Reduction of the fluorescence lifetime of quantum dots in presence of plasmonic nanostructures

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Abstract. Developing a single photon source in the near infrared spectrum for optical fibre communications implies the control of the spontaneous emission of quantum dots. In this paper we show that the fluorescence lifetime of lead sulphide quantum dots can be drastically decreased due to the presence of plasmonic nanostructures specially designed to confine the electromagnetic field to which the emitted photons could decay at $\lambda=1550\,\text{nm}$. To demonstrate this, we first measured the fluorescence lifetime of colloidal quantum dots in toluene solution and took this as a reference measurement. Then, we compared this value with the fluorescence lifetime of quantum dots in two different plasmonic nanostructures. The measurement of lifetime was made using the Time-Correlated Single Photon Counting technique. We obtained for the quantum dots in solution a fluorescence lifetime of 0.98084\,$\mu$s and for the quantum dots in the nanostructures, fluorescence lifetimes of 0.06227\,$\mu$s and 0.11789\,$\mu$s. We also numerically calculated the distribution of the electromagnetic field near the plasmonic nanostructures. These results demonstrate that the plasmonic nanostructures modified the fluorescence lifetime of the quantum dots, and that these plasmonic nanostructures with the lead sulphide quantum dots could work as a single photon source that could be integrated in a photonic circuit for infrared optical fibre communications.

1. Introduction

A quantum dot (QD) can be modelled as a two-level system. When a two level system absorbs a photon there is an electronic transition and the system becomes excited. After a time $\Delta T$ (known as lifetime fluorescence) the two level system decays by spontaneous emission emitting a photon of lower energy, as shown in Figure 1. This process is described by the spontaneous emission rate $\Gamma$ of the quantum dot (QD) \cite{1} given by Equation 1. Where $P$ is the emitted power, $E$ the energy of the emitted photons, $p_{eg}$ is the dipole moment associated to the QD, $\omega_{eg}$ is the frequency of the emitted photon and $\rho_{e,u}$ is the Local Density Of States \cite{2, 3}. The lifetime fluorescence of the quantum dot $\tau$ is defined as the inverse of $\Gamma$.

The Purcell factor is defined by Equation 2, it compares the emission rate of the quantum dots (QDs) in a particular environment $\Gamma$ with the emission rate in vacuum $\Gamma_0$. What is more,
it can be expressed as a function of the lifetime fluorescence, here $\tau$ is the lifetime fluorescence of the QDs in a particular environment and $\tau_o$ is the lifetime fluorescence in vacuum.

Figure 1. Spontaneous emission process in a quantum dot.

\[
\Gamma = \frac{P}{\mathcal{E}} = \frac{\pi \omega_{eg}^2}{\epsilon_o} |p_{eg}|^2 \rho_{e,u}(r, \omega_{eg}) \left( \frac{1}{\hbar \omega_{eg}} \right) \left[ \frac{\text{photons}}{s} \right] \tag{1}
\]

\[
P_{factor} = \frac{\Gamma}{\Gamma_o} = \frac{\tau_o}{\tau} \tag{2}
\]

In a resonant cavity the Purcell factor is expressed as a function of the quality $Q$ and effective volume $V$ of the resonant mode of the cavity, as shown in Equation 3 [1, 4]. So, there are two main ways to change the spontaneous emission of a QD, the first is to create a cavity with high quality factor, and the second is to reduce the effective mode volume, that is to confine the electromagnetic field.

\[
P_{factor} = \frac{3}{4\pi^2} \lambda_{eg}^3 \frac{Q}{V} \tag{3}
\]

Controlling the spontaneous emission of QDs is a critical issue if we want to obtain highly-efficient and deterministic single photon sources. Modification and enhancement of the spontaneous emission has been studied in different ways [5–9], for example, it has been demonstrated that different geometries and shapes of plasmonic optical antennas have high Purcell factors.

A single photon source is of particular interest for quantum information because of its advantages over attenuated classical sources [10, 11]. Here arises the need of developing a single photon source in the near infrared which is the region of the electromagnetic spectrum used in optical fibre communications. In an attempt to develop such single photon source, we studied the spontaneous emission of QDs in an electromagnetic environment with LDOS enhanced due to the confinement of the electromagnetic field in plasmonic nanostructures. These QDs are made of lead sulphide (PbS) and emit in the near infrared at $\lambda = 1550\text{nm}$.

This paper presents numerical calculations of the distribution of infrared ($1550\text{nm}$) electromagnetic field near the plasmonic nanostructures, and the experimental measurement of the Purcell factor. The idea is to integrate the plasmonic nanostructures onto silicon photonic waveguides, compatible with standard optical fibres.

2. Materials and methods

The plasmonic nanostructures shown in Figure 2, are made of gold on a glass substrate and were fabricated using the electron beam lithography technique, following a design proposed in [12]. The primary nanostructure, Figures 2(a) and 2(b), is a triangular nanotaper with length of $800\text{nm}$ and base width of $300\text{nm}$, the complementary, Figures 2(c) and 2(d), has the same dimensions, but the materials (gold-air) are interchanged. The complementary nanostructures is complementary of the primary nanostructures, Figures 2(a) and 2(b), by means of Babinet’s principle [13–15], this implies that the distribution of the electric field produced by the primary
structure should be the same as the magnetic field distribution of the complementary structures, with rotated polarisation characteristics [12].

![Figure 2](image-url)

**Figure 2.** Plasmonic nanostructures. (a) SEM image of primary nanostructure of gold on glass substrate. (b) Topography of primary nanostructure. (c) SEM image of complementary nanostructure of gold on silicon substrate. (d) Topography of complementary nanostructure.

We used lead sulphide (PbS) QDs as the quantum emitters, they absorb in the visible region with a peak in the green wavelength, and emits in the near infrared around $\lambda = 1550$ nm. The QDs were spin-coated over the samples and the fluorescence lifetime measurements were done using the Time Correlated Single Photon Counting technique (TCSPC) [16–19]. As shown in Figure 3, the laser pulse signal triggers a timer, this pulse excites the PbS quantum dots, and then the fluorescence photon is detected, the output signal of the detector stops the timer. This measurement consists of cyclical experiments to obtain statistical data.

![Figure 3](image-url)

**Figure 3.** Time correlated single photon counting technique. Measurement of start-stop times in time-resolved fluorescence measurement with TCSPC, image taken from: https://www.picoquant.com/images/uploads/page/files/7253/technote_tcspc.pdf.

The experimental setup is shown in Figure 4. The pump signal is a pulsed laser of 12 picoseconds with repetition rate of 200kHz. The wavelength of the laser is 520nm, a cutoff filter is used. We used the ID210 Infrared Single-Photon Detector which has its peak detection efficiency in the near infrared. To employ the TCSPC technique we used the HydraHarp 400. The experimental calculation of the Purcell factor is given in terms of the fluorescence lifetime as shown in equation 2. The experimental data is fitted with an exponential decay of the form $e^{-t/\tau}$, where the value $\tau$ represents the lifetime fluorescence.

We simulated the near-field distribution of the electric field in the vicinity of the plasmonic nanostructures using the commercial software *LUMERICAL*. This software uses the Finite
Difference Time Domain (FDTD) technique which is broadly used in numerical calculations to solve electrodynamics systems [20–22]. Originally, this calculation should be done by placing an electric dipole in every point of observation near the plasmonic nanostructures. However, to simplify the simulation of the scanning probe we made use of the electromagnetic reciprocity theorem [23], so we exchanged the detector with a source placed in far field, and instead of the scanning probe we placed detectors at different distances above the plasmonic nanostructures.

3. Results and discussion
The numerical calculations of the electric field distribution is shown in Figure 5. The calculations were made for using an unpolarised electric dipole. To do this, the the results for the horizontal (Figures 5(a) and 5(b)) and the vertical (Figures 5(c) and 5(d)) polarisation of the dipole were averaged (Figures 5(e) and 5(f)). For the primary structure, the electric field is confined at the apex of the triangular plasmonic nanostructure as expected, the total enhanced near-field distribution is of 55 times. On the other hand, the complementary plasmonic nanostructure should confine the magnetic field, also at the apex of the triangle. However, in order to experimentally measure the near field of the complementary structure, it was simulated using an electric dipole as well. This is because a special scanning tip would be needed to measure the magnetic field.

The experimental results of the fluorescence lifetime of the QDs in different environments is shown in Figure 6. The black points show the results of the fluorescence of quantum dots in its toluene solution, we took this as the reference measurement to calculate the Purcell factors. The green and red points represent the results of the fluorescence of QDs placed in the complementary and primary nanostructures, respectively. As we can see, the decay of the QDs in the plasmonic nanostructures is quicker than in solution, that is, we have enhanced the spontaneous emission with the plasmonic nanostructures.

The experimental lifetime measurements Purcell factors are shown in Table 1. As we can see, the lifetime is different in each case, the lower lifetime is 0.06227 µs, and was obtained for the complementary nanostructure. As shown in Figure 5, these nanostructure have higher confinement of the electric field than the primary nanostructure. Using Equation 2, we obtained Purcell factors of 15.75 for the complementary nanostructure and 8.32 for the primary nanostructure. So, the more confinement of the electromagnetic field the higher Purcell factor and the lower lifetime fluorescence, as Equation 3 dictates. The difference between the numerical and the experimental results are due to the fact that, when simulated, the electric dipole is placed in a specific, well controlled manner. Meanwhile, for the moment, the practical positioning of the QDs is not perfectly controlled, they are randomly placed by the spin-coating process. The controlled positioning of the QDs constitutes the next step of this project.
Figure 5. Numerical calculations of distribution of the electric field on the surface of the plasmonic nanostructures. The colour bar represents the intensity of the electric field. The source is placed in the far field condition and its wavelength is 1550nm. The detector is placed 5nm above the nanostructures.
4. Conclusions
We studied the lifetime fluorescence of lead sulphide quantum dots in different plasmonic nanostructures, the results showed that the lifetime is enhanced in presence of these nanostructures. We also studied the distribution of the electromagnetic field near the plasmonic nanostructures and showed that the electromagnetic field at $\lambda = 1550\text{nm}$ is confined. Our results demonstrate that these plasmonic nanostructures with the PbS quantum dots could work as a single photon source that could be integrated in a photonic circuit for infrared optical fibre communications.

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