, purchased from Refs. 22 and 23. This size was chosen because it provides a stronger overall scattering response as compared with smaller nanostructures whose plasmonic resonance peak may be closer to the laser wavelength used in this work but at a lower scattering level (as shown in Fig. 29 of Ref. 22). Each of these samples had a mass density of 0.05 g/mL. These gold nanoparticles were chosen because they were well characterized by Ref. 23, had a strong spectral response, and had a relatively long wavelength. To prepare the samples, first the one square centimeter silicon substrates are cleaned with acetone and isopropyl alcohol. Next, after sonicating the QD solution to evenly suspend the quantum dots, the QDs are drop-cast onto the silicon substrate, covering 40% of the substrate. For the QD-AuNP sample, the gold nanoparticles are subsequently drop-cast on the sample after the QD solution was allowed to dry, a few minutes later, so adding the AuNPs did not change the QD surface density. For these samples, single drop of QDs and a single drop of AuNPs are deposited. For both samples, after the nanostructures are drop-cast onto the substrate, the sample is then left to dry for 48 h to ensure all of the water from AuNP solution has time to fully evaporate.²²

3 Results

First, we measured the photoluminescence of the plain QD sample and observed the photobrightening behavior of the ensemble without the presence of plasmonic AuNPs. The QD sample was

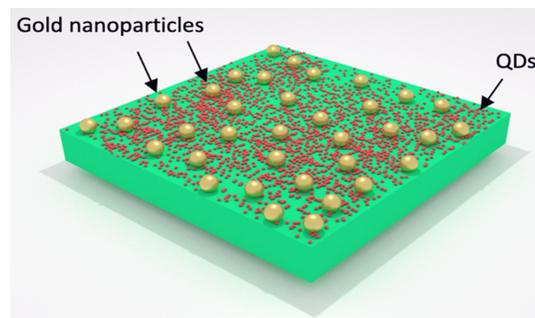


Fig. 1 Illustration of the QD-AuNP sample: CdSe quantum dots with 100-nm Au nanospheres.

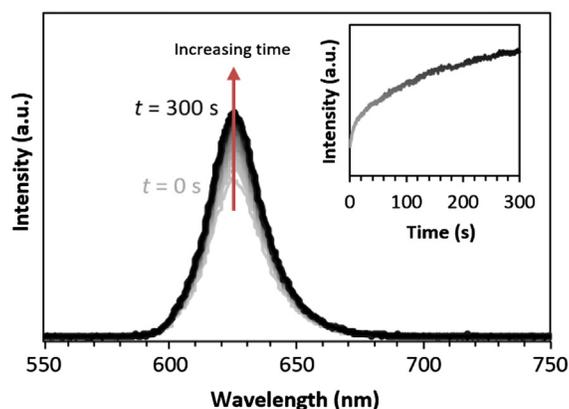


Fig. 2 The evolution of a quantum dot spectrum over time. The darker lines represent later times, illustrating the photobrightening that takes place under continuous excitation.

excited with a 532-nm laser at 1.74 W/cm^2 with a spot size of $50 \mu\text{m}$. Figure 2 shows the intensity of the emitted light over time as a small region of quantum dots are exposed to a laser. Under continuous excitation over time, the photobrightening increases. The inset in Fig. 2 shows the peak intensity at 627 nm change over time. This measurement was repeated over several different regions of interest.

Because each region of interest will have a different base intensity depending on how many quantum dots are in that region, comparing the intensity before and after excitation over several regions of interest will not give accurate results. To avoid the issue of the differing baselines, we measure the percent change in intensity $I_t/I_{(t=0 \text{ s})}$ to normalize the results.

To gain insight into baseline photobrightening as a function of laser intensity and confirm the idea that the intensity of the emitted light of the quantum dots increases with increased excitation intensity, we excite samples of quantum dots with different laser intensities. Figure 3 shows the average percent change in intensity of the emitted light under four different excitation laser intensities, 0.11, 1.74, 2.99, and 5.86 W/cm^2 . Each laser intensity was used to illuminate 10 different regions of interest for 300 s. The data in Fig. 3 are the average QD emission intensity value from all 10 regions as a function of time, after being normalized to their respective initial values.

Figure 3(a) shows that increased laser intensity causes greater photobrightening as measured as a percent change relative to the initial emission intensity $I_t/I_{(t=0 \text{ s})}$. The error bars show the standard error in the data. Figure 3(b) makes this even more clear, plotting the average percent change at 300 s versus laser intensity and showing there is a linear relationship between the photobrightening and the laser excitation intensity. The linearity between photobrightening and laser intensity means that it is significantly easier to estimate the excitation intensity given a photobrightening value.

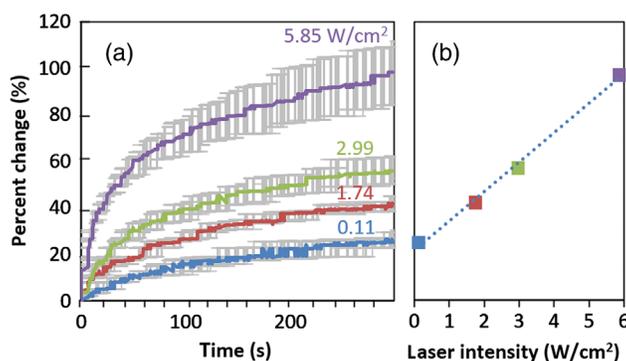


Fig. 3 (a) The percent change in the intensity of the quantum dot emission spectrum with different excitation laser intensities. (b) The percent change in intensity of QDs with changing laser intensities at $t = 300 \text{ s}$.

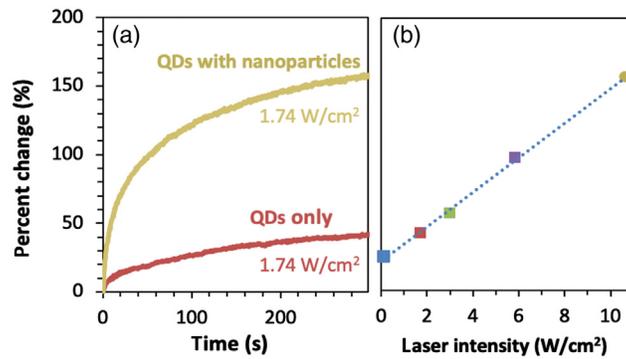


Fig. 4 (a) Percent change of the photo brightening effects by the addition of 100-nm gold nanoparticles. (b) The percent change in intensity of QDs with changing laser intensity including the percent change with gold nanoparticles. This shows that with the presence of gold nanoparticles, the observed photobrightening is equivalent to that produced by hitting the QD sample with a laser intensity that is effectively 10.7 W/cm².

Figure 4 shows the average percent change of photobrightening with an excitation laser intensity of 1.74 W/cm² for both the sample with only QDs and for the sample with both QDs and AuNPs, 100-nm gold nanospheres. By fitting the data to the linear relationship obtained from the measurements in Fig. 3(b), we were able to plot the photobrightening after 300 s of the sample with gold nanoparticles, showing that the presence of gold nanoparticles produced a percent change in intensity that is effectively equivalent to a 10.7-W/cm² incident laser intensity. This is a clear and dramatic increase in the rate of photobrightening and shows that we can get a greater percent increase of photobrightening with less excitation energy by adding gold nanoparticles. Because we only sampled photobrightening out to 300 s, saturation effects are not seen here, but an unbounded increase of photobrightening is physically impossible. By dividing the effective laser intensity by the actual laser intensity, we got an overall plasmonic enhancement of around 6.

4 Discussion

The plasmonic enhancement shown in this study is impressive, considering that most of the QDs in the ensemble that is being measured are not in the plasmonic hotspot regions, within a few nanometers of the AuNPs since both nanostructures have been randomly deposited on the substrate as shown in Fig. 1, so many of the QDs being measured here should not be affected by the presence of the plasmonic structure. Therefore, these QDs bring down the ensemble's plasmonic enhancement. If one were able to measure the effects of a single QD in the plasmonic hotspot region, with near-field optical microscopy for example, then it is expected the plasmonic enhancement effect would be 10 or 100 times greater than the value measured here since only 1% to 10% of the QDs in this work are in the plasmonic hotspot regions.

Other studies have shown that quenching can occur when a light source is too close to a nanoparticle, preventing any light emission.²⁴ This behavior is not seen here likely due to the low enough surface density that allows the measured enhancement to come from the QDs that are not too close but close enough to the nanoparticles. If the density of our sample was much higher, quenching may have been observed due to the much smaller distance between the nanoparticles and QDs.

5 Conclusion and Future Work

In this study, we examined the plasmonic enhancement of photobrightening in cadmium selenide quantum dots. First, we showed that there is a linear relationship between the QD photobrightening rate and the incident laser intensity. By exciting quantum dot samples with multiple

different laser intensities, the increase in laser intensity has not only been shown to have a clear effect on photobrightening but also a linear effect as well. The linear relationship makes it possible to verify the excitation energy, allowing for characterization of the electric field causing the photobrightening in the quantum dots.

Next, we measured the effects of the presence of AuNPs on these samples. While previous studies have shown that photobrightening can be quenched by the addition of plasmonic nanoparticles, in this study the photobrightening increases substantially, reaching an intensity value at 300 s that was 158% greater than the initial excitation intensity at $t = 0$ s. Using the linear relationship between incident laser intensity and photobrightening from plain QDs samples, we determined that the presence of AuNPs on a QDs sample has a laser intensity of effectively 10.7 W/cm^2 , a sixfold intensity increase. This experimental method of determining plasmonic enhancement from a fabricated gold nanostructure can be used in further studies and the results shown here can be applied in quantum dot technologies.

This work can inspire other future work and provides interesting results that contribute and grow the field of photobrightening in quantum dots, though it is not without limitations. For future work, we would encourage others to determine the exact density and arrangement of the quantum dots and gold nanoparticles on the surface with an electron microscope, a measurement we were unable to perform. However, sample preparation or substrate used for electron microscopy may need a different preparation method, which would alter the results shown here. Knowing the exact particle density could lead to more explanation of the results and more precise data.

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