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# Plasmon Mediated Energy Transfer in a Hybrid Quantum Well - Quantum Dot System

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A PhD Thesis

*by:*

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School of Physics  
Trinity College Dublin

2016



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## Summary

In this thesis silver plasmonic arrays, fabricated using both helium-ion lithography (HIL) and electron beam lithography (EBL), on an InGaN/GaN quantum well (QW) are used to enable localised surface plasmon (LSP) enhanced Förster resonance energy transfer (FRET) to a  $\sim 80$  nm layer of CdSe/ZnS quantum dots (QDs) embedded in a poly(methyl methacrylate) (PMMA) matrix. The thickness of the QD acceptor layer and the dimensions of the silver plasmonic nanoparticles (NPs) are large compared with previous reports of plasmon-coupled nonradiative energy transfer (ET). Whilst FRET has been observed between a QW and QDs before, the work presented in this thesis provides the first ever experimental demonstration of LSP enhanced FRET from a QW donor to a thick layer of QD acceptors. In particular, the carrier density dependence of the plasmon-coupled nonradiative energy transfer mechanism is investigated, which is a first step towards FRET based implementation in electrically pumped LEDs. By conducting the carrier density dependence the LSP enhanced mechanism within the system is found to be determined by the same physics as conventional FRET. The plasmon-coupled FRET efficiency is determined by the interplay between the QW donor spontaneous emission rate, the rate of nonradiative ET to the plasmonic array and the rate of plasmon-coupled nonradiative ET to the acceptors. TRPL and spectral measurements are used to demonstrate and quantify the LSP-FRET from the QWs to the QDs. Both the QW emission quenching rate and the plasmon-coupled nonradiative ET rate are found to increase with increasing QW carrier density. The quenching and energy transfer efficiencies are carrier density independent. Despite strong direct quenching by the metal nanoparticles, the LSP-FRET results in a plasmon-enhanced energy transfer efficiency of 25 % and a 16 % increase of the QD emission.

As the absorption and scattering spectra of plasmonic structures are tuneable by varying their shape and size, incorporating different plasmonic arrays into the hybrid system can impact the level of LSP enhanced absorption and emission processes for both the QW and the QDs. It can also modify the LSP-FRET within the system. Therefore, the impact of changing the plasmonic array geometry on the different mechanism is investigated. LSP-FRET is found to occur from the QW to the QDs for each of the plasmonic array geometries considered. The QD-NP array interaction is found to be understood by a combination of enhanced absorption and scattering processes due to the presence of the NP arrays. LSP-FRET efficiencies from 25 % to 51 % are observed from the QW to the QDs *via* the different NP array geometries and QD emission enhancements of up to 71 % are also seen.

Furthermore, the work presented in the earlier sections of this thesis explores LSP-FRET from a QW donor with a thin ( $\sim 3$  nm) GaN barrier layer. Thin QW barriers



can increase nonradiative losses within the QW donor and can be detrimental for carrier spreading. Attempting the remedy these issues, three different QW donors, with barrier thicknesses ranging from 3 nm to 7 nm, are used to enable LSP-FRET to a  $\sim 80$  nm layer of acceptor QDs using silver nanobox arrays fabricated by EBL. The plasmonic arrays enable LSP-FRET from each of the three QW donors to the QD acceptors. Once again, the QD-NP array interaction is found to be understood by a combination of enhanced absorption and scattering processes due to the presence of the NP arrays. For a given array, the FRET rate is observed to decrease as the QW barrier thickness is increased. This observation indicates that at smaller QW-array distances, the LSP-FRET process is faster and that the rate of FRET decreases as the QW-array distance increases, as expected. This result is consistent with observations of LSP-FRET in other material geometries. The change in the QD emission due solely to LSP-FRET is understood by a combination of the energy transfer efficiency and the donor field enhancement factor due to the plasmonic arrays. LSP-FRET efficiencies of up to 28 % are found from the QWs to the QDs, along with QD emission enhancements of up to 120 %.

The work presented in this thesis signifies a substantial improvement to the body of work already published in this field and the novelty of the 3-component (QW-Array-QD) layered geometry system allows for considerable enhancement of the FRET efficiency. The work presented in this thesis demonstrates a substantial increase of the range over which QWs can nonradiatively pump QDs. This provides promising results regarding the implementation of FRET for color conversion in white light LEDs.

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# List of publications and conference contributions

## List of publications

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3. L. J. Higgins, V. D. Karanikolas, C. A. Marocico, P. J. Parbrook, and A. L. Bradley, "Plasmon-enhanced energy transfer in a hybrid system using silver nanobox array geometries." *Advanced Electromagnetic Materials in Microwaves and Optics (METAMATERIALS)*, 2015 9th International Congress on (pp. 106-108). IEEE. (2015)
4. L. J. Higgins, V. D. Karanikolas, G. P. Murphy, X. Zhang, C. A. Marocico, P. J. Parbrook, and A. L. Bradley, "Plasmon-enhanced non-radiative energy transfer in a hybrid quantum well structure." In *Transparent Optical Networks (ICTON)*, 2015 17th International Conference on (pp. 1-4). IEEE. (2015)
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## Conference contributions

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3. L. J. Higgins, V. D. Karanikolas, G. P. Murphy, X. Zhang, C. A. Marocico, P. J. Parbrook, and A. L. Bradley, "Plasmon Enhanced Nonradiative Energy Transfer in a Hybrid Quantum Well Structure." ICTON 2015, 5th-9th July 2015, Budapest, Hungary.

### Selected list of poster presentations:

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2. L. Higgins, J. Gough, G. Murphy, V. Karanikolas, V. A. Gerard, C. Hanley, Y. K. Gun'ko, A. L. Bradley, "Metal Nanoparticle Arrays for Enhanced Light-Matter Interactions." NanoWeek Conference 2012, September 2012, Dublin, Ireland.
3. L. Higgins, V. Karanikolas, and A.L. Bradley, "Plasmonic Structures for Enhancement of Light-Matter Interactions." IoP Rosse Medal Spring Event 2012, March 2012, Dublin, Ireland.



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# 1 Motivation

Global warming is undisputedly one of the most pressing problems facing humankind today. Much of this is caused by human activity, in particular the burning of fossil fuels and deforestation [1,2]. This has resulted in an increase of the average global surface temperature by about 0.75 degrees Celsius over the past century [3]. The underlying root cause of this problem is humankind's increased demand for cheap energy. This evergrowing global thirst forces us to create novel, renewable and efficient ways in which we both generate and consume the energy we require. In order to keep pace with this growing demand, immediate action is required before the increase in global temperatures threaten Earth's wildlife further. Solar energy or photovoltaics generates electricity by converting sunlight, the earth's most abundant source. Much progress has been made in solar cell technology with the worldwide energy production from solar cells in 2009 being  $>10$  GW, a tenfold increase from 2000 [4]. However, better device performance with lower cost is still required. Along with the improvements made within the area of light harvesting devices, there has been considerable effort made towards the improvement of light emitting devices.

The development and optimization of highly-efficient semiconductor light emitting diodes (LEDs) for applications in solid-state lighting (SSL) and displays is an area that has received a great deal of attention in recent years. In such devices, white light generation is typically achieved by using phosphor coatings on top of a blue or UV emitting quantum well (QW) LED [5]. Some of the drawbacks of phosphors include emission in the far-red and near IR parts of the spectrum, poor colour rendering and scattering [6]. For this reason inorganic nanocrystal quantum dots (QDs) can provide an alternative to phosphors. This is due to the fact that QDs have narrow, tunable emission spectra and so can be selected to reduce losses due to emission in unwanted spectral regions. Within such LED devices radiative pumping is the most commonly used energy transfer mechanism. Radiative pumping is not very efficient, this is due to the fact that it involves many steps. These include emission of the photon, extraction of the photon from the LED and reabsorption of the photon. Due to limited photon extraction and light scattering issues, losses occur throughout this process. Many different strategies to efficiently extract photons from LEDs have been a topic of considerable research. These include modification of the surface roughness of the LED to increase the extraction efficiency [7,8]. More



recent researchers have considered nonradiative energy transfer mechanisms, such as Förster resonance energy transfer (FRET) which may have the potential to be more efficient [9,10]. Nonradiative energy transfer does not require the emission and extraction of the photons but rather the energy is transferred directly to the QDs, this provides for the possibility of FRET being used as an alternative to radiative pumping in such devices. FRET was successfully demonstrated from an InGaN/GaN QW to a monolayer of QDs over a decade ago [9]. At that time it was shown that the FRET process was fast enough to compete with both radiative and non radiative relaxation processes within the QW itself. However, as FRET is a near-field dipole-dipole interaction the efficiency is extremely sensitive to QW-QD separation, and consequently only a monolayer of QDs could benefit from nonradiative pumping by the QW in this way. Since then many studies have focussed on exploration of alternative geometries; such as dry etched nanopillars [11–13], with a view to bringing a higher number of acceptor QDs close enough to benefit from nonradiative energy transfer from the QW. Other researchers have explored graded QDs [14] or optimized donor-acceptor ratios [15]. Whilst these studies improved on the what had come before, each also brought its own fabrication complexities, such as the need for complex etching processes. The successful pumping of larger volumes of QDs from a QW *via* nonradiative energy transfer still proved to be elusive, and is a principal objective.

A significant drawback for FRET-based devices is its strong dependence on the separation between the donor and acceptor, showing an  $r^{-6}$  dependence for a single donor-acceptor pair with a characteristic distance of typically less than ten nanometers. Therefore, in order to implement FRET for color conversion in LEDs would require small separations between the donor QWs and a large number of QD acceptors, or a method to increase the energy transfer distance. In recent times there have been numerous reports on the use of plasmonic structures, based on both metal nanoparticles and films, to enhance the emission of QWs [16–21] and QDs [22–27]. The enhanced emission can arise due to increased absorption under optical pumping, increased radiative recombination rates and/or scattering by the plasmonic nanostructures themselves [27]. Along with coupling to a single emitter, plasmonic NPs can also be used to couple light between two emitters. In the 1980s it was theoretically proposed that localised surface plasmons (LSPs) could modify FRET between two molecules [28, 29]. Work completed in the Bradley group by Komarala *et al.* was the first experimental observation of plasmon enhanced FRET between mixed monolayers of QDs [30]. LSP-FRET has been demonstrated in a variety of material systems and geometries over the last decade, with reported enhancements of the nonradiative energy transfer distance, rate and efficiency [30–37]. Incorporating plasmonic structures into an LED device consisting of a QW donor



and QD acceptors could allow for the possibility to achieve higher energy transfer efficiencies over larger distances, in which one could nonradiatively pump a larger volume of QDs. This could potentially be exploited to improve the efficiency of nonradiatively pumped down-conversion for white LEDs. The strength of the QW-plasmon coupling is reflected in the modified spontaneous emission rate of the donor. Plasmon-coupled nonradiative energy transfer is sensitive not only to the spectral overlap of the donor and acceptor with each other, but also with the spectrum of the plasmon mode [25,34]. The plasmon-coupled nonradiative energy transfer efficiency is determined by the interplay between the QW spontaneous emission rate, the rate of nonradiative energy transfer to the plasmonic structure and the rate of plasmon-coupled nonradiative energy transfer to the acceptors. The plasmon-coupled energy transfer must compete with the nonradiative energy transfer from the QW to the plasmonic structure.

It has been almost two decades since Govorov *et al.* proposed that the geometry for the LSP mediated FRET which has the strongest enhancement of the FRET rate, is to position the metal NP with the donor and acceptor at opposite poles [38]. Extensive studies on LSP mediated FRET within layered QD systems was completed in recent times in this group [35,39,40]. These studies demonstrated the capability of LSP-FRET within layered systems. Whilst FRET between a single donor-acceptor pair shows a  $r^{-6}$  distance dependence, within different material geometries this can be modified. Essentially the distance dependence is dictated by the acceptor's dimensionality [41], and this is driven by the level of quantum confinement within the acceptor. So as the level of confinement within the acceptor goes from 3D (QD) to 2D (quantum wire) to 1D (QW) to 0D (bulk), the FRET distance dependence goes from  $d^{-6}$  to  $d^{-5}$  to  $d^{-4}$  to  $d^{-3}$ , respectively. In this way, the distance dependence of a layer of acceptors (i.e. a 2-D like monolayer of QDs) is the same as a 1D confined structure, like a QW, resulting in a distance dependence of  $d^{-4}$ . With this in mind, planar geometries such as a QW donor with a layer of QD acceptors possess an advantage to enable FRET over distance. Moreover, the optical properties of plasmonic NPs can be tuned by varying their material, size and shape [42]. This allows them to interact more strongly with emitters by tuning the level of spectral overlap between the two species. Within an arrayed design these optical properties can be controlled even further by tuning the level of interaction between individual NPs within the array, by varying the gap between consecutive units. Therefore, combining a QW donor with an array of plasmonic elements and a layer acceptor QDs generates a 3-component hybrid system that contains all the necessary elements required to observe efficient LSP-FRET between a QW and a thick layer of QD acceptors. This is the 3-component system that will be discussed in this thesis.

In brief, in this thesis Ag plasmonic arrays, fabricated using both helium-ion

lithography (HIL) and electron beam lithography (EBL), on an InGaN/GaN QW are used to enable LSP enhanced FRET to a  $\sim 80$  nm layer of CdSe/ZnS QDs embedded in a poly(methyl methacrylate) (PMMA) matrix. The thickness of the QD acceptor layer and the dimensions of the Ag plasmonic NPs are large compared with previous reports of plasmon-coupled nonradiative energy transfer [34, 43]. Whilst FRET has been observed between a QW and QDs before [9], the work presented in this thesis provides the first ever experimental demonstration of LSP enhanced FRET from a QW to a thick layer of QDs. The work presented in this thesis signifies a substantial improvement to the body of work already published in this field and the novelty of the 3-component layered geometry system allows for considerable enhancement of the FRET efficiency. This work also clearly demonstrates a substantial increase of the range over which QWs can nonradiatively pump QDs. The work presented in this thesis shows promising results regarding the implementation of FRET for color conversion in white light LEDs.

Chapter 2 will introduce FRET theory and discuss how it is characterised within the material system under study. The basics of FRET within different material systems and geometries will also be outlined. LSPs and their effect on the emission properties of the emitters will be concisely introduced. The main theoretical and experimental reports of FRET and LSP-FRET with different NPs will be discussed. Finally, the theoretical and experimental reports of FRET between QWs and QDs will be presented.

An introduction to the different materials used throughout this thesis and sample preparation methods can be found in chapter 3. Details on the properties of the materials and methods of characterisation will be outlined. The methods for fabrication of the plasmonic NPs will also be given and their characterisation will be discussed.

In chapter 4 the first ever experimental demonstration of LSP mediated FRET from a QW donor to QD acceptors will be presented. An array of Ag nanoboxes have been chosen to investigate this plasmon-coupled process. These nanoboxes are fabricated directly onto both the QW and bulk GaN substrates. More specifically, the carrier density dependence of the plasmon-coupled nonradiative energy transfer mechanism is examined. By conducting such a study we determine if the same physics as for conventional FRET underpins the LSP enhanced interaction.

In chapter 5 the effect that the plasmonic array has on both the LSP-FRET and the enhanced emission processes within the QW-QD system is presented. To do this, a range of different Ag plasmonic arrays, consisting of NPs with varying shape and size are fabricated onto both a QW and bulk GaN substrate. The interaction between both the donor QW and the acceptor QDs with the plasmonic arrays alone are characterised separately. To quantify the strength of the enhanced absorption



and emission processes arising from coupling to the enhanced local field around the NPs, measurements for the QDs are taken on the bulk GaN substrate. Subsequently, the impact that the arrays have on the LSP-FRET from the QW to the QDs is determined. These measurements are taken on the QW substrate. Signatures of LSP-FRET are seen in the QW and QD photoluminescence (PL) spectra and in the PL decays. The total change in the acceptor QDs emission is shown to be explained solely by the LSP-FRET from the QW to the QDs *via* the NP arrays.

In chapter 6 the impact of changing the QW barrier thickness on the LSP-FRET process from the QW donor to the QD acceptors will be presented. Thin QW barriers can increase nonradiative losses within the QW donor and can be detrimental for carrier spreading across the device area [10, 44]. This is a product of the fabrication process and is driven by the quality and purity of the barrier itself. Having a thicker QW barrier can help to alleviate both of these problems. As a result, demonstrating FRET from a QW with a thicker barrier ( $\sim 7$  nm) to QDs could be considerably advantageous. To do this, Ag nanobox arrays were fabricated directly onto QW samples with barrier thickness varying from 3 nm to 7 nm in steps of 2 nm. The impact that the barrier thickness has on the LSP-FRET rate and efficiency is discussed. Once again, the total change in the acceptor QDs emission is shown to be explained solely by the LSP-FRET from the QW to the QDs *via* the NP arrays.

The major conclusions of this work will then be presented in chapter 7 and some discussion of the future work to be completed in this exciting area of research will be presented.





## 2 Background

### 2.1 Förster Resonance Energy Transfer Theory

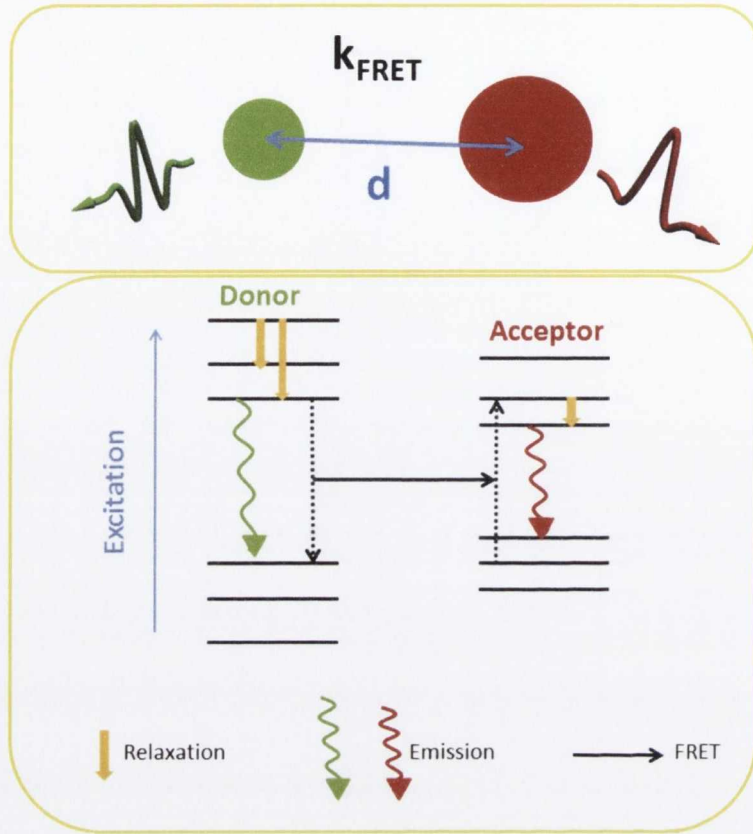
Förster Resonance Energy Transfer (FRET), is a nonradiative energy transfer process that is mediated by a near field dipole-dipole interaction. It is named after the German physical chemist Theodor Förster [45, 46]. An schematic of FRET between a single donor and acceptor pair is shown in Fig. 2.1. When the donor is excited by a light source which is at a higher energy than the bandgap energy of the donor, it is excited to a higher energy state [47]. It vibrationally relaxes to the lowest excited state over a picosecond timescale [48–50]. In the absence of an acceptor, the donor will relax to its ground state by emitting a photon via radiative recombination, with a rate  $k_r$  *via* nonradiative recombination with a rate  $k_{nr}$ , where  $k_r + k_{nr} = \tau^{-1}$ .  $\tau_D$  is the intrinsic decay lifetime of the donor by itself without any acceptor present. If there are available acceptor states with resonant energy levels with the excited donor state and that are at proximal distance to the donor, typically less than 10 nm, then nonradiative energy transfer can occur from the donor to the acceptor. The acceptor vibrationally relaxes very fast which prevents back transfer to the donor and then eventually the acceptor returns to the ground state *via* radiative or nonradiative recombination. The rate of the dipole-dipole resonance energy transfer,  $k_{FRET}$ , between a donor and acceptor that are separated by a fixed distance,  $d$ , was shown to be [51]

$$k_{FRET} = \frac{1}{\tau_D} \cdot \left( \frac{R_0}{d} \right)^6 \quad (2.1)$$

where  $R_0$  is a characteristic distance known as the Förster distance. The FRET efficiency is then

$$\begin{aligned} E_{FRET} &= \frac{k_{FRET}}{k_{FRET} + \tau_D^{-1}} \\ &= \frac{1}{1 + \left( \frac{d}{R_0} \right)^6} \end{aligned} \quad (2.2)$$

and it can be seen that the Förster distance,  $R_0$ , is the donor-acceptor distance at



**Figure 2.1:** Schematic of FRET process between a donor-acceptor pair

which the intrinsic rate equals the energy transfer rate or where the energy transfer efficiency is 50 %. Clearly, the  $E_{\text{FRET}}$  is very sensitive to the donor-acceptor distance,  $d$ , and therefore, FRET has been used as a spectroscopic ruler, particularly in the area of biology [52, 53].

Eq:2.1 and eq:2.2 are only applicable for a single donor-acceptor pair. If the donor is interacting with several acceptors, the energy transfer rate  $k_{\text{FRET}}$  is the sum of each of the energy transfer rates,  $k_i$ , giving

$$k_{\text{FRET}} = \sum_i k_i = \frac{1}{\tau_D} \sum_i \left( \frac{R_0}{d_i} \right)^6 \quad (2.3)$$

and the energy transfer efficiency

$$\begin{aligned} E_{\text{FRET}} &= \frac{k_{\text{FRET}}}{k_{\text{FRET}} + \tau_D^{-1}} \\ &= \frac{1}{1 + \left[ \sum_i \left( \frac{R_0}{d_i} \right)^6 \right]^{-1}} \end{aligned} \quad (2.4)$$

$R_0$  can therefore be used to compare FRET ranges for various donor-acceptor

pairs. It is determined by the spectral properties of the donor-acceptor pair and described by [54]

$$R_0 = 0.0211 \left[ \frac{\kappa^2 \varphi_D J(\lambda)}{n^4} \right]^{\frac{1}{6}} \quad (2.5)$$

which yields  $R_0$  in units of nm where  $n$  is the refractive index,  $\kappa^2$  is the dipole orientation factor between the donor and the acceptor,  $\varphi_D$  is the emission quantum yield of the donor in the absence of the acceptor and  $J(\lambda)$  is the spectral overlap of the area-normalized donor emission spectrum,  $f_D$ , and the acceptor extinction spectrum,  $\varepsilon_{Acc}(\lambda)$ . The spectral overlap

$$J = \int_0^\infty f_D(\lambda) \cdot \varepsilon_{Acc}(\lambda) \cdot \lambda^4 d\lambda \quad (2.6)$$

with

$$f_D(\lambda) = \frac{F_D(\lambda)}{\int F_D(\lambda) d\lambda} \quad (2.7)$$

where  $f_D(\lambda)$  is the donor emission per unit wavelength integrated over the donor emission spectrum, in units of  $\text{nm}^{-1}$ . The extinction spectrum of acceptors  $\varepsilon_{Acc}$  is in units of  $\text{M}^{-1}\text{cm}^{-1}$ , whilst  $J$  is in units of  $\text{nm}^4\text{M}^{-1}\text{cm}^{-1}$ .

The orientation factor  $\kappa$  is given by

$$\kappa = \hat{d} \cdot \hat{a} - 3 \left( \hat{d} \cdot \hat{r} \right) \cdot \left( \hat{r} \cdot \hat{a} \right) \quad (2.8)$$

where  $\hat{d}$ ,  $\hat{a}$  are the vectors along donor and acceptor dipoles, respectively.  $\hat{r}$  is the vector along the donor-acceptor direction. The detailed discussion of  $\kappa^2$  can be found in ref [46]. All systems studied in this thesis are isotropic, resulting in an orientation factor  $\kappa^2 = 2/3$ .

## 2.2 FRET Characterization

For the structures studied in this thesis the donor is a quantum well. For a donor-only system the QW has a PL decay lifetime,  $\tau_D$ , determined by its radiative recombination rate,  $k_r$ , and its nonradiative rate,  $k_{nr}$  [46]

$$\tau_D = \frac{1}{k_r + k_{nr}} \quad (2.9)$$

The quantum yield of the donor,  $\varphi_D$ , is determined by

$$\varphi_D = \tau_D \cdot k_r = \frac{k_r}{k_r + k_{nr}} \quad (2.10)$$



If there are available acceptors in proximity to the donor, the donor PL decay lifetime becomes

$$\tau_{DA} = \frac{1}{k_r + k_{nr} + k_{FRET}} \quad (2.11)$$

The quantum yield of the donor in the presence of the acceptor,  $\varphi_{DA}$ , is then given by

$$\varphi_{DA} = \tau_{DA} \cdot k_r = \frac{k_r}{k_r + k_{nr} + k_{FRET}} \quad (2.12)$$

Therefore, the FRET efficiency,  $E_{FRET}$ , can be characterized as [54]

$$\begin{aligned} E_{FRET} &= \frac{k_{FRET}}{k_r + k_{nr} + k_{FRET}} \\ &= 1 - \frac{\varphi_{DA}}{\varphi_D} \\ &= 1 - \frac{\tau_{DA}}{\tau_D} \\ &= 1 - \frac{I_{DA}}{I_D} \end{aligned} \quad (2.13)$$

where  $I_D$  and  $I_{DA}$  are the integrated emission intensities of the donor in the absence and presence of the acceptor, respectively.  $\tau_D$  and  $\tau_{DA}$  are experimentally measured decay lifetimes of the donor in the absence and presence of the acceptor, respectively. Whilst the reduction of both the donor emission intensity and donor PL decay lifetime are the primary signatures of the FRET process, an emitting acceptor will also have an emission enhancement as well as an increase in the rise-time of the time-dependent acceptor emission, signifying an increase in the effective pumping of the acceptor.

## 2.3 Distinguishing FRET From Other Energy Transfer Mechanisms

The FRET efficiency can be characterized as discussed above, however, it is not always straight-forward to establish whether the donor emission quenching or the energy transfer mechanism is explicitly FRET or is due to another mechanism, such as Dexter transfer [55] or charge transfer.

When we have an excited donor close to an acceptor, energy transfer can occur via radiative and/or nonradiative channels. Nonradiative energy transfer is a single-step

process, whereby



where  $D^*$ ,  $A^*$  denotes the excited state of the donor and acceptor respectively, while  $D$ ,  $A$  denotes the ground state of the donor and acceptor respectively.

By contrast, radiative energy transfer is a two-step process [56], whereby an emitted photon from the donor is reabsorbed by the acceptor. In this case a real photon mediates the energy transfer. This process has a relatively long range, exhibiting an  $r^{-2}$  dependence [36] as



Dexter transfer is a nonradiative process which occurs as a result of an electron exchange mechanism, which requires overlapping wavefunctions of the energy donor and energy acceptor [55]. The Dexter transfer rate,  $k_{DET}$ , decays exponentially with distance,  $d$ , with a range of  $\sim 1$  nm [57] as

$$k_{DET} = K \cdot J_{DT} \cdot e^{[-2d/L]} \quad (2.16)$$

where  $K$  is a constant related to specific orbital interactions.  $J_{DT}$  is the spectral overlap integral, which is similar to spectral overlap  $J$  in FRET but does not depend on the acceptor extinction coefficient, and  $L$  is the sum of the donor and acceptor Van der Waals radii. Similar to Dexter transfer, the charge transfer rate  $k_{CET}$  also decays exponentially with distance  $d$  as

$$k_{CET} = K_0 \cdot e^{[-\beta d]} \quad (2.17)$$

$\beta$  characterizes the energy transfer and  $K_0$  is a pre-exponential factor. In this case the energy transfer range can be  $\sim 2$  nm, with full details found in ref [58].

The Dexter mechanism is an electron exchange mechanism that requires both spectral overlap and wavefunction overlap, whereas charge transfer requires and electron (hole) donor and acceptor. This requires wavefunction overlap but not spectral overlap [58].

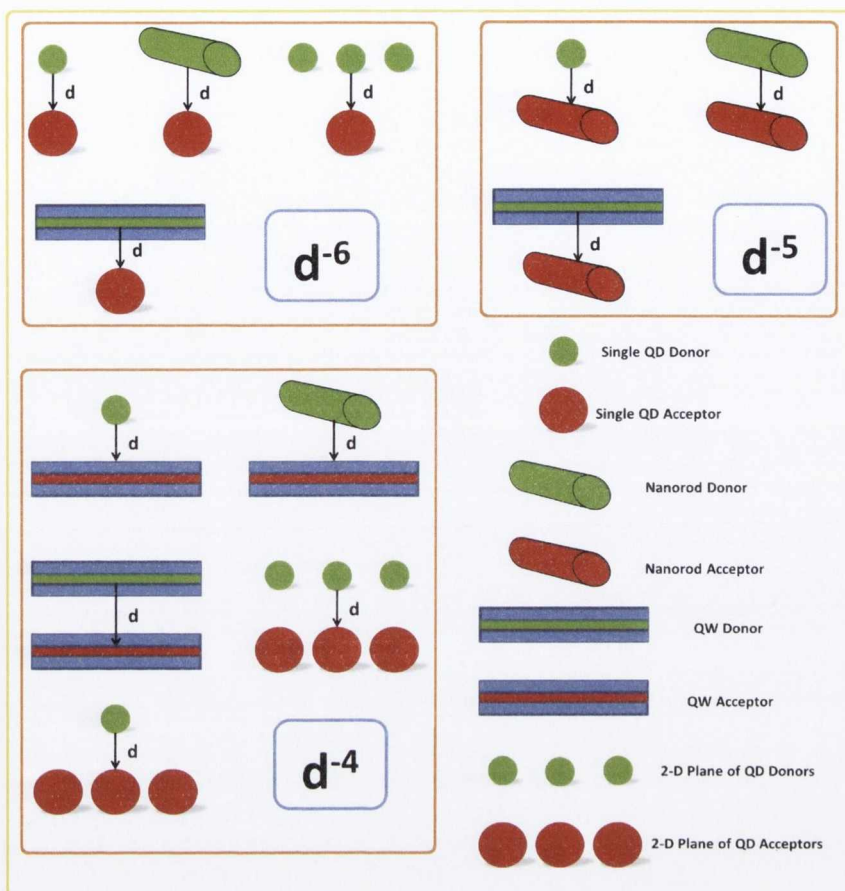
In the hybrid QW-QD system studied in this thesis, the minimum centre-to-centre distance between the donor and acceptor is much larger than 2 nm and therefore Dexter transfer and charge transfer can be excluded. As mentioned earlier, the FRET process is mediated by a nonradiative dipole-dipole interaction with length scales of  $\sim 10$  nm [59], with a  $d^{-6}$  distance dependence for a single donor-single acceptor

pair. Due to the ideal dipole approximation, which assumes that the dipole-dipole separation is much larger than the dipole itself, FRET breaks down for  $d < 1$  nm. However, as both emission and lifetime quenching are characteristic processes in both FRET and charge transfer, in some systems it can be difficult to establish if the energy transfer mechanism is FRET or charge transfer purely from quenching experimentally. However, by tracking the energy transfer efficiency by monitoring the spectral or distance dependence, one can provide further evidence to determine the mechanism. This is because FRET depends on the spectral overlap while charge transfer does not, and they both have different distance dependences. Once again, as mentioned earlier, in this work we are dealing with distances  $> 2$  nm and no evidence of charge has been observed, therefore we can isolate the mechanism involved uniquely as FRET.

## 2.4 FRET Distance Dependence

As mentioned earlier, FRET is a highly distance sensitive process. The distance dependence between a single donor and a single acceptor, as discussed earlier, follows a conventional  $d^{-6}$  dependence. However, it can be altered for different donor-acceptor geometries. Essentially the distance dependence is dictated by the acceptor's dimensionality, as detailed in ref [41], and this is driven by the level of quantum confinement within the acceptor. So, for example, for 2D and 1D confined quantum wire (Q-wire) and quantum well (QW) acceptors, the distance dependences vary with  $d^{-5}$  and  $d^{-4}$ , respectively [41]. So as the level of confinement within the acceptor goes from 3D (QD) to 2D (Q-wire) to 1D (QW) to 0D (bulk), the FRET distance dependence goes from  $d^{-6}$  to  $d^{-5}$  to  $d^{-4}$  to  $d^{-3}$ , respectively. Furthermore, different assemblies of the acceptors can also alter the distance dependence, as in the case where a 2D-like assembly of the semiconductor QDs (i.e. a monolayer of QDs) act as a 1D confined structure, like a QW, which consequently results in a distance dependence of  $d^{-4}$ . So in all of these cases, the dimensionality of the donor does not play a role in deciding what the distance dependence will be. Instead, only the acceptor indicates what the distance dependence of FRET will be within the system. A schematic showing the distance dependence within different donor-acceptor geometries is shown in Fig. 2.2.





**Figure 2.2:** Schematic of distance dependence regimes in different donor-acceptor geometries

## 2.5 FRET in Quantum Dots Systems

QDs can be assembled in 2D or 3D geometries through bottom-up methods, such as Layer-by-Layer assembly [60, 61] and Langmuir-Blodgett [62], or through top-down methods, such as lithography [63] or molecular beam epitaxy [64]. All of these methods allow for the investigation of QD-QD interactions in close proximity. As FRET is a short range process, it cannot occur in dilute solutions because the QDs are too far apart from one another. However, in densely packed layers, the QDs are sufficiently close to satisfy the requirement for donor-acceptor proximity.

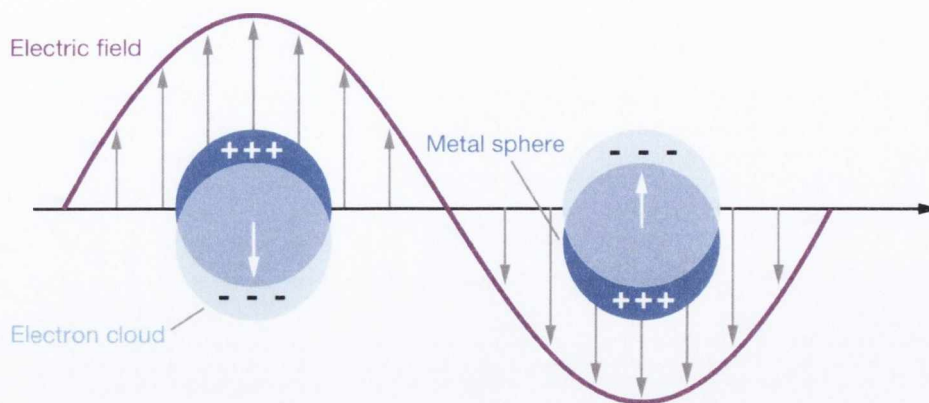
The first report of FRET observed between QDs was by Kagan *et al.* [60, 65]. They reported energy transfer in CdSe core-only QDs of different sizes, showing evidence of energy transfer from smaller to larger QDs. However, it was Crooker *et al.* [66] who firstly revealed that FRET could be optimized by arranging QDs of different sizes to create an energy gradient. Crooker *et al.* studied the energy transfer mechanism by time-resolved photoluminescence and spectrally-resolved photoluminescence. It should also be noted that energy transfer has been reported in monodispersed QDs

due to the size distribution within an ensemble [67], therefore a large size disparity is not a requirement to observe FRET. Furthermore, producing an energy gradient by the sequential stacking of green, yellow, orange and red emitting QDs was as shown to facilitate efficient directional FRET. These structures [68] yielded approximately a 28-fold emission enhancement, which was much higher than expected from conventional FRET, and was attributed to the presence of exciton recycling within the system. Exciton recycling allows for excitons captured by defect states in smaller QDs to be transferred to bright states in the larger QDs. Theoretical studies have probed the validity of FRET in QD systems [69, 70] and have demonstrated that the interaction between QDs can be well described by FRET. The QD behaves as a potential formed by a positive charge and a negative charge separated by  $\sim 0.7\text{nm}$  that are localised at the centre of the QD [70], confirming the approximation of a QD as a point dipole. FRET has also been observed in several other material systems, including in QD-QD [66, 71, 72], QD-dye [73, 74], QD-graphene [75], QD-QW [9] and QD-protein [76] systems.

## 2.6 Localised Surface Plasmon Resonance

Surface plasmons (SPs) are collective oscillations of electrons at the interface between a metal and a dielectric [42]. SPs can display a resonance behaviour and produce enhanced near-field amplitudes at the resonance wavelength. This enhanced field can be highly localised, and the large electric field enhancements produced are the reason why metallic NPs in particular are so extensively used in research today. Localised surface plasmon resonances (LSPR) are non-propagating excitations of the conduction electrons of a metallic NP coupled to an electromagnetic field, as seen in Fig 2.3. Considering the simplest case of a gold nanosphere, for example, incident light induces a coherent oscillation of electrons between opposite surfaces of the nanosphere. Under a plane wave excitation the light can be absorbed or scattered by the nanosphere. Scattering by the nanosphere will usually occur at higher wavelengths than the LSPR peak wavelength due to absorption dominating at the LSPR peak wavelength and also at lower wavelengths (or higher energies). The combination of absorption and scattering, is the extinction of the NP. More specifically, the extinction cross-section,  $C_{ext} = C_{abs} + C_{scatt}$ , where  $C_{abs}$  is the absorption cross-section and  $C_{scatt}$  is the scattering cross-section. Oscillation of the free electrons of the nanosphere due to the incident electromagnetic wave also causes a large electromagnetic field enhancement to be generated around the nanosphere. Due to this field enhancement, MNPs such as this have effective extinction cross-sections that can be up to ten times larger than their physical size. They therefore interact strongly with light, leading such plasmonic elements to be viewed as nano-antennae.





**Figure 2.3:** Schematic of LSPs reprinted from Willets *et al.* [77].

Plasmonic NPs like these can also be coupled with emitters. The coupling between an emitter, viewed as a dipole, and a MNP, such as the gold nanosphere considered earlier, can modify the emitter properties. The enhanced field around the nanosphere can modify the radiative and nonradiative decay rates of the emitter. The change in the radiative rate is due to an increase in the pumping of the emitter in the presence of an enhanced electric field. This change can also be viewed as modifying the quantum yield of the emitter dipole. Changes in the nonradiative decay rate are due to nonradiative energy transfer to the nanosphere, which can also result in a decrease in the emitter PL (quenching) or an increase in the emitter PL (enhancement or increased scattering) [27]. Various plasmonic NPs have been used throughout the literature as non-fluorescent acceptors due to their LSPR in the visible range. They can allow for increases or decreases in the donors emission [78–81]. Several examples, such as Au NPs discussed above, have been used due to their high molar extinction coefficients, making them very effective quenchers [82]. As the absorption and scattering properties of MNPs can be tuned by simply changing the size and shape of the NP, nanostructures can be designed to be resonantly incorporated with different emitters for the purposes of increasing or decreasing emission.

## 2.7 Localised Surface Plasmon Mediated Energy Transfer

As mentioned earlier, the distance dependence of Förster resonance energy transfer (FRET) is well-defined by a dipole-dipole interaction [83, 84]. However, due to this, it can only conventionally occur over short length scales, typically  $\sim 10$  nm. Along with coupling to a single emitter, plasmonic NPs can also be used to couple light between two emitters. It was theoretically proposed in the 1980s that LSPs could modify FRET between two molecules [28, 29], that were regarded as two point



dipoles. Let us consider the simplest case of a donor-acceptor pair of emitters and a gold nanosphere, once again. In this case the nanosphere can modify the radiative and nonradiative decay rates, and the PL of both the donor dipole and the acceptor dipole, independently. The donor can also transfer energy radiatively or nonradiatively to the acceptor in the absence of the nanosphere. However, the enhanced electric field around the nanosphere can also facilitate an enhancement of nonradiative energy transfer between the donor and the acceptor. In this way the donor-nanosphere can be viewed as an enhanced donor dipole which couples to the acceptor dipole. The enhancement of the FRET process strongly depends on the distance from the metal NP, the shape of the metal NP, and orientation of the dipoles with respect to the metal NP. Although LSP enhanced FRET still decreases with distance, LSPs could extend the FRET range substantially compared to traditional FRET in the absence of the metal NPs, increasing it from the sub 10 nm range up to  $\sim 70$  nm. A wide range of experimental investigations with various geometries and emitters have demonstrated enhancement of nonradiative energy transfer *via* MNPs. These include experiments which demonstrate that enhancement of the energy transfer rate, efficiency, and range can be achieved in different geometries with a variety of fluorophores and metal NPs [25, 26, 30, 34, 43, 85–89].

Govorov *et al.* proposed that the optimum geometry for the LSP mediated FRET, which has the strongest enhancement of the FRET rate, is to position the metal NP with the donor and acceptor at opposite poles [38]. More recent work by Marocico *et al.* has shown the dependence of LSP FRET on a number of factors, such as the size of the NP, the emission wavelength and the quantum yield [40]. Lakowicz *et al.* showed that the presence of silver island films near donor-acceptor pairs increased the Förster radius from 3.5 nm to 16.6 nm [90]. Zhang *et al.* reported a 60% increase in the Förster radius between oligonucleotide donor-acceptor pairs bound to a single MNP [91]. Also, work completed in this group by Komarala *et al.* was the first experimental observation of plasmon enhanced FRET between mixed monolayers of QDs [30].

Studying FRET from a conjugated polymer to fluorescent multilayer core-shell NPs, Lessard-Viger *et al.* observed a 50 % increase in the Förster distance coupled with an 173 times increase in the FRET rate [92]. Plasmonic resonators have also been used in single MNP LSP enhancement reports [33]. The other LSP enhanced FRET reports include donor ZnO NPs and acceptor CdSe/ZnS core-shell QDs with silver prisms in a spin coated layer [37]; other layered geometries such as mixed CdSe QDs layer with silver NPs layer [86]; mixed CdSe/ZnS and CdSe/ZnTe QDs with a Au NP layer [93] and also metallic NPs in planar structures [30, 34, 43, 85]. Wang *et al.* showed that FRET could be switched on and off by varying the spectral position of the LSP resonance relative to the donor emission and acceptor absorp-

tion [94] through studying a core-shell geometry, whereby the donor and acceptor fluorophores were embedded in a shell coating a Au-Ag core-shell nanocrystal.

Further reports in planar stacked structures consisting of dyes and/or QDs, which act as donors and acceptors, placed on a metal NP layer demonstrate that selective coupling to the donor or acceptor is possible by changing the order of QD and NP layers [43]. Depending on how the LSP coupled FRET rate competes with the LSP modified decay rates of the donors and acceptors it has been shown that the result can be PL quenching or enhancement [95–100]. Extensive studies on LSP mediated FRET was completed in recent times in this group [35, 39]. Investigating separated planes of donor and acceptor QDs with a layer of Au NPs sandwiched between, it became clear that the signatures of LSP coupled FRET depend strongly on the position of the intermediate Au NP layer and on the concentration of the Au NPs. The largest rates and efficiencies were observed for higher Au NP concentrations, smallest donor-Au NP and acceptor-Au NP separations. However, the donor-Au NP separation was found to be more sensitive for impacting the LSP FRET within this system. As discussed in detail earlier, the distance dependence of the LSP coupled FRET efficiency has the same  $d^{-4}$  form as conventional FRET within an acceptor layer geometry. The independence of the Förster radius on the acceptor-Au NP separation indicates that the donor-plasmon coupling is dominant, and since it can fit with FRET theory, this suggests that the strongly coupled donor-plasmon system can be considered as an enhanced donor dipole.

## 2.8 Energy Transfer Between Quantum Wells and Quantum Dots

Quantum wells display many unique properties compared to their 3D bulk crystals. For example, the exciton binding energy is 4 times larger than that for the 3D-case [42]. QWs also demonstrate heightened sensitivity of their absorption spectra to an applied electric field, which can allow for their integration with existing CMOS technology [101, 102]. More specifically, InGaN/GaN QWs have been promising to explore in terms of opto-electronic devices, such as LEDs [103–105] and light harvesting devices [106, 107].

Combining QWs and QDs has, to date, played a significant role in many devices for both white light generation [108–110] and colour conversion [6, 10, 111, 112]. Radiative pumping of QDs by QWs, whereby the emission of a photon from the QW is re-absorbed by the QDs which subsequently re-emit a photon, is a multi-step process that is inherently lossy. The reasons for this include issue in extraction of the photon from the LED and reabsorption of the photon by the QD acceptors.



Many different strategies to efficiently extract photons from LEDs have been a topic of considerable research. These include modification of the surface roughness of the LED to increase the extraction efficiency [7, 8]. However, as nonradiative energy transfer does not require the emission and extraction of the photons but rather the energy is transferred directly to the QDs, this provides for the possibility of FRET being used as an alternative to radiative pumping in such devices. There have been many approaches to attempt to circumvent radiative pumping by utilising nonradiative energy transfer from a QW to a layer of QDs. It was theoretically predicted by Basko *et al.* [113] that pumping from a QW to organic molecules via non radiative energy transfer or FRET was possible. However, it was Achermann *et al.* who experimentally confirmed that the efficient pumping through non radiative energy transfer from an InGaN/GaN QW to a monolayer of QDs could be achieved, and showed that this process is fast enough to compete with both radiative and non radiative relaxation processes within the QW itself [9, 10]. However, as FRET is a near-field dipole-dipole interaction and the efficiency is extremely sensitive to QW-QD separation, only a monolayer of QDs could benefit from nonradiative pumping by the QW in this way. Also, as this QW-QD distance is crucially important, the capping layer of the QW should remain as thin as possible. This provides its own complications because thin QW barriers can increase nonradiative losses within the QW donor and can be detrimental for carrier spreading across the device area [10, 44]. Having a thicker QW barrier can help to alleviate both of these problems [10]. However, FRET has not been observed from a QW with a thicker barrier to date. Instead, many other studies have focussed on optimisation of the geometries, such as dry etched nanopillars [11, 12] to bring a higher number of acceptor QDs close enough to benefit from nonradiative energy transfer from the QW, graded QDs [14] or optimized donor-acceptor ratios [15]. Whilst there were some performance improvements made due to the etching process in such devices, they also provide their own drawbacks, such as fabrication complexity or the need to carefully position emitters.

As mentioned earlier, plasmonic coupling can enhance the efficiency of non radiative energy transfer, and also metal structures displaying plasmonic properties have been used to enhance the emission of QWs and/or LED devices [16–21]. Plasmonics have also been utilised to enhance photovoltaic devices [114]. Therefore, if one could achieve pumping of a thick layer of QDs *via* nonradiative ET from a QW by using plasmonic structures, this could be highly promising for device applications. This highlights why incorporating plasmonic elements into a hybrid QW-QD system could be so beneficial. This provides the motivation for the work completed in this thesis, which will be presented in detail in chapters 4, 5 and 6.



# 3 Materials and Characterisation

The quantum well (QW) structures used in this thesis were fabricated using metal organic vapour phase epitaxy (MOVPE) by collaborators in Tyndall National Institute. There are several different QWs used throughout this thesis, the details for each case are specified for the studies presented in chapters 4, 5 and 6. In all cases considered in this thesis, CdSe/ZnS core-shell quantum dots (QDs) with a diameter of 6.3nm and a peak emission wavelength of 649 nm are dispersed within a poly(methyl methacrylate) (PMMA) matrix and deposited on to the bulk GaN and QW substrates *via* a spin coating technique. Plasmonic arrays are fabricated directly on to the bulk GaN and QW substrates using both helium-ion and electron beam lithography. Once again, the details for each study are specified in chapters 4, 5 and 6. A general introduction to the materials used throughout this thesis is presented in this chapter, along with the methods used to characterise them. Also, the signatures of Förster resonance energy transfer within the structures considered in this thesis will be discussed.

## 3.1 Quantum Dots

Semiconductor quantum dots (QDs) are semiconductor material with spatial confinement in three dimensions. This confinement is made possible because an electron's de Broglie wavelength,  $\lambda_e$ , is more than one order of magnitude larger than the lattice constant of many crystals, allowing for spatial confinement of electrons while keeping the crystal lattice structure relatively unperturbed. To illustrate this we consider the de Broglie wavelength; assuming the effective mass seen in real crystals and using room temperature as a measure of the electrons kinetic energy ( $k_B T = 26.7 \text{ meV}$ ) [42], described by

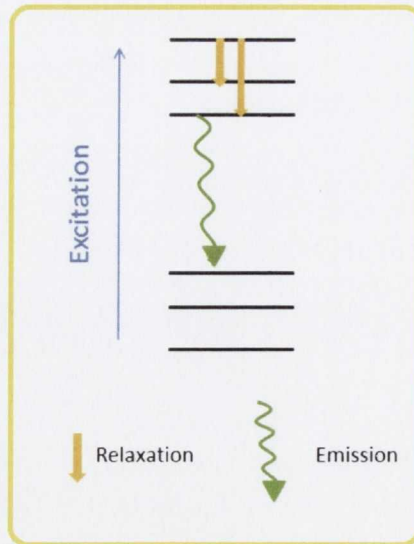
$$\lambda_e = \frac{h}{\sqrt{2m_e^*k_B T}} \quad (3.1)$$

Due to the quantum confinement, the electronic structure of the QDs is described by discrete energy levels [42], and can be understood by applying the quantum mechanical “particle in a box” problem to bound electron and hole states, i.e. excitons. Excitons are formed when an absorbed photon excites an electron from the

valence band (VB) of a semiconductor into the conduction band (CB), leaving behind a positive hole in the VB. There is then a Coulomb attraction between the electron and hole, leading to the formation of an exciton which has slightly less energy than the unbound electron and hole. This exciton can then be described as an exotic hydrogenic atom using quantum mechanics. Similar to the electron and proton in a hydrogen atom, excitons have an average physical separation between the electron and hole, referred to as the exciton Bohr radius, denoted  $a_B^*$ , which is material dependent. The expression for the exciton Bohr radius is  $a_B^* = \frac{m\epsilon r}{\mu} a_0$  where  $a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$ . In bulk semiconductor crystals the dimensions are much larger than  $a_B^*$  and the energy levels can be considered as continuous. However, if the size of the semiconductor becomes comparable to  $a_B^*$  then the energy levels of the exciton must be treated as discrete. This situation of discrete energy levels is known as quantum confinement. The energy gap of the quantum dots can be estimated using the following [42]

$$E_g^{QD} = E_g^{Bulk} + \frac{\hbar^2 \pi^2}{2r^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) - 1.786 \frac{e^2}{\epsilon r} - 0.248 E_{Ry}^* \quad (3.2)$$

where  $r$  is the radius of the QD,  $m_e$ ,  $m_h$  are the electron and hole effective masses,  $\epsilon$  is the dielectric constant of the semiconductor, and  $E_{Ry}^*$  is the Rydberg energy for the electron hole pair. The first term,  $E_g^{Bulk}$ , is the bandgap energy of the bulk solid. The second term is the "particle in a box" term and the third term arises from the electron-hole coulomb attraction. Therefore from this expression we see that as the radius of the QD decreases the band gap increases which enables the emission spectrum to be tuned with size. The band structure for a single QD is shown in Fig. 3.1.



**Figure 3.1:** Band structure of single QD (2-level system)

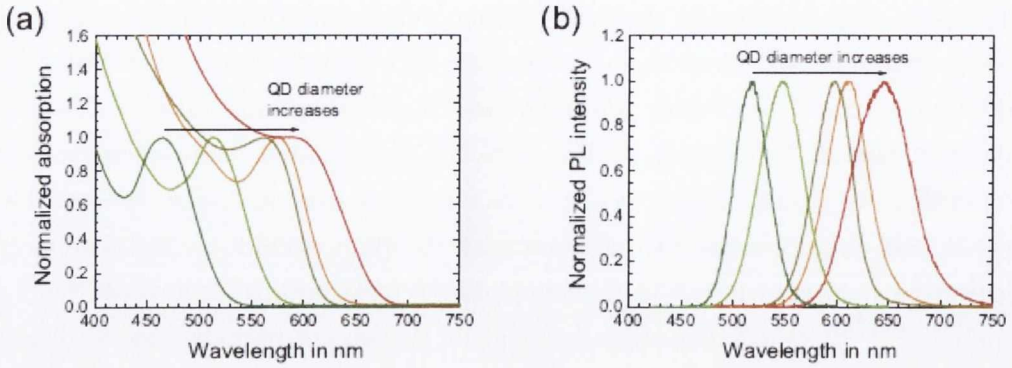


The possibility to tune the emission by simply changing the size of the QD makes them very useful, but in addition to this, the QDs have a broad absorption range which enables free selection of excitation wavelength as multiple QDs can be excited with the same excitation source. This gives QDs a distinct advantage over molecular dyes which would require multiple excitation sources for different dyes due to their narrow absorption bands. Furthermore the photostability, resistance to photobleaching, and quantum yields of colloidal QDs have improved in recent years due to refinement of the chemical synthesis [115–119], giving them a further advantage in many areas over traditional molecular dyes. These properties make QDs of great interest in research as well as in applications such as bio-sensing [120,121], photodetectors [122] and, as has already been mentioned above, in LEDs and photovoltaic devices [16–21,114].

### 3.1.1 Optical Properties of Quantum Dots

Absorption of a photon by a QD occurs if the photon energy is higher than the band gap energy. Due to quantum confinement, decreasing the size of a QD results in a blue shift of the absorption onset ( $E \propto \frac{1}{L^2}$ , from the particle in a box problem) [123]. The excess energy can then be re-emitted as light through photoluminescence (PL). Rapid excitation and de-excitation resulting in photoluminescence is known as fluorescence. The emission rates (denoted  $k$ ) are of the order of  $10^8$  Hz which means that fluorescence lifetimes are typically around 10 ns ( $1/k$ ) for QDs [42]. The lifetime ( $\tau$ ) of a species is defined as the average time between excitation and return to the ground state. It is interesting to note that the lifetimes of other low dimensional systems such as quantum wells can be much shorter, of the order of pico-seconds, however in real samples the purity of the material and presence of defects have an impact on the measurable lifetime. For example time dependent photoluminescence (PL) decays of QDs should be monoexponential, reflecting only the intrinsic exciton recombination rate. However, due to the fact that QDs which are in solution are an ensemble of various sizes, and also due to defects, multi-exponential decays are observed. Normalised absorption and emission (luminescence) spectra of different sizes of quantum dots are shown in Fig. 3.2 (a) and 3.2 (b), respectively. One can see the relatively sharp first absorption peak and the red shift of both this peak and the emission wavelength peak with increasing size. One can also see that the spectra are quite broad, all with FWHM (full-width-at-half-maximum) around 40-70 nm. As mentioned above, very narrow emission lines would be expected for single QDs, however, scattering at surfaces and at defects cause homogeneous broadening of the peaks [42]. In addition, since these spectra are measured for a QD ensemble in solution there will be inhomogeneous broadening due to the finite size distribution,





**Figure 3.2:** (a) Absorption spectra of CdTe QDs in water with diameter increasing from left to right. (b) Photoluminescence spectra of the same samples shown in (a) for an excitation wavelength of 400nm. Figure taken from [124].

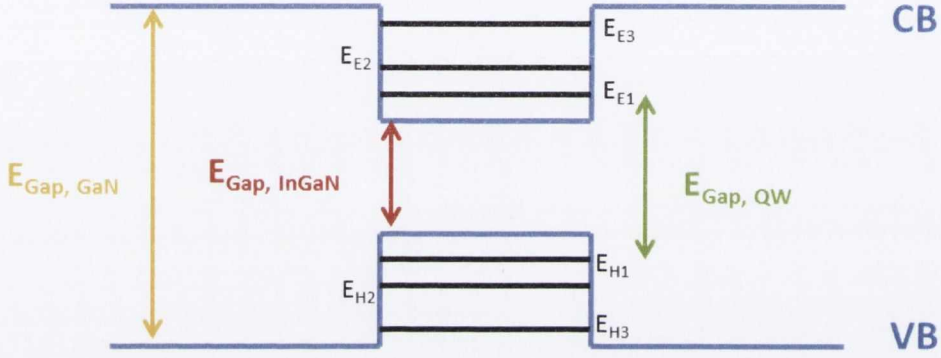
and variations in stoichiometry and charge, as well as other factors [42]. In the spectra shown it is the inhomogeneous broadening that dominates.

When the absorption and emission peak wavelengths are examined more closely, it can be seen that emission peaks always occurs at higher wavelengths to the absorption peak, i.e. they are always red shifted from the absorption peak. It is a general property of fluorescence that the energy of emission is less than that of absorption and the resulting red shift of the emission spectra is called the Stokes shift. The Stokes shift is caused by exciton-phonon interactions as the exciton rapidly relaxes to the lowest vibrational level of the electronic excited state. This relaxation process is called internal conversion. The decay which results in emission is generally to an excited vibrational level of the ground electronic state. This then relaxes, also *via* exciton-phonon interactions, to the lowest level, further increasing the energy difference between the absorbed photon and emitted photon [54]. It is worth noting that all of the QDs used throughout this thesis are chemically synthesized colloidal nanocrystal QDs. The QDs used throughout this thesis were commercial Sigma Lumidot 640 QDs. For the QDs used in all work throughout this thesis the concentration was low enough such that there was no evidence of intra-energy transfer.

## 3.2 Quantum Wells

Quantum Wells (QWs) are the two-dimensional analogue of QDs. Instead of charge carriers being confined in all three spatial directions they are confined in only one, and are therefore free to move in a two-dimensional sheet. QWs are made by sandwiching a thin layer of narrow bandgap material between two layers of higher bandgap material, this creates the band structure observed in Fig. 3.3. As the middle layer is decreased in thickness carriers will become more and more confined in

one direction and eventually this will lead to quantised energy levels [42, 125]. The single InGaN/GaN QW structure used in this thesis was grown by metal-organic vapour-phase epitaxy (MOVPE) [126] on a thick GaN layer on a c-plane sapphire substrate. The active InGaN layer is 2 nm thick capped with a 3 nm GaN barrier. The thin top barrier GaN layer was selected to allow for strong near-field coupling between the QW and the subsequently-added plasmonic nanostructures. No evidence of guided modes were observed in the QWs used throughout this thesis.



**Figure 3.3:** Band Diagram for an InGaN/GaN QW showing the Conduction Band (CB) and Valence Band (VB)

Quantum wells display many unique properties compared to their 3D bulk crystals. For example, the exciton binding energy is 4 times larger than that observed for the 3d-case [42]. QWs also demonstrate heightened sensitivity of their absorption spectra to an applied electric field, which can allow for their integration with existing CMOS technology [101, 102]. More specifically, InGaN/GaN QWs have been promising to explore in terms of opto-electronic devices, such as LEDs [103–105] light harvesting devices [106, 107] and lasers [42, 127, 128].

As mentioned earlier, the greatest signature of Förster resonance energy transfer (FRET) is a reduction in the energy donor fluorescence decay lifetime. As the QW is the energy donor in the work presented in this thesis, its decay lifetime must be monitored to determine if FRET occurs.

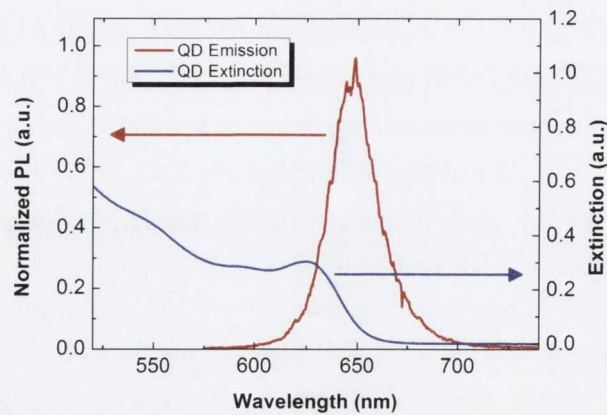
### 3.3 Characterisation of the Emitters

#### 3.3.1 Absorption

For the QW-QD energy transfer study in this thesis, CdSe/ZnS core-shell QD samples were prepared using a spin coating technique. QDs, dissolved in toluene, were dispersed within a (PMMA) matrix before being spun down onto the various substrates. Quartz substrates were used for initial characterisation before utilising bulk GaN for reference and the single QW samples for the energy transfer (ET) study. Absorption spectra of the QD samples provides information about the concentration of the QDs in solution and subsequently in a layer. The measurements were carried out on a Cary 50 UV-Vis Spectrophotometer. The spectra of the QDs in PMMA matrix in a solution of toluene were recorded between 300nm and 800nm with a resolution of 1 nm. Absorption of a material is characterised by the Lambert-Beer Law:

$$A(\lambda) = \epsilon(\lambda) \cdot c \cdot l \quad (3.3)$$

where  $\epsilon(\lambda)$  is the extinction coefficient of the sample,  $l$  is the length of the path of light through the sample and  $c$  is the concentration of the material in the sample. As mentioned in the previous chapter, extinction is the sum of absorption and scattering, however as the QDs have a diameter of 6.3 nm scattering is negligible therefore their extinction is equivalent to their absorption. One can now see how information on concentration can be determined from absorption measurements. Once  $l$  and  $\epsilon(\lambda)$  are known for the material being investigated, then the concentration can be determined by measuring the absorption. The extinction and emission spectra of the CdSe/ZnS core-shell quantum dots used in this thesis are shown in Fig 3.4.



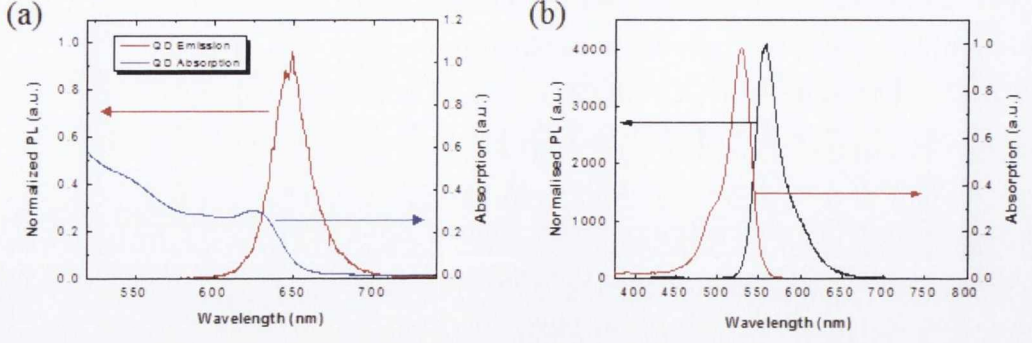
**Figure 3.4:** The extinction (right axis) and emission (left axis) of CdSe/ZnS QDs in PMMA solution



The concentration of the QDs when in a layer can then be calculated by using equation 3.3, where we take the measured absorption value at the  $\lambda$  value of the 1-S peak. Therefore with  $A = 0.92$ ,  $\epsilon = 5.88 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$  and  $l = 0.5 \text{ cm}$ , this gives  $c = 3.1 \times 10^{-6} \text{ M}$ . As the QDs are embedded in the PMMA matrix, the concentration of the QDs in solution is the same as the concentration in a layer. So we can convert this concentration from a molar concentration into a total number of QDs in a given 3D space within the PMMA matrix. To do this we need to use a conversion factor which includes a conversion from mol/L to mol/m<sup>-3</sup> ( $1 \text{ mol/L} = 10^3 \text{ mol/m}^{-3}$ ) and also includes Avogadro's number,  $N_A$ , whereby the QD particle concentration  $N = c \cdot N_A \cdot 10^3$ , gives  $N = (1.9 \pm 0.1) \times 10^{21} \text{ m}^{-3}$  or  $(1.9 \pm 0.1) \times 10^3 \mu\text{m}^{-3}$ . This is the concentration of QDs in a layer used throughout this thesis. This QD concentration is used throughout this thesis as it is low enough such that there is no evidence on intra-energy transfer between the QD ensemble but yet high enough such that through the range of excitation powers used the QD emission does not saturate at the high power ranges used.

### 3.3.2 Photoluminescence and Quantum Yield

The photoluminescence (PL) spectra of the QD solutions were recorded with a Perkin-Elmer LS 55 fluorescence spectrometer for quantum yield (QY) calculations. A pulsed Xenon lamp was used as a light source and it provided variable excitation wavelengths for the measurements. The spectra of the QDs were recorded using an excitation wavelength of 400 nm, a wavelength where QDs absorb well. The spectra were recorded over a range of 420-700 nm with a resolution of 0.5 nm. In order to prevent saturation of the detector neutral density filters (with 1% transmission) were used when acquiring the spectra of QDs in solution. To determine the QY of the samples, a comparison is done with a standard Rhodamine 6G fluorescent dye, seen in Fig. 3. 5 (b), which has a well known QY of 95%. The differences in number of photons absorbed between the two samples (due to differences in extinction coefficient and concentration) is taken into account by the ratio of the sample absorption and the Rhodamine absorption at the excitation wavelength,  $A_{\text{sample}}(\lambda_{\text{ex}})$  and  $A_{\text{Rho}}(\lambda_{\text{ex}})$ , respectively. To determine the number of emitted photons the PL spectra of the sample,  $I_{\text{sample}}(\lambda)$ , and the Rhodamine,  $I_{\text{Rho}}(\lambda)$ , are integrated in the range 400 nm to 700 nm. The emission spectra of the sample and the standard are recorded at the same excitation wavelength to ensure that the excitation intensity is the same in both cases. In addition, the QD samples and the rhodamine are dissolved in different solvents so the difference in refractive index must be accounted for in the calculation. Overall the formula for the QY of the QDs in solution,  $Q_{\text{QD}}$ , is given by



**Figure 3.5:** Absorption (right axis) and Photoluminescence (left axis) spectra of (a) QDs and (b) Rhodamine 6G excited at 400nm

$$Q_{QD} = \frac{A_{Rho}(\lambda_{ex})}{A_{sample}(\lambda_{ex})} \cdot \frac{\int_{400nm}^{700nm} I_{sample}(\lambda) d\lambda}{\int_{400nm}^{700nm} I_{Rho}(\lambda) d\lambda} \cdot \left( \frac{n_{sample}}{n_{Rho}} \right)^2 \cdot Q_{Rho} \quad (3.4)$$

The value of rhodamine absorption at 400 nm was 0.0233 and the integrated PL of the rhodamine with an excitation wavelength of 400 nm was 1799 (with 1% filter). The rhodamine was dissolved in methanol so  $n_{Rho} = 1.329$  and since the QDs were dissolved in toluene  $n_{sample} = 1.5$ . Substituting all these values into equation (3.4) and using the values from the QD solution spectrum one obtains

$$Q_{QD} = \frac{0.0233}{0.0178} \cdot \frac{28453}{179900} \cdot \left( \frac{1.5}{1.329} \right)^2 \cdot 0.95 = 0.251 \text{ or } \approx 25.1\%$$

Additional PL measurements are obtained from an Andor Shamrock sr-303i spectrometer with an Andor Newton 970EMCCD. This spectrometer is fiber coupled to an output port of the fluorescence lifetime imaging microscope (FLIM) used to measure time-resolved PL (TRPL) decays. Having the PL spectrometer coupled to the FLIM system allows for the acquisition of TRPL and PL spectra from the same area of the sample with the same excitation source. The samples are excited through a x40 objective using a 90 picosecond laser pulses at 405 nm with a repetition rate of 10 MHz, emission was collected back through the same objective.

### 3.3.3 Time Resolved Photoluminescence

Time resolved PL decays were measured on a PicoQuant Microtime 200 FLIM system with 90 ps time-resolution. Samples were excited using picosecond laser pulses at 405 nm, repetition rates were set to 10 MHz. Signals were recorded using a single-photon avalanche diode using a x40 objective. Decays were measured over  $20 \times 20 \mu m^2$  areas with a usual integration time of 4 ms. The spot size is  $0.43 \mu m$  and the laser powers used throughout this thesis varied from approximately 250 nW to 9  $\mu W$ . Broadband filters with a FWHM of approximately  $70 \pm 5$  nm were used to



spectrally resolve the QW and QD emission when required.

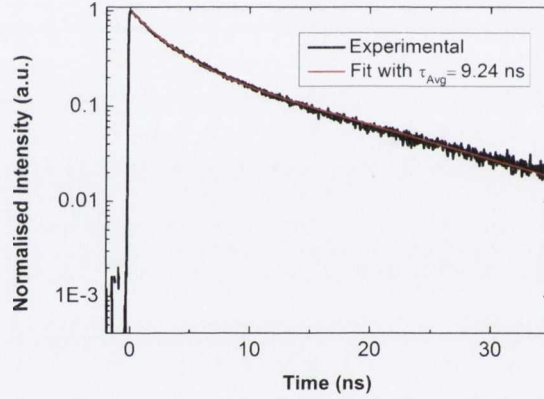
The intensity decays were found to be well-fitted with a two-exponential decay function:

$$I(t) = A_1 \cdot e^{-t/\tau_1} + A_2 \cdot e^{-t/\tau_2} + A_0 \quad (3.5)$$

where  $A_1$  and  $A_2$  are the intensity amplitudes of the decays with the two different lifetimes  $\tau_1$  and  $\tau_2$ , and  $A_0$  is the background intensity. Average lifetimes were calculated from an intensity weighted mean:

$$\tau_{Avg} = \frac{A_1 \cdot \tau_1^2 + A_2 \cdot \tau_2^2}{A_1 \cdot \tau_1 + A_2 \cdot \tau_2} \quad (3.6)$$

Fig. 3.6 shows an example of the decay curve and the two-exponential fitting, the average decay rate is then easily determined from this lifetime,  $k_{Avg} = 1/\tau_{Avg}$ .



**Figure 3.6:** Time resolved photoluminescence decay of QDs in PMMA layer. The red line is a two-exponential fit with  $\tau_{Avg} = 9.24$  ns

### 3.3.4 Thickness of the Quantum Dot Layers

Once the QDs are embedded in the PMMA matrix, they are spun down on to our GaN substrates. It is important to know how thick the acceptor QD layer is, so that the total number of available acceptors that are within a given scanning area can be calculated. To do this a Dektac profilometer is used. This is effectively an AFM tip that rasters across the layer until it drops down into a channel that has been etched out by a blade. The edge of the blade is hard enough to remove the soft PMMA but not scratch into the GaN surface. This measurement generates a height profile between the top of the QD layer and the substrate. This method has a resolution of 5 nm in the thickness of the layer. For all of the investigations in chapters 4, 5 and 6 we have a QD layer thickness of  $\sim 80$  nm on all of the plasmonic arrays. This QD layer thickness was selected because it is approximately 40 nm higher than the



height of the plasmonic arrays. As the field enhancement around the arrays drops off over approximately 20 nm above the arrays, the QDs that are much further away from this will not likely benefit from either enhanced absorption or enhanced FRET. Therefore a QD layer thickness of somewhere above 60 nm was thought to be necessary for observing both processes in this hybrid system. Therefore a layer thickness of  $\sim 80$  nm was selected.

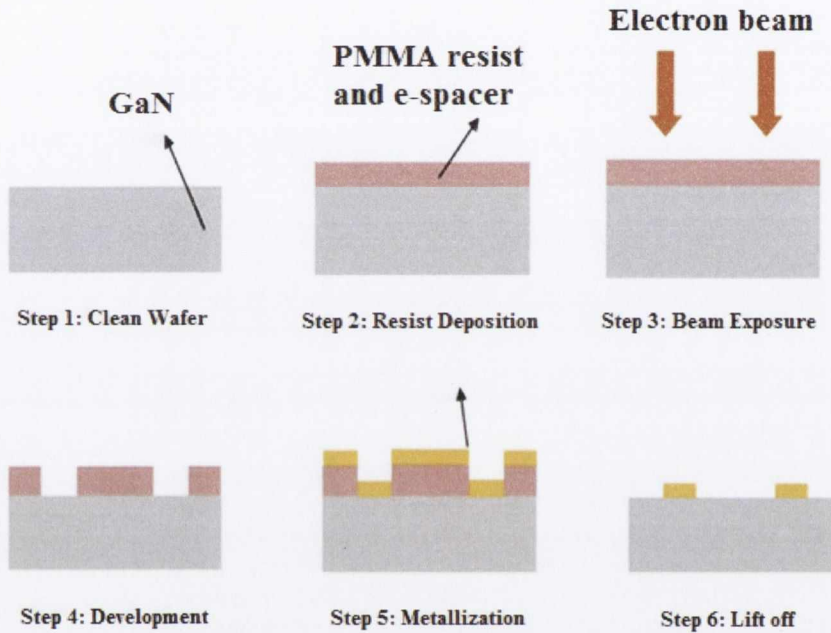
### 3.4 Fabrication of Plasmonic Arrays

In recent times, there have been numerous reports on the use of plasmonic structures, based on both metal nanoparticles and films, to enhance the emission of QWs [16–20] and QDs [22–24]. The enhanced emission can arise due to increased absorption under optical pumping, increased radiative recombination rates and/or scattering by the plasmonic nanostructures. Also, the enhanced local field generated by the plasmonic structures has been shown to facilitate plasmon-enhanced nonradiative energy transfer. This has been demonstrated in a variety of material systems and geometries, with reported enhancements of the nonradiative energy transfer distance, rate and efficiency [30–37]. The possibility to achieve higher ET efficiencies over larger distances, allows for nonradiative pumping of a larger volume of QDs, and can potentially be exploited to improve the efficiency of nonradiatively pumped down-conversion for white LEDs.

The degree to which plasmonic structures can enhance nonradiative ET between or modify the emission of various emitters depends strongly on the optical properties of the plasmonic structures themselves. Ag was chosen as the plasmonic material throughout this thesis rather than Au because the bulk absorption of Ag is blue-shifted compared to Au, therefore using Ag allows for better spectral overlap between the QW donor emission and the plasmonic structure absorption. The optical properties are sensitive to not only the material, size and shape of the structures, but within an array geometry also depend on the separation between the individual particles themselves. It is for this precise reason that careful control of the size, shape, aspect ratio and separation of metal plasmonic structures within an array geometry is vitally important. Therefore, a fabrication method that is highly diverse in the range of nanoparticles it can make with consistent reproducibility is required. For this reason two methods in particular, electron beam lithography (EBL) and helium-ion lithography (HIL) will be discussed.

### 3.4.1 Electron Beam Lithography

EBL is a fabrication process whereby a controlled, focused beam of electrons is used to draw specific patterns in an electron-sensitive layer called a resist, for the purpose of fabricating nanoscale features. A schematic of the process can be seen in Fig. 3.7. The first step in the fabrication process is to deposit the resist layer onto



**Figure 3.7:** Schematic of EBL process

the substrate *via* a spin coating technique. The resist layer used to fabricate all of the nanostructures in this thesis is PMMA. A conducting polymer layer called e-spacer is also spun down onto the sample to reduce any charging effects during exposure. Through the process of field electron emission, a beam of electrons is generated from a heated W/ZrO source. This beam is then controlled *via* magnetic lenses, so that it can be focused onto the resist layer. The electron beam modifies the resist (PMMA) by causing the long-chained PMMA to break up into smaller-chained regions. These smaller-chained areas, exposed by the electron beam, are then soluble in methyl-isobutylketone (MIBK) which allows for selective removal of these regions within the resist. This is the development process, seen as step 4 in Fig. 3.7. Following this development process, metal can be added through the use of an evaporation process, whereby the desired metal is deposited everywhere on the sample. Finally, a lift-off process can take place in which metal in the regions that were not exposed by the electron beam can be removed by immersing the sample in acetone. This dissolves the remainder of the resist layer, leaving only metal in the areas that were exposed by the electron beam. The resolution of individual plasmonic units in EBL for



positive-tone resists like PMMA is  $\sim 10$  nm [129]. However, due to both proximity and charging effects [130,131], especially on non-conducting substrates such as those used in this work, EBL can have drawbacks when attempting to fabricate features on the order of 10's of nm. This is especially true when such features are of complex shape and are tightly packed within an array. The proximity effect is predominantly a result of back-scattered electrons, which are reflected from the substrate back into the resist layer above, causing exposure of the resist in areas that are away from the original region of the incidence beam [130,131]. The backscattered electrons originate from collisions with atoms in the substrate and traverse through the resist at wide angles compared to electrons in the primary beam. For this reason helium-ion lithography can present clear advantages over EBL. This is due to the fact that helium ions have a higher resolution in direct-write lithography ( $\sim 1 - 2$  nm) and do not suffer from proximity effects like electrons do. Helium-ion lithography is discussed in the next section. It is the preferred and primary fabrication tool used.

### 3.4.2 Helium-ion Lithography

As mention earlier, helium ion lithography is a nanofabrication process, similar to EBL, except that a focused beam of helium ions are used instead of electrons to exposed the resist layer.



**Figure 3.8:** Image of Zeiss Orion Plus Helium ion Microscope

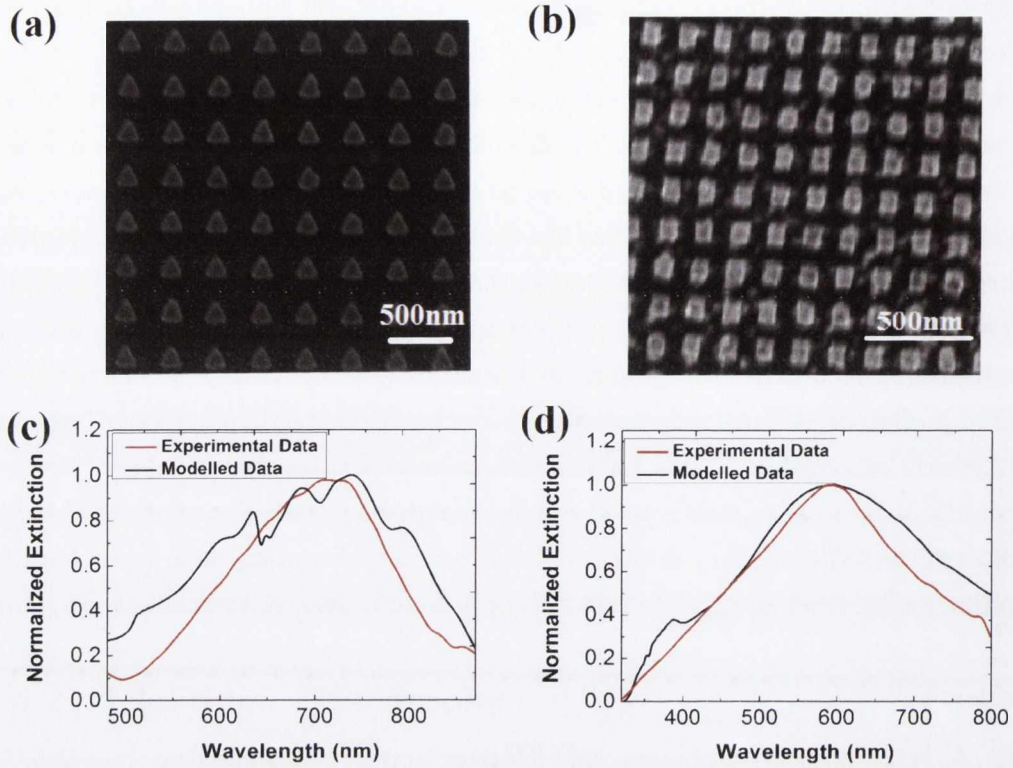
The fabrication steps are the same as for EBL, except in this case the source



consists of a sharpened needle that is at high positive voltage and low temperature in the presence of helium gas [132,133]. A trimer of atoms is generated at the tip of the source and through a process called field ionization allows for the creation of a very bright ion beam at the tip of the needle. Fig. 3.8 shows an image of the Zeiss Orion Plus helium ion microscope used to fabricate the plasmonic arrays considered in this thesis. At the tip of the source the electric field can become intense enough, over just a few atoms, that gas atoms impinging on the surface of the tip are stripped of an electron and are emitted as ions. As helium ions have a higher resolution in direct-write lithography, and produce less back-scattered electrons, the proximity effect does not impact on the ability to fabricate tightly packed arrays of well-defined nanoscale features. This explains why HIL presents clear advantages over EBL for fabricating the type of arrayed plasmonic structures considered in this thesis, and was the primary fabrication tool used. An example of a typical helium ion lithography recipe, used to fabricate a plasmonic array is shown in Appendix A.

### 3.5 Characterisation of Plasmonic Arrays

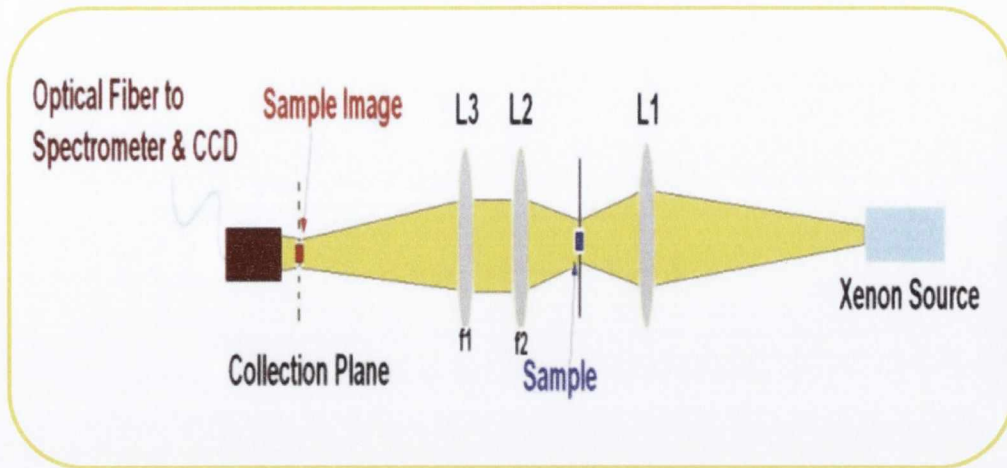
Once we have fabricated the plasmonic arrays we must characterise them, in order to confirm that they have all of the necessary properties we require. These properties include the size and shape of the nanoparticles within an array, as well as the optical properties of the array itself. One of the most straightforward ways to characterise the structures is simply to image them. To do this Scanning Electron Microscopy (SEM) was used. This is a nanoscale imaging technique in which the same electron source that is used for EBL, rasters across a magnified area of the sample and the backscattered electrons are used to generate an image of the surface. SEM images of two different plasmonic arrays fabricated on a quartz substrate are shown in Fig. 3.9 (a) and (b). Fig. 3.9 (a) shows a gold nanoprism array, where the length of the base of each triangle is 150 nm and they are each separated by a 200 nm gap. Fig. 3.9 (b) shows a silver nanobox array, where each box is 125 nm x 95 nm in size and they are each separated by a 95 nm gap. In both cases a 5 nm adhesion layer of Ti was deposited first, then the Au and Ag were deposited on top. The SEM images show that there is a large degree of uniformity across the array and the yield (or number of correctly-shaped units within the array compared to total number of units) is very high.



**Figure 3.9:** SEM image of (a) a gold nanoprism array and (b) a silver nanobox array. Experimental and theoretical extinction spectra of (c) a gold nanoprism array and (d) a silver nanobox array on a quartz substrate. Simulation data of the extinction spectra was provided by Dr. Vasilios Karanikolas.

As mention earlier, the optical properties of plasmonic structures are sensitive to the material, size, aspect ratio and shape of the individual units. The motivation behind fabricating plasmonic arrays on quartz substrates is to confirm that that fabricated arrays have the optical properties required and that those properties are the ones that were designed. The optical properties are also modified when the effective refractive index of the environment changes. We require plasmonic arrays which have an absorption peak overlapping with the donor QW emission [35, 134]. However, as the bulk GaN reference samples and single QW samples are opaque and have a roughened sapphire substrate, it is not possible to measure the extinction spectra of the arrays when fabricated directly onto the QW samples. Therefore we must fabricate plasmonic arrays on an optically transparent substrate, such as quartz, and measure the extinction of the arrays on it, by using a magnified transmission set-up to validate the fabrication. A schematic of the set-up used to measure the extinction of the arrays on quartz substrates is shown in Fig. 3.10. The transmission set-up allows us to measure the total light that is lost when passing through the arrays on quartz and therefore the extinction can be determined.





**Figure 3.10:** Schematic of magnified transmission set-up

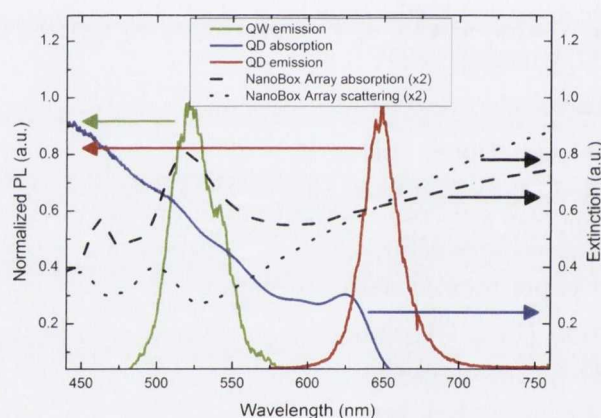
Once this optical system was built, extinction spectra were measured for a number of different plasmonic arrays and these spectra were compared to a Finite Difference Time Domain (FDTD) model. FDTD is a numerical analysis technique used for modelling computational electrodynamics by finding approximate solutions to the associated differential equations. Since it is in the time domain, it can cover a wide frequency range with a single simulation run. The extinction spectra were simulated using the FDTD Solutions from Lumerical. The dielectric permittivity of the substrate and experimental data for the dielectric permittivity of the metal used, were chosen from [135]. A plane wave excitation was used, to simulate the laser excitation used in the experiment, and periodic boundary conditions were used to simulate the fabricated array. The absorption is calculated by integrating the absolute value of the field over the volume of the lossy nanostructure. For the scattering measurements planar monitors record the field transmitted above and below by once again integrating over the area of the nanostructure as a measure of the total emission into the far-field.

Careful validation between the measured and modelled extinction spectra is of vital importance, as it allows us to test how accurately the arrays were fabricated. This then enables us to have confidence when simulating the extinction spectra of the arrays when on a GaN substrate instead of a quartz substrate. Once we confirm that the measured and modelled extinction spectra on quartz match well with one another, we can proceed to tune the physical parameters of the plasmonic arrays in an effort to tailor them to a specific QW donor. An example of the measured and modelled extinction spectra of two different plasmonic arrays are shown in Fig. 3.9 (c) and (d). We can see that there is good agreement between the overall shape and peak position for both spectra. Both the experimental and simulated extinction spectra are quite broad in Fig. 3.9 (c) as they are from a gold nanoprism array



which can have broad SPR signals. In Fig. 3.9 (d) however the spectral feature is somewhat narrower. There is also a slightly better fit between the modelled and measured results. It is worth noting that the slight differences in the peak positions between the experimental and theoretical SPR signals can be attributed to slight variation in the aspect ratio of the nanoparticles themselves.

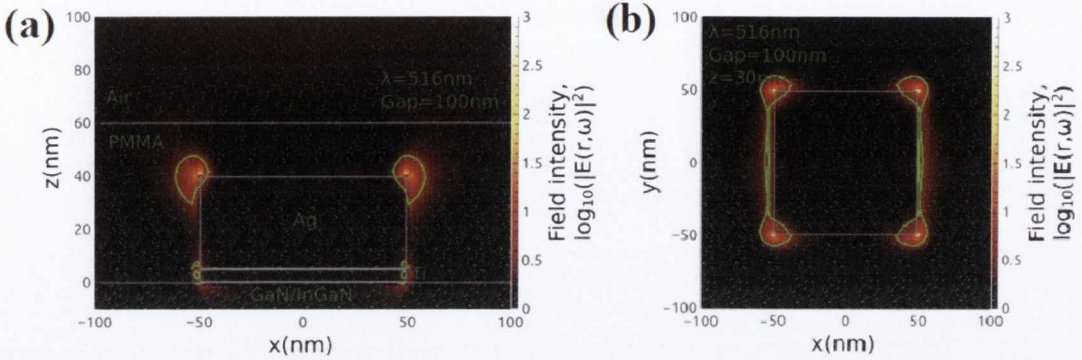
Once the absorption and scattering spectra have been simulated, this allows us to more carefully select an array that has an absorption peak which is tuned to our QW donor. It also allows us to examine how the scattering profile of the array chosen may effect the acceptor QDs in the layer independently. An example of the calculated absorption and scattering spectra of a silver plasmonic nanobox array is shown in Fig. 3.11. The particular silver nanobox array was chosen to allow for strong overlap between the peak in the array absorption with the donor QW emission.



**Figure 3.11:** Modelled absorption (dashed black line) and scattering (dotted black line) spectra for silver nanobox array, along with the absorption spectrum of the acceptor QDs (blue line) and the emission spectra of both the QW (green line) and the QDs (red line), respectively. Absorption and scattering spectra simulations were carried out by Dr. Vasilios Karanikolas.

For this silver nanobox array each box has a side length of 100 nm and a separation between consecutive units of 100 nm. It can be seen clearly in Fig. 3. 11 that the nanobox array has a peak in its absorption spectrum that is overlapping with the donor QW emission spectrum. You can also see from Fig. 3.11 that there is significant spectral overlap between the absorption and scattering spectra of the nanobox array with the acceptor QD emission spectrum. Therefore, we can expect there to be significant interaction between the QD layer and the plasmonic array by themselves, independent of the presence of the QW. Along with simulating the absorption and scattering spectra of the plasmonic arrays, we can also use FDTD simulations to generate a map of the local electric field around the plasmonic particles. This can

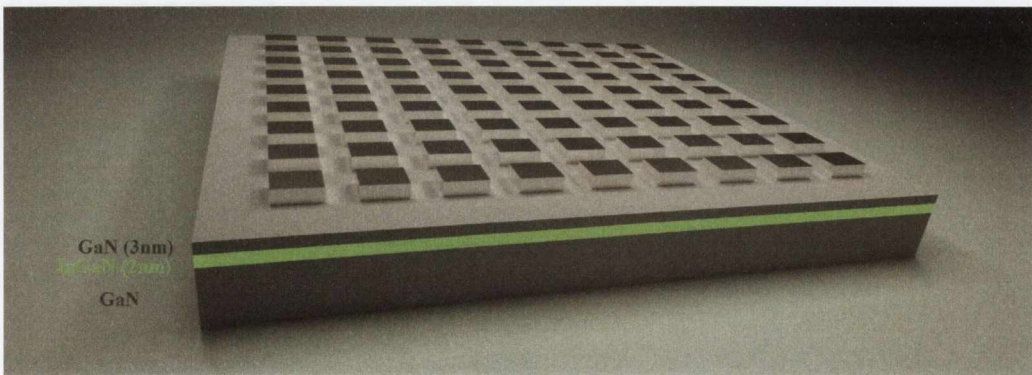
be done by using either a plane wave or a dipole excitation. An example of the electric field around a silver nanobox, the same one that was discussed in Fig. 3.11, when excited by a plane wave is shown in Fig. 3.12.



**Figure 3.12:** Electric field intensity map in (a) x-z plane and (b) x-y plane for a plane wave excitation at 516nm, for a silver nanobox with a base length of 100nm. Simulations were carried out by Dr. Vasilios Karanikolas.

It can be seen clearly from Fig. 3.12 what the electric field strength is, and how localised the field is to the edges of the nanobox. The electric field maps can be very useful in comparing one structure to another, by examining both the relative field strength and also the degree of field penetration into the surrounding media.

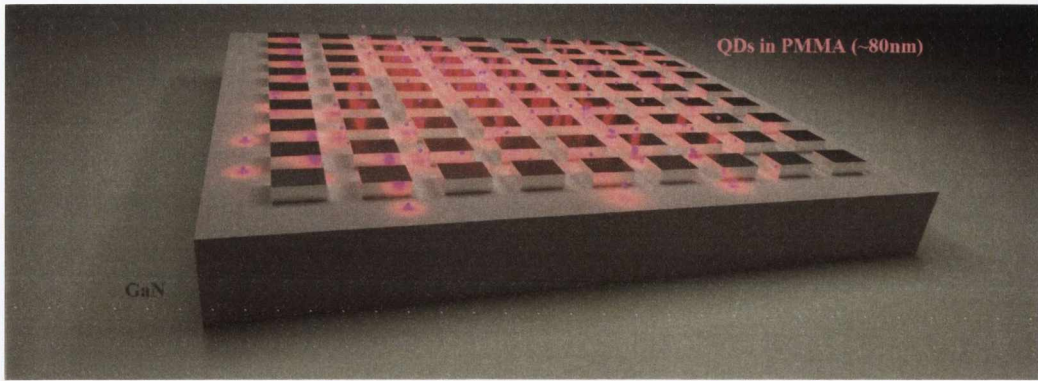
It is worth noting that in all of the work completed in chapters 4, 5 and 6, two types of reference samples (QW-Array and QD-Array) are used. These allow us to investigate how the plasmonic array interacts with both our energy donor (QW) and our energy acceptors (QD), independently. A schematic of the QW-Array reference sample is shown in Fig. 3.13.



**Figure 3.13:** Schematic of QW-Array reference sample. Schematic kindly generated by Dr. Cristian Marocico.

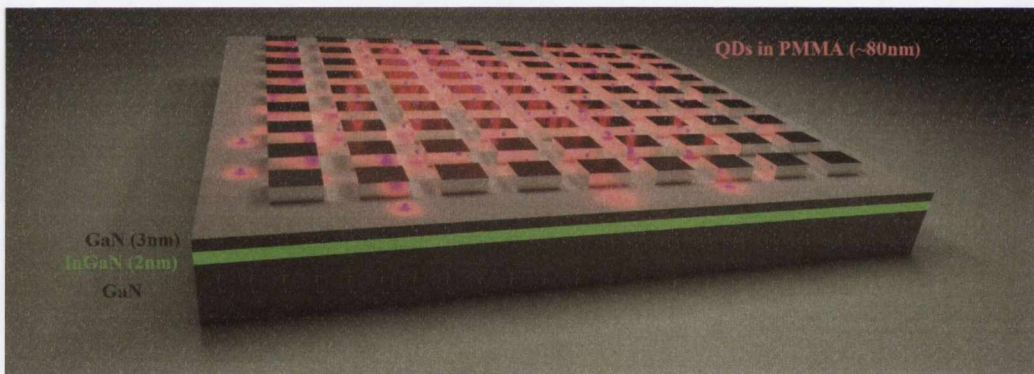
The interaction between the plasmonic array and the QW only is investigated using this sample. In this schematic, a nanobox array geometry is depicted. Next, a schematic of the QD-Array reference sample is shown in Fig. 3.14.





**Figure 3.14:** Schematic of QD-Array reference sample. Schematic kindly generated by Dr. Cristian Marocico.

Once again, the interaction between the plasmonic array and the layer of QDs only is investigated using this sample. The contribution of the plasmonic element on the QD emission and lifetime can be probed by using this sample. Finally, the full 3-component system can be used to investigate the LSP-FRET process. A schematic of the full 3-component structure (QW-Array-QD) can be seen in Fig. 3.15.



**Figure 3.15:** Schematic of 3-component system. Schematic kindly generated by Dr. Cristian Marocico.

## 3.6 Conclusion

In conclusion the materials used throughout this thesis and the methods by which we characterise them have been introduced. The different samples that are necessary for the work in this thesis have been identified and the structures for the observation of FRET in the QW donor-Array-QD acceptor system were described. The motivation for the choice of fabrication technique has been provided and the specific characterisation methods for the plasmonic arrays that were fabricated have been introduced. Interestingly, the QW-Array-QD system seems remarkably stable as the same level of acceptor emission enhancements can be seen approximately two years after initial measurements.



In chapter 4 the first experimental demonstration of LSP mediated FRET from a QW to a layer of QDs will be presented. Furthermore, a deeper understanding of the carrier density dependence of LSP-FRET within our QW-QD system will be provided, to both identify the nature of our donor carriers and to understand how the plasmonic arrays influence the process.



# 4 Carrier Density Dependent Study of LSP mediated FRET

## 4.1 Introduction

As mention in chapter 1, the development of high-efficiency semiconductor light emitting diodes (LEDs) for applications in solid-state lighting (SSL) has received a great deal of attention in recent years. The white light generation is typically achieved using phosphor coatings on top of a blue or UV emitting LED [5]. Phosphors have some considerable drawbacks including emission in the far-red part of the spectrum, poor color rendering and scattering [6], this is why inorganic nanocrystal quantum dots (QDs) can be used as an alternative to phosphors in such devices. Radiative pumping is the most commonly used energy transfer mechanism within these LED devices even though FRET has the potential to be more efficient [9, 10]. This is due to losses that can occur in the multi-stepped radiative pumping process such as limited photon extraction and light scattering. Strategies to efficiently extract photons from LEDs have been a topic of considerable research [7, 8]. However, as nonradiative energy transfer does not require the emission and extraction of the photons but rather the energy is transferred directly to the QDs, this provides for the possibility of FRET being used as an alternative to radiative pumping in such devices. A significant drawback for FRET-based devices is its strong dependence on the separation between the donor and acceptor, showing an  $r^{-6}$  dependence with a characteristic distance of typically less than ten nanometers. In recent times, there have been numerous reports on the use of plasmonic structures, based on both metal nanoparticles and films, to enhance the emission of QWs [16–20] and QDs [22–24]. Also, the enhanced local field generated by the plasmonic structures has also been shown to facilitate plasmon-enhanced nonradiative energy transfer between emitters. The possibility to achieve higher energy transfer efficiencies over larger distances allows for nonradiative pumping of a larger volume of QDs, and can potentially be exploited to improve the efficiency of nonradiatively pumped down-conversion for white LEDs. In this chapter we report on the use of an array of Ag nanoboxes, fabricated using helium-ion lithography (HIL), on an InGaN/GaN QW to enable localised surface plasmon (LSP)-enhanced nonradiative energy transfer to a  $\sim 80$



nm layer of CdSe/ZnS QDs. The thickness of the QD acceptor layer and the dimensions of the Ag nanoboxes (100 nm x 100 nm x 40 nm) are large compared with previous reports of plasmon-coupled nonradiative energy transfer [34, 43]. Secondly, there has been no report on the carrier density dependence of the plasmon-coupled nonradiative energy transfer, which is a first step towards implementation in electrically pumped LEDs. In this chapter we specifically investigate if the carrier density dependence of the plasmon-coupled nonradiative energy transfer is determined by the same physics as conventional nonradiative energy transfer. FRET from QWs to QDs is known to strongly depend on the QW excitations, excitons or unbound electron-hole pairs [136]. There are some factors which may influence the plasmon-coupled nonradiative energy transfer efficiency, such as, when a plasmonic element is introduced, it can influence the carrier density dependence of the QW emission rate and spectral profile. For example, it has been demonstrated that coupling to plasmonic structures can suppress the efficiency droop in QW LEDs. The emission spectrum from the coupled QW-plasmon system may also be modified relative to the bare QW [137]. The strength of the QW-plasmon coupling is reflected in the modified spontaneous emission rate. Plasmon-coupled nonradiative energy transfer is sensitive not only to the spectral overlap of the donor and acceptor with each other, but also with the spectrum of the plasmon mode [25, 34]. The plasmon-coupled nonradiative energy transfer efficiency is determined by the interplay between the QW spontaneous emission rate, the rate of nonradiative energy transfer to the plasmonic structure and the rate of plasmon-coupled nonradiative energy transfer to the acceptors. In this chapter the carrier density dependence of plasmon-coupled FRET efficiency is investigated by probing the carrier density dependences of the individual rates and it is found that in the system under study, the plasmon-enhanced nonradiative energy transfer efficiency is constant over the full carrier density range. We also show enhancement of the emission of the CdSe/ZnS QDs acceptors embedded in a  $\sim 80$  nm thick poly(methyl methacrylate) (PMMA) layer on top of the QW structure. The work presented in this chapter is published in Optics Express (see list of publications).

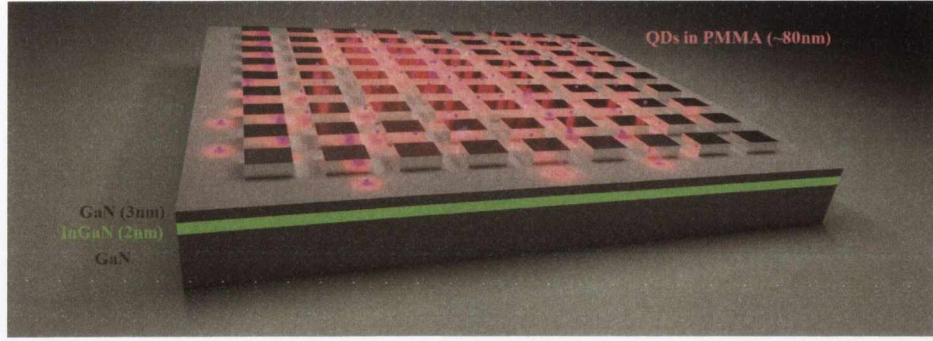
## 4.2 Experimental Methods

A schematic of the complete structure is shown in Fig. 4.1 (a). A Ag nanobox array has been fabricated on a single InGaN QW structure and, subsequently, covered in a layer of CdSe/ZnS core-shell QDs embedded in a  $\sim 80$  nm thick layer of PMMA. The single QW structure used in this chapter was grown by metal-organic vapour phase epitaxy (MOVPE) on a thick GaN layer on a c-plane sapphire substrate. The QW is 2 nm thick InGaN capped with a 3 nm GaN barrier. It has a peak emission

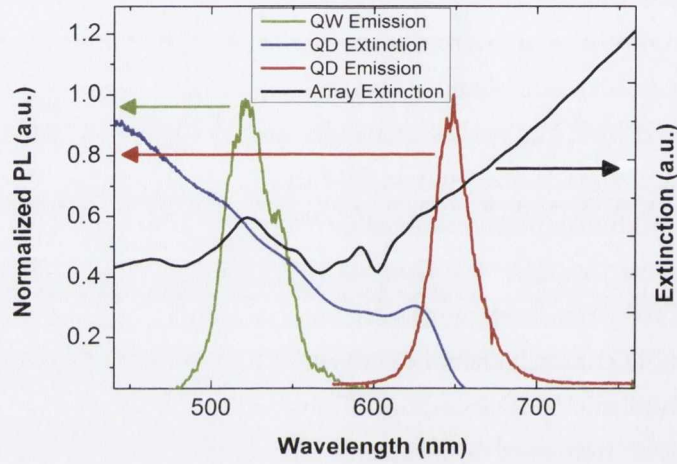
wavelength of 516 nm, shown in Fig. 4.1. The thin top barrier GaN layer was selected to allow for strong near-field coupling between the QW and the plasmonic nanoparticles. A Ag nanobox array was fabricated on top of the GaN barrier using Helium-Ion Lithography (HIL) and a standard lift-off procedure. A 100 nm thick layer of PMMA was first spun onto our GaN top surface and patterned using a Zeiss Orion Plus helium-ion microscope (HIM). After the development of the PMMA, a 5 nm thick layer of Ti followed by a 35 nm thick layer of Ag was deposited using a metal evaporation process. The Ag nanobox array was finally created by a lift-off process. The array consists of nanoboxes arranged in a two-dimensional square lattice with overall dimensions of  $52\ \mu\text{m} \times 52\ \mu\text{m}$ . A HIM micrograph of the array of 100 nm square boxes with 160 nm gap is shown in Fig. 4.2. The image shows that there is a large degree of uniformity across the entire array and that the aspect ratio of each individual unit is well maintained. The QDs are CdSe/ZnS core-shell nanocrystals with a diameter of 6.3 nm and a peak emission wavelength of 649 nm, shown in Fig. 4.1. The QDs are embedded in PMMA by first adding the QDs in toluene to a 2.5 % wt. PMMA (also dissolved in toluene) solution. This mixture is then sonicated to ensure the QDs are thoroughly dispersed. The solution is then spun down onto the QW decorated by the NP array to create a layer of QDs in PMMA. The layer has a QD concentration of  $(1.9 \pm 0.1) \times 10^{21}\ \text{m}^{-3}$ . The QD layer thickness has been measured with a Dektac6 profilometer. It is found that the thickness of the PMMA layer is increased by  $(19 \pm 5)$  nm on the array compared with a  $(60 \pm 5)$  nm thickness off the array. The QD concentration used represents approximately 5-6 QDs per unit cell for the nanobox arrays, for example. The deposition of the QD layer completes the hybrid structure.

The emission and energy transfer processes were characterised using photoluminescence (PL) spectroscopy and time-resolved photoluminescence (TRPL). For PL measurements the samples were excited at normal incidence using a pulsed 405 nm laser diode focused using a x40 objective lens. The PL spectra were measured using a fiber-coupled Andor grating spectrometer. The PL decays were measured using a PicoQuant Microtime 200 time-resolved confocal microscope with 90 ps time resolution. The QW or QD emission bands were selected using broad-band filters with a full-width-at-half-maximum of  $(70 \pm 5)$  nm centred at 500 nm and 650 nm, respectively. The decay signals and spectra were recorded over an area of  $20\ \mu\text{m} \times 20\ \mu\text{m}$ . All measurements were made at room temperature. The dimensions and periodicity of the Ag nanoboxes were selected to have overlap of the surface plasmon resonance with the QW donor emission. The nanobox arrays were designed using finite difference time domain commercial software FDTD Solutions from Lumerical Inc. The simulations took account of the PMMA layer on top of the Ag nanoboxes and the 5 nm Ti layer. The dielectric permittivity of the Ag and Ti materials are





(a)

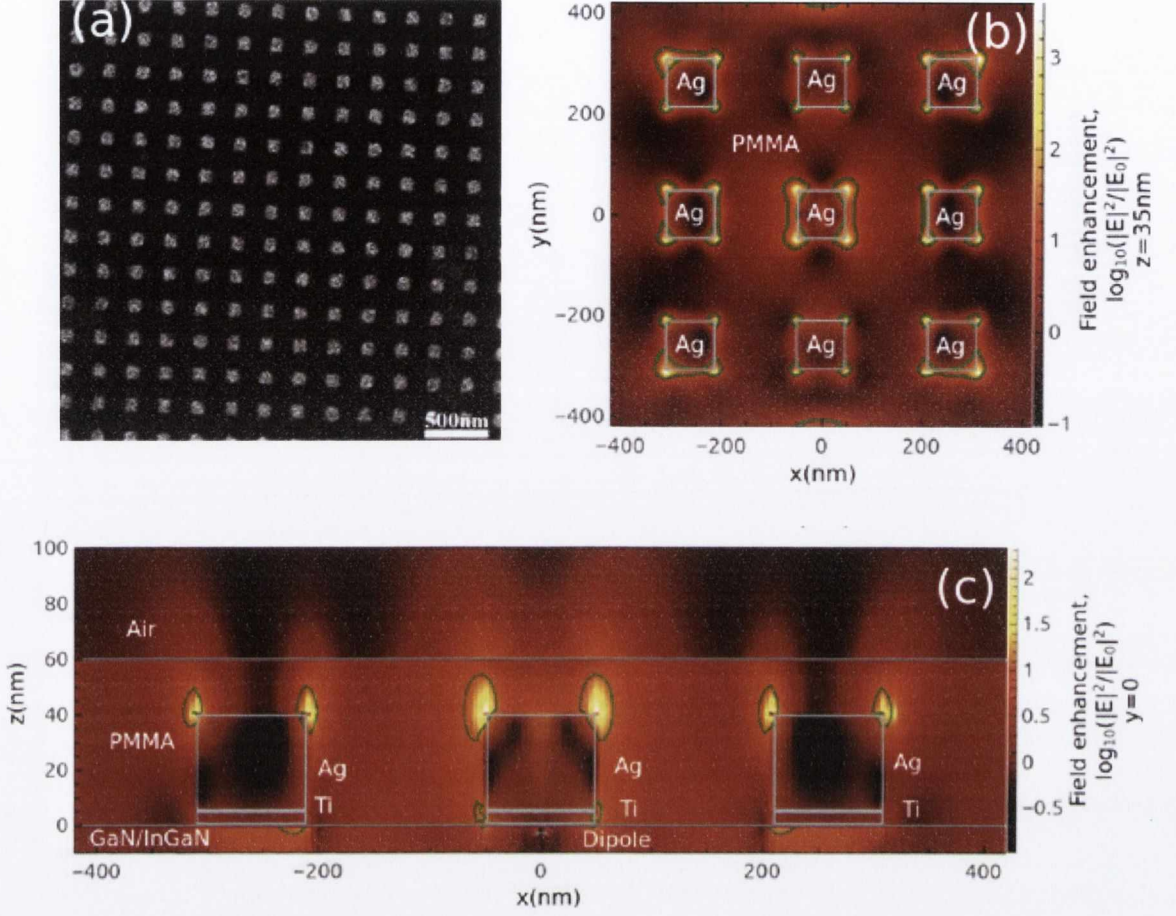


(b)

**Figure 4.1:** (a) A schematic of the complete structure. (b) The normalized emission spectra of the QW and QDs (left-hand axis) along with the extinction spectrum of the QDs and the extinction spectrum of the Ag nanobox array (right-hand axis). Schematic kindly generated by Dr. Cristian Marocico. Extinction spectrum simulations carried out by Dr. Vasilios Karanikolas.

included using experimentally measured data [135]. The GaN and PMMA layers are modelled with a constant dielectric permittivity of  $\epsilon_{GaN} = 5.35$  and  $\epsilon_{PMMA} = 2.2$ , respectively. The extinction spectrum of the Ag nanobox array is simulated using plane-wave excitation. A map of the electric field intensity enhancement due to a dipole source, emitting at 516 nm and placed in the QW below the centre of a nanobox, is shown in Fig. 4.2. The field enhancement is calculated relative to the same layered structure without the Ag nanoboxes. Fig. 4.2 (b) and (c) show the x-y and x-z maps respectively. It can be seen that for this dipole position the field intensity is enhanced over an extended volume in the vicinity of the Ag nanobox array. It should be noted that the field intensity enhancement is highly dependent on the position of the dipole source.





**Figure 4.2:** (a) HIM image of a square array of Ag nanoboxes with 100 nm lateral dimension and 160 nm gap fabricated by HIL on top of the GaN barrier. The field intensity enhancement map in (b) the x-y plane and (c) the x-z plane for a dipole excitation at 516 nm, positioned in the QW layer directly below the Ag nanobox at  $x=y=0$ . The olive line indicates where the field intensity is enhanced by a factor of 10. Field intensity simulations carried out by Dr. Vasilios Karanikolas.

### 4.3 Results and Discussion

The dependence of the QW emission properties are considered first. The calculation of the injected carrier density,  $n$ , is given by Eqn. 4.1,

$$n = \frac{P}{(h\nu) \cdot \theta \cdot d_{active} \cdot f} \cdot [1 - \exp(-\alpha_{InGaN} \cdot d_{active})] \cdot (1 - R) \quad (4.1)$$

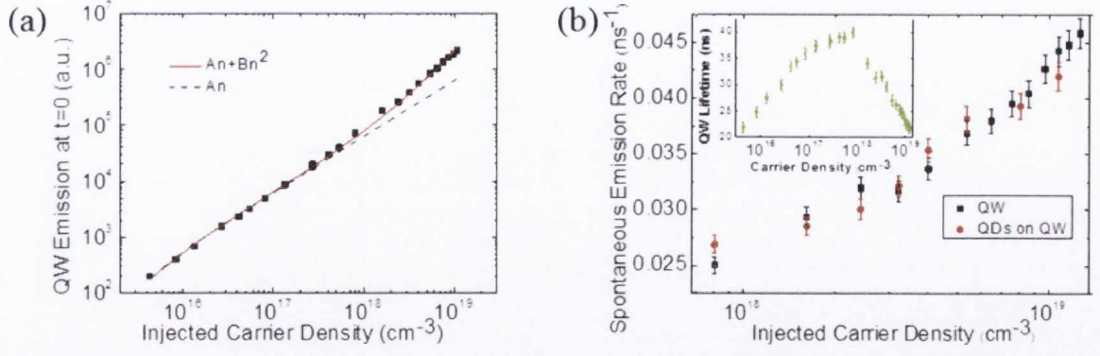
where  $P$  is the laser pumping power,  $h\nu$  is the energy of the injected photons,  $\theta$  is the spot size of pumping laser,  $d_{active}$  is the thicknesses of the active region,  $f$  is the repetition rate of pumping laser,  $\alpha_{InGaN}$  is the absorption coefficient of the InGaN QW, and  $R$  is the reflectance at the wavelength of the pump laser at 405 nm, respectively [138]. Here the spot diameter is 0.43  $\mu\text{m}$ ,  $d_{active}$  is 2 nm,  $f$  is 10 MHz,  $\alpha_{InGaN}$  is  $10^4 \text{ cm}^{-1}$  and  $R$  is 0.15. The laser powers used throughout this chapter

varied from approximately 250 nW to 9  $\mu$ W. The PL intensity of the single QW as a function of injected carrier density,  $n$ , is shown in Fig. 4.3 (a). The intensity is measured from the PL decay at  $t = 0$ . At lower carrier densities the PL increases linearly while at higher excitation powers a quadratic dependence is present, which is characteristic of free-carrier recombination. There is some evidence of saturation at the highest carrier densities which may be due to carrier leakage, however there is no evidence of any Auger effects present even at the highest carrier density ranges investigated. In the inset of Fig. 4.3 (b) we show the average PL lifetime of the single QW, over the same range of injected carrier densities. The PL decay curves for both the QW and the QDs are fit with a bi-exponential and the average PL lifetime is given by Eqn. 4.2,

$$\tau_{avg} = \frac{I_1 \cdot \tau_1^2 + I_2 \cdot \tau_2^2}{I_1 \cdot \tau_1 + I_2 \cdot \tau_2} \quad (4.2)$$

where  $I_1$  and  $I_2$  are the intensity amplitudes of the exponential decays with two different lifetimes  $\tau_1$  and  $\tau_2$ , respectively. It can be seen that in the lower carrier density range, up to approximately  $1 \times 10^{18} \text{ cm}^{-3}$ , the lifetime increases. This is attributed to the presence of defect related nonradiative recombination centres [139]. At higher carrier densities these defect states become saturated and the average lifetime begins to decrease as the excitation intensity is further increased. In this range the radiative recombination processes dominate. We concentrate on the higher carrier density range from  $1 \times 10^{18} \text{ cm}^{-3}$  to  $2 \times 10^{19} \text{ cm}^{-3}$  from this point forward. Figure 4.3 (b) shows the spontaneous emission rate of the QW as a function of injected carrier density with and without the addition of the QDs in the absence of the Ag nanobox array, and , respectively. The introduction of the QDs has no measurable effect on the QW PL decay rate indicating that there is insignificant direct nonradiative energy transfer from the QW to the QD layer in the absence of the plasmonic nanostructures. It should be noted that for all measurements, of the bare QW and the nanobox decorated QW, there is a layer of PMMA deposited on top to facilitate direct comparison of the QW PL lifetime with the structures having QDs embedded in the PMMA host layer.





**Figure 4.3:** (a) The QW emission at  $t=0$  as a function of injected carrier density. (b). The spontaneous emission rate of the QW with (red circles) and without (black squares) QDs as a function of injected carrier density. Inset: The average QW PL lifetime as a function of injected carrier density.

Next the interaction of the QW and QDs with the Ag nanobox array is examined. Fig. 4.4 (a) shows the PL decays of the bare QW, the QW with the Ag nanobox array deposited on top, and the completed structure with the QD layer. The decays were recorded at an injected carrier density of  $5.4 \times 10^{18} \text{ cm}^{-3}$ . It is noted that the QW PL lifetime and emission are dramatically reduced due to the presence of the Ag nanobox array. They are further reduced by the addition of the QDs. Considering, firstly, the effect of the Ag nanobox array on the QW emission, the reduction in PL lifetime and emission signifies a quenching process due to nonradiative energy transfer from the QW to the metal nanoparticles. Emission quenching by energy transfer to metal nanoparticles has been extensively reported by the literature [134, 140, 141]. This can be quantified as a quenching efficiency,  $\eta_Q$ , which is given by Eqn. 4.3,

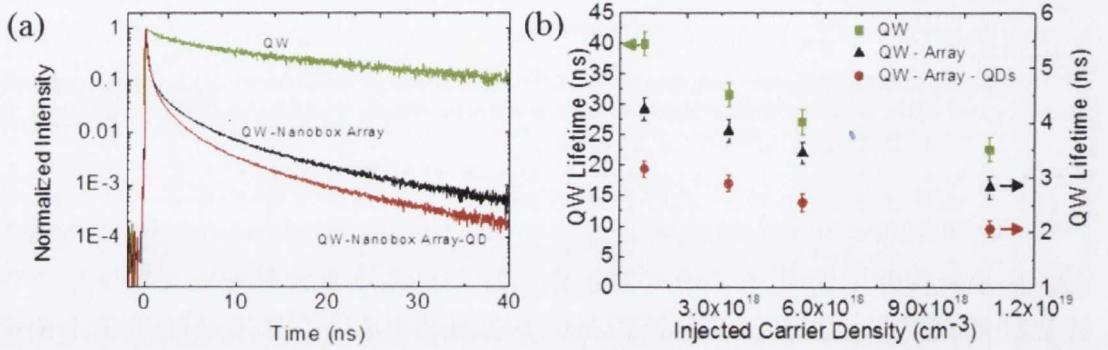
$$\eta_Q = 1 - \frac{\tau_{QW-Array}}{\tau_{QW}} \quad (4.3)$$

where  $\tau_{QW} = (27 \pm 2) \text{ ns}$  is the average PL lifetime measured for the bare QW and  $\tau_{QW-Array} = (3.5 \pm 0.2) \text{ ns}$  is the average PL lifetime for the QW decorated with the Ag nanobox array. The quenching is  $(90 \pm 10)\%$  indicating a very strong interaction between the QW and Ag nanoboxes. The further reduction of the QW lifetime and emission after the addition of the QDs indicates the presence of Forster-like nonradiative energy transfer from the QW to the QDs. This is evidence for LSP enhancement of the nonradiative energy transfer process mediated by the Ag nanoboxes since, as noted earlier, in the absence of the Ag nanobox array no measurable signatures of nonradiative energy transfer from the QW to the QDs could be observed. The plasmon-coupled nonradiative energy transfer efficiency,  $\eta_{FRET}$ , is defined by Eqn. 4.4,

$$\eta_{FRET} = 1 - \frac{\tau_{QW-Array-QD}}{\tau_{QW-Array}} \quad (4.4)$$



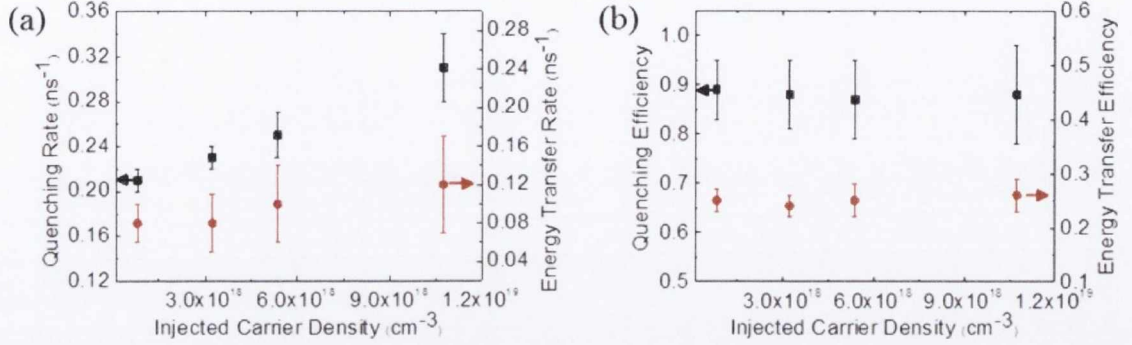
where  $\tau_{QW-Array-QD} = (2.6 \pm 0.2)$  ns is the QW PL lifetime after the addition of the QD layer. For the example shown in Fig. 4.4(a) a plasmon-enhanced nonradiative energy transfer efficiency of  $(25 \pm 3) \%$  is observed. Fig. 4.4 (b) shows the average PL lifetime of the bare QW, the QW decorated with the Ag nanobox array and the QW with both the Ag nanoboxes and QDs, as a function of the injected carrier density. The average lifetime of the QW-Ag nanobox-QD structure is shorter relative to the QW-Ag nanobox structure at all carrier densities.



**Figure 4.4:** (a) The normalized PL decays of the bare QW (green line), the QW with nanobox array (black line) and the QW with nanobox array and QD layer (red line) at a carrier density of  $5.4 \times 10^{18} \text{ cm}^{-3}$ . (b) The average PL lifetime of the bare QW (green squares), the QW with nanobox array (black triangles) and the QW with nanobox array and QD layer (red circles) as a function of injected carrier density.

Fig. 4.5 (a) shows the carrier density dependence of the quenching and QW to QD nonradiative energy transfer rates. Both increase with increasing carrier density. As previously reported the carrier density dependence of the Förster nonradiative energy transfer rate from a QW is determined by whether the electronic excitations in the QW are free electrons and holes or bound electron hole pairs (excitons) [9,136]. For donor QW free carriers the energy transfer rate is proportional to the carrier density, whereas it is independent of carrier density for donor QW excitons. A linear dependence of the direct nonradiative energy transfer rate from an InGaN QW to a monolayer of CdSe QDs has been experimentally reported and found to be in good agreement with a theoretical model for free carrier QW excitations [136]. The QW PL quenching by the Ag nanobox array is also considered to arise due to nonradiative energy transfer to the metal nanoparticle acceptors. The observed linear dependence of the quenching rate on the carrier density therefore suggests nonradiative energy transfer from free carrier excitations in the donor QW. This is consistent with the earlier analysis of the QW emission properties, presented in Fig. 4.3, which showed evidence of free carrier recombination in this carrier density range. The plasmon-coupled nonradiative energy transfer from the QW to the QDs indicates a similar behaviour, though it is noted that the errors on the measured rates in this case are larger due to smaller lifetimes (see Fig. 4.4 (b)). The QW excitations are the donors

for both nonradiative energy transfer to the metal nanoparticles and to the QDs, therefore, a similar carrier density dependence might be expected for both cases. However, further evidence for the trend of the plasmon-coupled energy transfer rate can be obtained by looking at the energy transfer efficiency and this will be discussed below.



**Figure 4.5:** (a). The QW emission quenching rate (black squares) and the plasmon-coupled non-radiative energy transfer rate (red circles) as a function of the injected carrier density. (b) Quenching efficiency (black squares) and plasmon-coupled nonradiative energy transfer efficiency (red circles) as a function of injected carrier density.

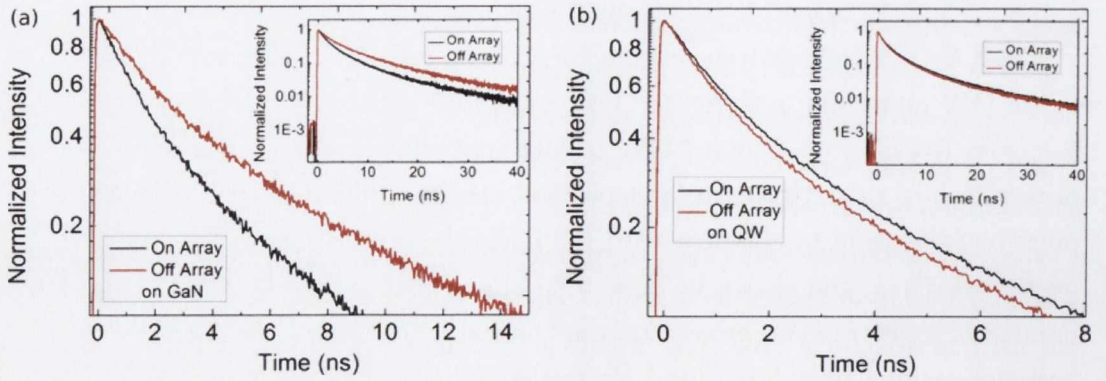
The quenching efficiency, and plasmon-coupled QW to QD nonradiative energy transfer efficiency, were calculated from the QW lifetimes using Eqns. 4.3 and 4.4. Both efficiencies are found to be independent of the injected carrier density, as seen in Fig. 4.5 (b). The quenching efficiency is approximately 90% across the full carrier density range, while the plasmon-coupled QW to QD nonradiative energy transfer has an efficiency of approximately 25 %. The nonradiative energy transfer efficiency can also be expressed as

$$\eta_{FRET} = \frac{k_{FRET}}{k_{QW} + k_{QW-Array} + k_{FRET}} \quad (4.5)$$

where  $k_{QW}$  is the spontaneous emission decay rate for the bare QW,  $k_{QW-Array}$  is the QW quenching rate for the QW decorated with the Ag nanobox array and  $k_{FRET}$  is the plasmon-coupled QW to QD nonradiative energy transfer rate. The observation of a carrier density independent energy transfer efficiency confirms that must be increasing to compete with the increasing QW spontaneous emission and quenching rates, and shown in Figs. 4.3 (b) and 4.5 (a), respectively. There are a number of aspects of this process that are noteworthy. Firstly, the Ag nanobox array provides a sufficiently large local electromagnetic field to allow for a nonradiative energy transfer path between the QW and QDs that is otherwise too weak to measure in the absence of the plasmonic nanostructures. Secondly, the plasmon-enhanced nonradiative energy transfer rate is sufficiently fast to compete with the efficient QW quenching across the full carrier density range. Thirdly, the increase in the



nonradiative energy transfer efficiency indicates an increase in the distance over which the energy transfer occurs. The conventional nonradiative energy transfer efficiency can be written as  $(1 + \frac{r^n}{R_0^n})^{-1}$  where  $r$  is the separation between the donor and acceptor dipoles,  $R_0$  is the characteristic distance at which the energy transfer efficiency is 50% and the exponent  $n$  depends on the geometry. For example, for nonradiative energy transfer between two point dipoles  $n=6$  and from a point dipole to a plane of acceptors  $n=4$ . Therefore, the increase in the nonradiative energy transfer efficiency can be expressed as a plasmon-enhanced  $R_0$ . Finally, the plasmon-enhanced nonradiative energy transfer is found to have the same dependence on carrier density as conventional Forster-like energy transfer from QW free carriers excitations to colloidal QDs in the absence of the plasmonic structures. Up to this point we have focussed on the properties of the plasmon-coupled energy transfer in this hybrid system extracted from the changes in the QW lifetime, however, there is also evidence of the plasmon-coupled energy transfer in the QD emission. Fig. 4.6 (a) shows the QD PL decays on and off a Ag nanobox array fabricated on a bulk GaN layer. This allows us to investigate the interaction between the QDs and the Ag nanoboxes with the same excitation source but in the absence of the QW. A  $(27 \pm 3) \%$  reduction in the QD average PL lifetime is observed on the array relative to off the array. Furthermore, Fig. 4.6 (b) shows the QD PL decays both on and off the Ag nanobox array on the QW sample. In this case the QDs on the array show an  $(12 \pm 2) \%$  increase of the PL lifetime relative to QDs off the array. Therefore, the influence of the plasmon-enhanced energy transfer is sufficiently strong that the QD PL lifetime not only recovers from the reduction on the array but is even further increased. The decay over 40 ns is presented in the inset, while the decay over the first 8 ns is given in the main Fig. to more clearly show the change in the PL decay.

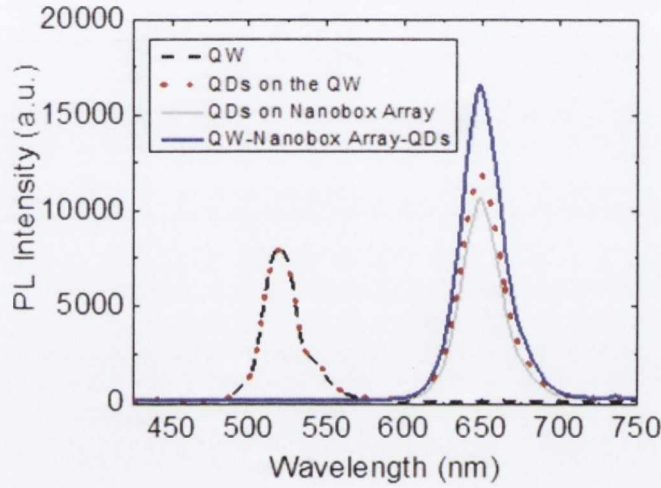


**Figure 4.6:** (a) The QD PL decay on and off the Ag nanobox array on a GaN bulk layer. (b) QD PL decay on and off of Ag nanobox array on the QW sample. The insets show the PL decays over 40 ns.

The PL spectra for the QW and QDs, with and without the Ag nanobox array,



are shown in Fig. 4.7. Firstly, from the PL spectra for the bare QW and the QW with the QDs in the absence of the Ag nanobox array it is clear that the presence of the QDs alone have little influence on the QW emission. The influence of the nanobox array on the QD emission is observed in the PL spectrum for the QDs on the Ag nanobox array on the bulk GaN layer. The direct interaction between the Ag nanoboxes and the QDs results in quenching of the QD emission by  $(11 \pm 4)\%$ . This reduction in QD emission is also confirmed by integrating the TRPL decays for the QDs on and off the array on the bulk GaN layer. As discussed earlier the QW emission is highly quenched by the Ag nanobox array.



**Figure 4.7:** PL spectra of the bare QW (dashed black line), QDs on the QW (red dotted line), QDs on the Ag nanobox array on the bulk GaN layer (grey line), and complete QW-Ag nanobox-QD system (blue solid line).

Finally, when we look at the PL spectrum of the complete QW-Ag nanobox-QD structure, it can be seen that the QW emission is effectively completely quenched and that the QD emission not only recovers from the direct quenching by the Ag nanobox array but exhibits an emission enhancement of  $(41 \pm 10)\%$  relative to the QW-QD structure. Again, this enhancement of the QD emission is confirmed by integrating the TRPL curves for the QDs on and off the Ag nanobox array on the QW. These QD PL quenching and enhancement factors are measured by direct comparison of the PL on and off the Ag nanobox array. However, taking account of the difference in the PMMA layer thickness on the Ag nanobox array compared with off the array, and the volume filled by the Ag nanoboxes, the corrected QD PL quenching and enhancement are 27 % and 16 %, respectively. It is noted that the plasmon-coupled nonradiative energy transfer has compensated for the direct quenching of the QD PL by the Ag nanobox array to yield an overall enhancement of the QD layer emission. Comparing the emission from the QDs on the nanobox

array with the QD emission in the full structure (spectra shown in Fig. 4.7) shows that the enhancement due to the plasmon-coupled energy transfer mechanism alone is 58%.

## 4.4 Conclusions

In conclusion, we have investigated plasmon-enhanced nonradiative energy transfer from an InGaN/GaN SQW to core-shell CdSe/ZnS QDs embedded in a  $\sim 80$  nm host PMMA layer. The plasmonic structure is a Ag nanobox array fabricated by HIL and designed such that the QW emission peak spectrally overlaps with the LSP resonance. Both the QW emission quenching rate and the plasmon-coupled nonradiative energy transfer rate were found to increase with increasing QW carrier density. The quenching and energy transfer efficiencies were carrier density independent. A quenching efficiency of 90 % of the QW emission by the Ag nanobox array and a QW to the QD plasmon-enhanced energy transfer efficiency of 25 % were observed. Despite strong direct quenching by the metal nanoparticles, the plasmon-coupled energy transfer results in a 16 % increase of the QD emission. Further optimization of the properties of the nanobox array and the QD layer thickness may yield higher enhancement of the QD emission. The carrier density dependence of the nonradiative energy transfer from the QW to the Ag nanobox array and that of the plasmon-enhanced nonradiative energy transfer from the QW to the QD layer are found to be the same as for conventional Förster-like energy transfer. This indicates that secondary effects of the plasmon coupling, such as spectral shifts, do not have a significant effect in the system studied. It should also be noted that whilst very strong direct quenching of the QW emission was observed with the silver nanobox array, this is not necessarily our goal, however it may not represent a disadvantage for potential device application as strong quenching of a UV emitting QW for example would reduce the need for UV filtering in the LED device.

Whilst this chapter focussed mainly on the use of a particular Ag nanobox array geometry to facilitate plasmon-enhanced nonradiative energy transfer from a QW to a thick layer of QDs, other plasmonic structures were used to demonstrate this process. The details of the different nano-arrays used and how they influence both the LSP-NRET and the overall QD emission will be discussed in detail in chapter 5. It should be noted that in all other cases involving LSP-NRET within this system, whereby other nano-arrays were used, the carrier density dependence displayed similar effects. This is unsurprising as the same QW and QDs were used, and therefore as the donor carriers are once again free-carriers, the trends in the carrier density dependence studies were similar.



# 5 Nanostructure Dependent Study of LSP Mediated FRET

## 5.1 Introduction

In the previous chapter the first ever experimental demonstration of LSP-FRET from a QW donor to a layer of QD acceptors was presented. Whilst this is a significant result, as it shows that QWs can nonradiatively pump thicker layers of QDs by utilizing plasmonic elements, it was only demonstrated for one particular Ag nanobox array. As the optical properties of plasmonic NPs can be tuned by varying their material, size and shape [42], this allows them to interact more strongly with different emitters by tuning the level of spectral overlap between the two species and also by changing the local field enhancement factor and distribution. Within an arrayed design these optical properties can be controlled even further by tuning the level of interaction between individual NPs within the array, which can be achieved by varying the gap between consecutive plasmonic elements. Other work done on LSP-FRET within different geometries showed that by changing the size of colloidal NPs, for example, the spectral overlap with the donor is automatically lost [30,34,43, 85,86,142]. However, within the array geometry a systemic shape dependence study can be investigated where spectral overlap is maintained. Variation in the plasmonic array design can modify the level of LSP enhanced absorption and emission processes within the QW-QD system by changing the absorption and scattering profile. The change in the array geometry may also impact the LSP-FRET within the system. A range of silver plasmonic arrays, with varying shape and size were fabricated onto both QW and bulk GaN substrates. For each of the plasmonic arrays there was spectral overlap between the absorption of the array and the emission of the QW, a requirement for observing LSP-FRET [25,34]. The level of scattering of the plasmonic arrays at the acceptor wavelength varies from one array to another, which will impact the degree of interaction between the QDs and the arrays by themselves on the bulk GaN substrate. Therefore, within the range of plasmonic arrays selected, different levels of both LSP enhanced FRET and enhanced absorption and scattering processes can be expected. The ability to tune these processes could be exploited in applications as either a colour tuning or a colour switching plasmonic device. Colour

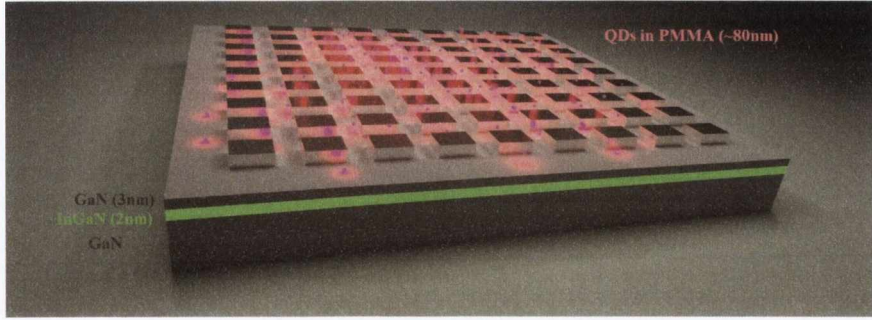


switching could be achieved by selecting a plasmonic array that quenches the donor emission strongly along with maintaining LSP-FRET to the acceptor. The colour tuning could be achieved by a combination of both LSP enhanced absorption and emission of either the donor or acceptor and enhanced FRET between them.

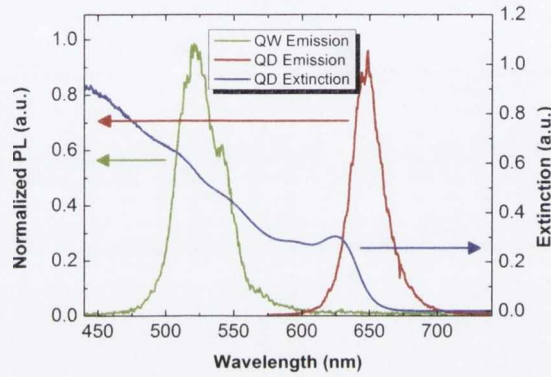
In this chapter an investigation into the effect that the different plasmonic arrays have on the LSP-FRET mechanism from a InGaN/GaN QW donor to QD acceptors embedded in an  $\sim 80$  nm layer of PMMA is presented. Once again, TRPL and spectral measurements are used to demonstrate and quantify the LSP-FRET from the QW to the QDs. Modification of the QD emission on the GaN substrate can be explained through a combination of both LSP enhanced absorption and emission processes. Furthermore, the change in the QD emission from the GaN substrate to the QW substrate is shown to be due to the LSP-FRET process alone. The work presented in this chapter is published in Nanoscale (see list of publications).

## 5.2 Experimental Methods

A schematic of the complete structure is shown in Fig. 5.1 (a). As in the previous chapter, Ag nanoparticle (NP) arrays were fabricated on a single InGaN QW structure and, subsequently, covered in a layer of CdSe/ZnS core-shell QDs embedded in a  $\sim 80$  nm thick layer of PMMA. The single QW was grown by metal-organic vapour phase epitaxy (MOVPE) on a thick GaN layer on a c-plane sapphire substrate. The QW is 2 nm thick InGaN capped with a 3 nm GaN barrier. The photoluminescence (PL) spectrum, given in Fig. 5.1 (b), shows a peak emission wavelength of 516 nm and a FWHM of 40 nm. The barrier thickness of 3 nm was selected to allow for strong near-field coupling between the excitons in the QW and the plasmonic NPs. The NP arrays were fabricated using Helium-Ion Lithography (HIL). PMMA is first spun onto the GaN capping layer surface and patterned using a Zeiss Orion Plus helium-ion microscope. Following the development, 5nm of Ti and 35nm of Ag are deposited using a metal evaporation process, and then the arrays are finally created by a lift-off process. The arrays consisted of various different shapes and sizes. The different structures and dimensions are described in Table 5.1 and the helium-ion microscopy (HIM) images are shown in Fig. 5.2. Each array contained units that were arranged in a symmetric two-dimensional square lattice with  $200 \times 200$  units in each array giving overall dimensions of between  $34 \mu\text{m} \times 34 \mu\text{m}$  to  $70 \mu\text{m} \times 70 \mu\text{m}$ .



(a)



(b)

**Figure 5.1:** (a) Schematic of complete hybrid structure. (b) QW PL (green line), QD absorption (blue line) and QD emission (red line) spectra. Schematic kindly generated by Dr. Cristian Marocico.

The QDs are CdSe/ZnS core-shell nanocrystals with a diameter of 6.3 nm and a peak emission wavelength of 649 nm. The spectrum is shown in Fig. 5.1 (b). The QDs are embedded in PMMA by first adding the QDs in toluene to a 2.5 % wt. PMMA (also dissolved in toluene) solution. This mixture is then sonicated to ensure the QDs are thoroughly dispersed. The solution is then spun down onto the QW decorated by the NP array to create a layer of QDs in PMMA. The layer has a QD concentration of  $(1.9 \pm 0.1) \times 10^{21} \text{ m}^{-3}$ . The QD layer thickness has been measured with a Dektac6 profilometer. It is found that the thickness of the PMMA layer is increased by  $(19 \pm 5) \text{ nm}$  on the array compared with a  $(60 \pm 5) \text{ nm}$  thickness off the array. The deposition of the QD layer completes the hybrid structure, shown in Fig. 5.1 (a). The same solution of QDs is spun down on the Ag array decorated GaN substrate for reference measurements.



| Label | Shape | Unit Dimension (nm) | Gap (nm) |
|-------|-------|---------------------|----------|
| B1    | Box   | 100                 | 100      |
| B2    | Box   | 100                 | 130      |
| B3    | Box   | 100                 | 160      |
| R     | Ring  | 250 Outer Diameter  |          |
|       |       | 150 Inner Diameter  | 100      |
| D1    | Disc  | 70 Diameter         | 100      |
| D2    | Disc  | 70 Diameter         | 130      |
| D3    | Disc  | 70 Diameter         | 160      |

**Table 5.1:** Shapes and sizes of nanostructures fabricated directly onto QW and bulk GaN substrates.

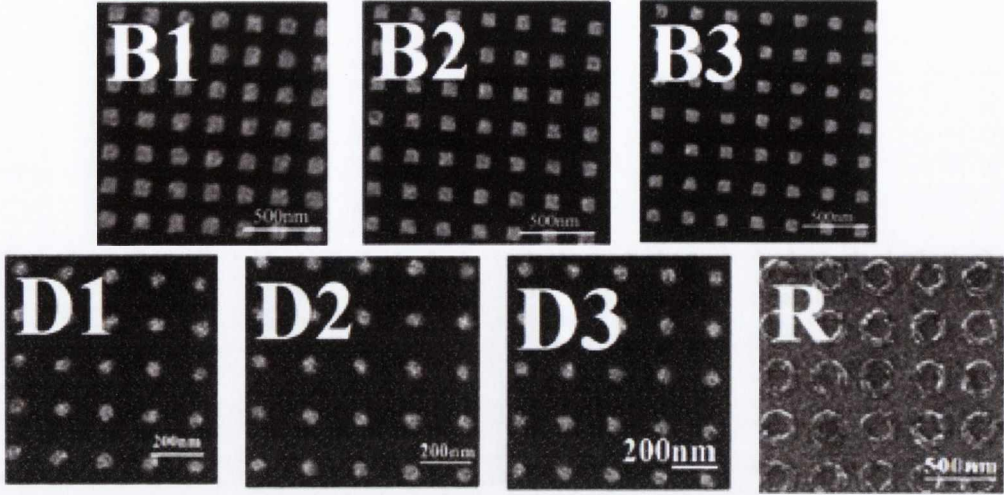
The emission and energy transfer (ET) processes were characterised using PL spectroscopy and time-resolved photoluminescence (TRPL). For PL measurements the samples were excited at normal incidence using a pulsed 405 nm laser diode focused using a x40 objective lens. The PL spectra were recorded using a fiber-coupled Andor grating spectrometer. The PL decays were measured using a PicoQuant Microtime 200 time-resolved confocal microscope with 90 ps temporal resolution. The QW or QD emission bands were selected using broad-band filters with a full-width-at-half-maximum of  $(70 \pm 5)$  nm centred at 500 nm and 650 nm, respectively. The PL decays and spectra were recorded over an area of  $20 \mu\text{m} \times 20 \mu\text{m}$ . All measurements were made at room temperature. The PL decay curves for both the QW and the QDs are fit with a bi-exponential and the average PL lifetime is given by Eqn. 5.1,

$$\tau_{avg} = \frac{I_1 \cdot \tau_1^2 + I_2 \cdot \tau_2^2}{I_1 \cdot \tau_1 + I_2 \cdot \tau_2} \quad (5.1)$$

where  $I_1$  and  $I_2$  are the intensity amplitudes of the exponential decays with two different lifetimes  $\tau_1$  and  $\tau_2$ , respectively.

The dimensions and periodicity of the Ag nanostructures were selected such that each array had overlap of the surface plasmon resonance with the QW donor emission [34, 35]. HIM micrographs of all of the seven nanostructure arrays are shown in Fig. 5.2. The images clearly show that there is a large degree of uniformity across the arrays and that the aspect ratio of each individual unit is also well maintained.





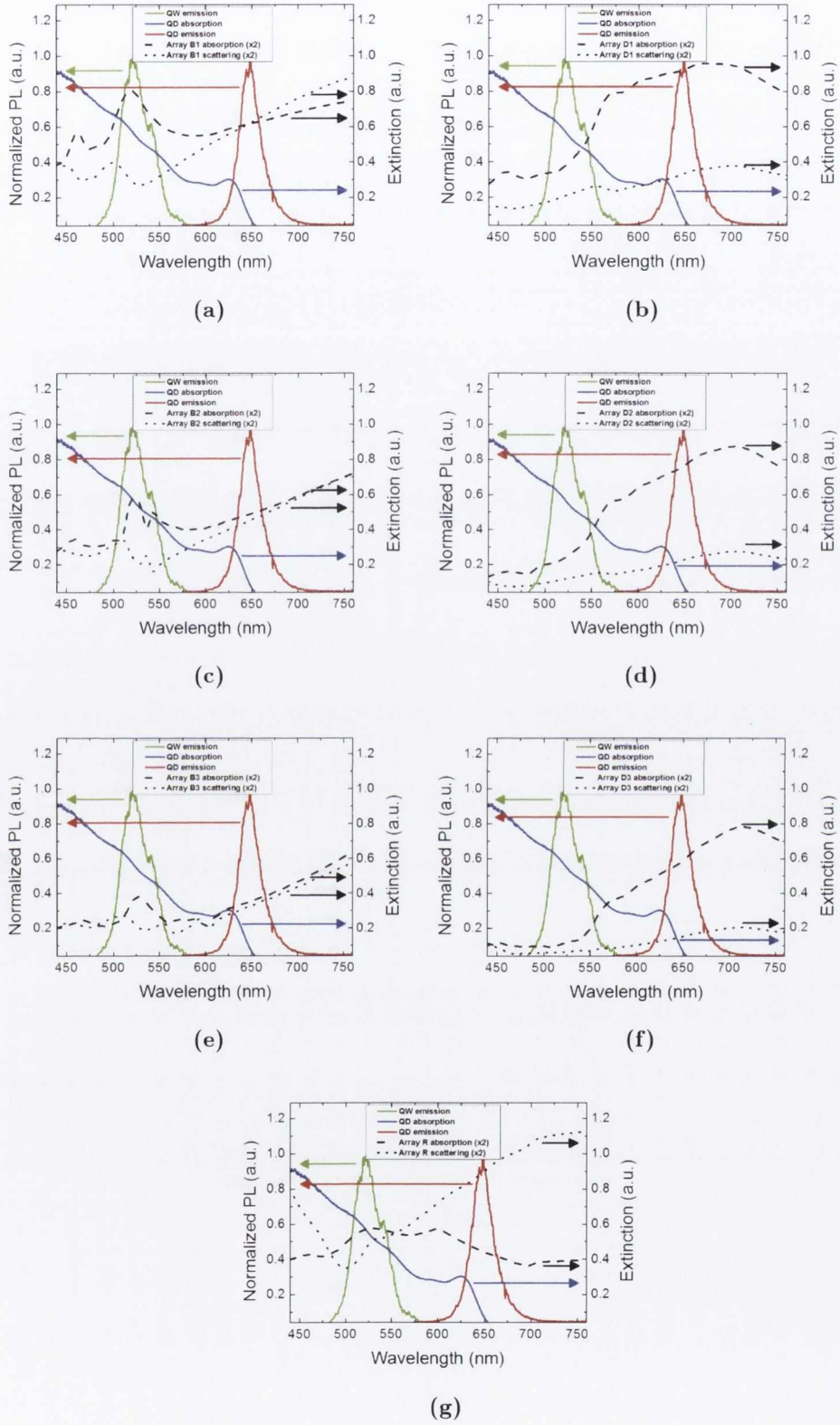
**Figure 5.2:** HIM images of B1, B2, B3 arrays (scale bar 500nm); D1, D2, D3 arrays (scale bar 200nm) and Ring array (scale bar 500nm).

The NP arrays were designed using Lumerical, a finite difference time domain (FDTD) commercial software. The absorption and scattering spectra of the Ag nanobox array are simulated using plane-wave excitation. The simulations took account of the PMMA layer on top of the Ag nanoboxes and the 5 nm Ti layer. The dielectric permittivity of the Ag and Ti materials are included using experimentally measured data [135]. The GaN and PMMA layers are modelled with a constant dielectric permittivity of  $\epsilon_{GaN} = 5.35$  and  $\epsilon_{PMMA} = 2.2$ , respectively.

As mentioned earlier, the optical properties of plasmonic nanoparticles can be tuned by changing their shape and size. This can modify both their absorption and scattering. As discussed in chapter 2, the extinction cross-section,  $C_{ext} = C_{abs} + C_{scatt}$ , where  $C_{abs}$  is the absorption cross-section and  $C_{scatt}$  is the scattering cross-section. By modifying the NPs absorption and scattering, one can control the level of interaction between NPs and different emitters. Therefore, a range of silver plasmonic arrays with varying absorption and scattering spectra were fabricated onto both QW and bulk GaN substrates. The change in the absorption of the different arrays at the QW donor emission wavelength can impact the level of LSP-FRET within the system. The calculated absorption and scattering spectra for each of the seven arrays are given in Fig. 5.3. It can be seen from Fig. 5.3 that for the box and nanoring arrays, a peak in the absorption spectra overlaps the donor emission spectrum in each case. For the nanodisc arrays there is overlap between the absorption spectra and the QW emission spectrum even though no clear peak in the array absorption spectra is present. Also, the level of scattering at the acceptor wavelength clearly varies from one array to another and this will impact the degree of interaction between the QDs and the arrays by themselves on the

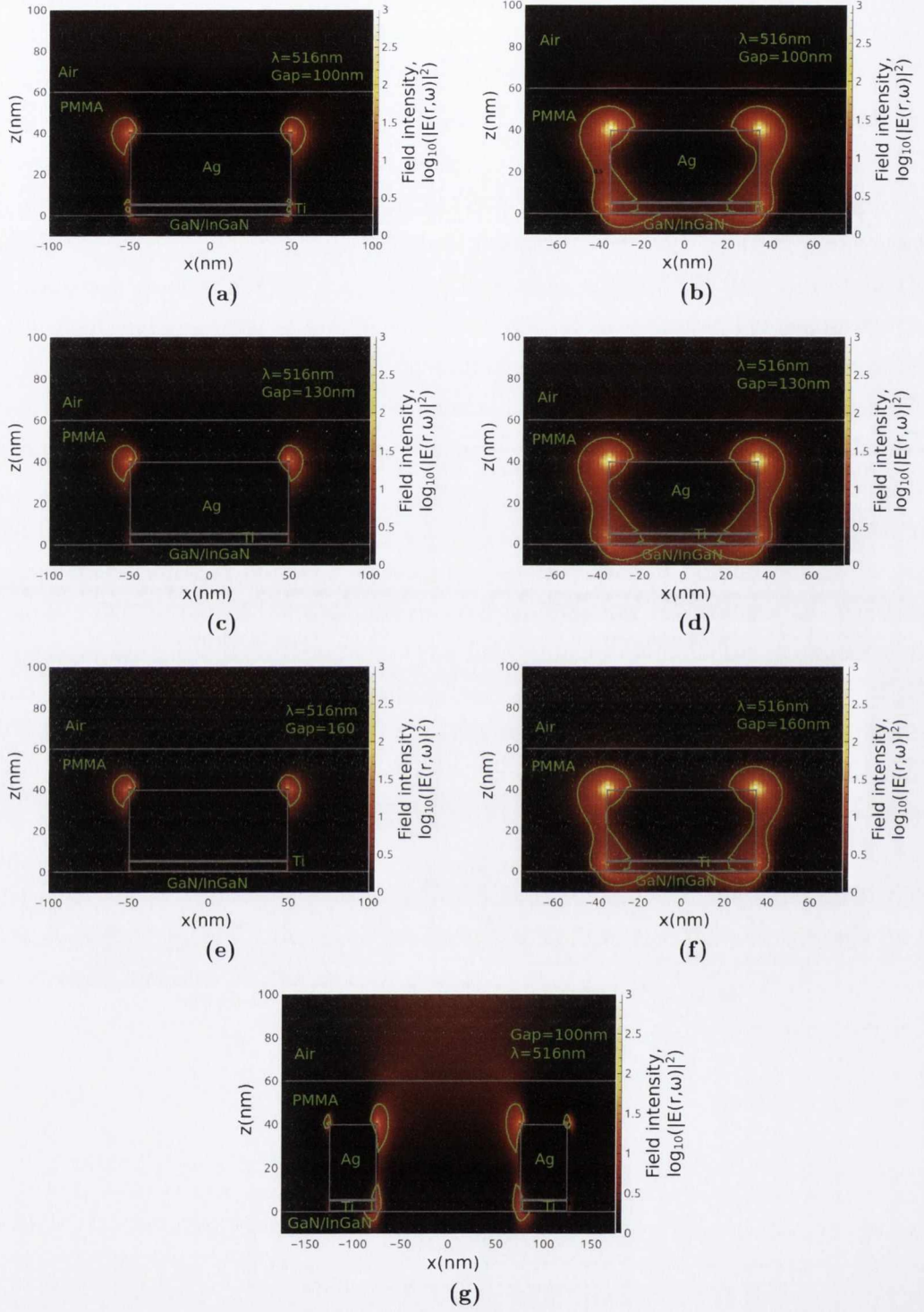
bulk GaN substrate. However, the absorption and scattering spectra of the different plasmonic arrays are not the only parameters to consider when trying to select a plasmonic geometry that could enable FRET. By examining the electric field enhancement generated around the NPs and the level of field penetration into the surrounding media, selecting a plasmonic array for a specific donor-acceptor FRET pair becomes more achievable. The local electric field intensity maps at the donor emission wavelength for the seven arrays studied, generated using a plane wave excitation are shown in Fig. 5.4. There is a clear variation of the extent of the electric field and the level of enhancement across the structures. For example, the field is more strongly localised to the nanoboxes and it extends for a much greater distance for the nanoring. This is emphasised by the green line which shows the position at which  $\log_{10} |E|^2 = 0.5$ , or where the electric field intensity is enhanced by a factor of  $\sqrt{10}$  compared to in the absence of the plasmonic array. It should be noted that the images presented in Fig. 5.4 are cropped so that they are easier to compare to one another but they do in fact represent different boundaries as the gap increases. The extent of the field is expected to influence the volume of QDs that can interact with the nanostructure. The field enhancement factor is expected to influence the absorption of the excitation laser source as well as the emission of the QW and QDs and the energy transfer between them. The local electric field intensity maps at the acceptor emission wavelength for the seven arrays studied, generated using a plane wave excitation are shown in Fig. 5.5. Once again, there is a clear variation of the extent of the electric field and the level of enhancement across the structures. For example, the field is more strongly localised to the nanobox arrays and it extends slightly for the nanodisc arrays. Also, the electric field extends for a much greater distance for the nanoring array.



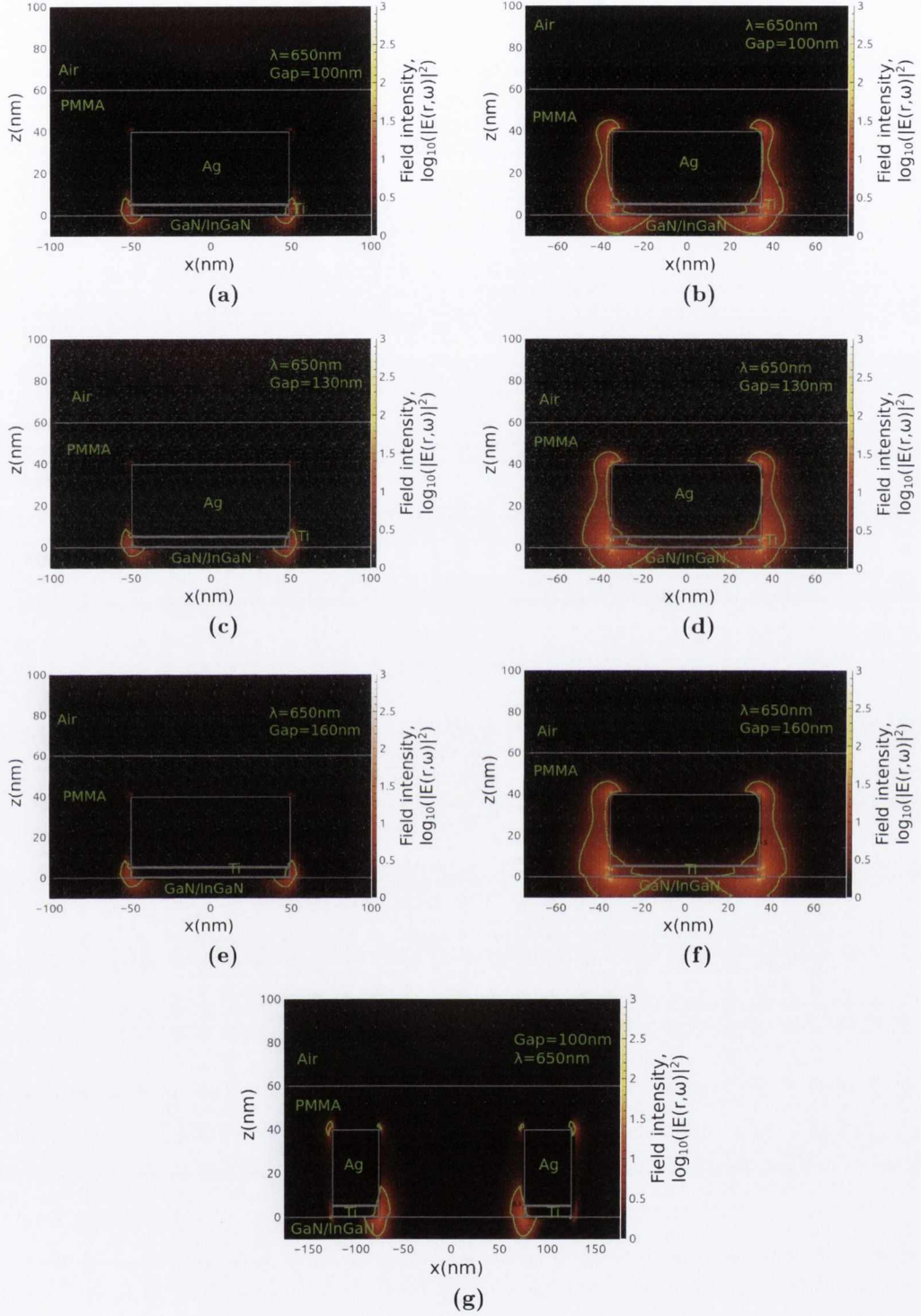


**Figure 5.3:** QW PL (green line), QD absorption (blue line) and PL (red line) spectra, along with absorption (dashed black line) and scattering (dotted black line) spectra for Box arrays B1, B2, B3 (a,c,e), Disc arrays D1, D2, D3 (b,d,f) and Ring array (g), respectively. The simulated absorption and scattering spectra were provided by Dr. Vasilios Karanikolas.





**Figure 5.4:** Maps of the field intensity in the x-z plane at the donor emission wavelength for Box arrays B1, B2, B3 (a,c,e), Disc arrays D1, D2, D3 (b,d,f) and Ring array (g), respectively under plane wave excitation. The green line gives  $\log_{10}(|E|^2) = 0.5$  for direct comparison. The simulation data was provided by Dr. Vasilios Karanikolas.

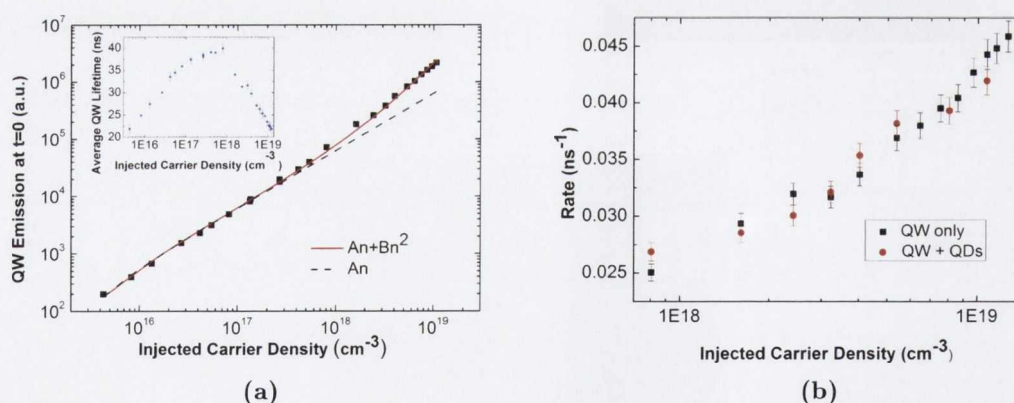


**Figure 5.5:** Maps of the field intensity in the x-z plane at the acceptor emission wavelength for Box arrays B1, B2, B3 (a,c,e), Disc arrays D1, D2, D3 (b,d,f) and Ring array (g), respectively under plane wave excitation. The green line gives  $\log_{10}(|E|^2) = 0.5$  for direct comparison. The simulation data was provided by Dr. Vasilios Karanikolas.



### 5.3 Results and Discussion

As in the previous chapter, all measurements are taken in the radiative recombination regime of the donor QW where the defects states have been saturated by excitation. The QW sample used in this chapter is the same as the one used in chapter 4, so the details of the decay dynamics are repeated here for completeness. The decay dynamics of the QW as a function of the injected carrier density are examined first. The PL intensity of the single QW as a function of injected carrier density,  $n$ , is shown in Fig. 5.6 (a). The inset of Fig. 5.6 (a) shows the average lifetime of the QW as a function of carrier density. It can be seen that in the lower carrier density range, up to approximately  $1 \times 10^{18} \text{ cm}^{-3}$ , the lifetime increases. This is attributed to the presence of defect related nonradiative recombination centres [139]. At higher carrier densities these defect states become saturated and the average lifetime begins to decrease as the excitation intensity is further increased. It can be seen from Fig. 5.6 (b) that the spontaneous emission rate of the donor QW increases with the carrier density in the range above  $1 \times 10^{18} \text{ cm}^{-3}$  and this increasing spontaneous emission rate combined with an  $n^2$  dependence on the QW emission, seen in Fig. 5.6 (a), indicates that within this carrier density range radiative recombination dominates. Therefore the FRET measurements will be carried out at a carrier density of  $5.4 \times 10^{18} \text{ cm}^{-3}$ .



**Figure 5.6:** (a) The QW emission at  $t=0$  as a function of injected carrier density. Inset: The average QW PL lifetime as a function of injected carrier density. (b). The spontaneous emission rate of the QW with (red circles) and without (black squares) QDs as a function of injected carrier density.

After the deposition of the QD layer on the QW, in the absence of the arrays, there is no measurable effect on the QW lifetime, as seen in Fig. 5.6 (b). This demonstrates that there is no significant direct FRET from the QW to the QDs away from the arrays. To facilitate direct comparison of measurements on structures



with and without the QDs, a layer of PMMA is deposited on top of the bare QW and NP decorated QW structures.

For each NP array, the influence that the NP array has on the emission properties of the QW and QDs, as well as the direct energy transfer from the QW to the QDs is characterised separately. Taking the nanoring array as an example, Fig. 5.7 shows the TRPL data for the QW by itself (green line), the QW with the nanoring array (black line), and the QW with the nanoring array after the addition of the QD layer (red line). It can clearly be seen that the QW lifetime is significantly reduced when on the nanoring array. This quenching process is quantified by the quenching efficiency term [25] as in chapter 4, with the details repeated here for completeness. In this case the quenching efficiency,  $E_Q$ , is given by Eqn. 5.2.

$$E_Q = 1 - \frac{\tau_{QW-Array}}{\tau_{QW}} \quad (5.2)$$

Here the quenching is  $(84 \pm 10) \%$  which indicates a very strong interaction between the QW and the nanoring array. This quenching efficiency for all seven arrays is shown in Fig. 5.8. It is fairly constant with an average value of  $(85 \pm 12) \%$ . To simulate this quenching process, the theoretical quenching efficiency of the QW is introduced as:

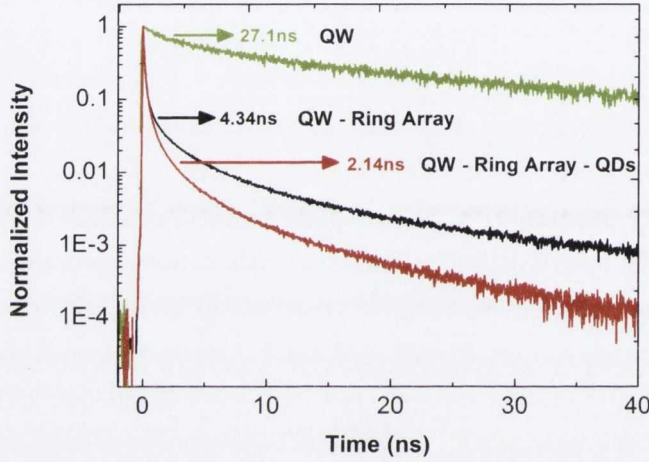
$$E_Q = \frac{k_{QW-NP}^{ET}}{k_{QW-NP}} \quad (5.3)$$

where  $k_{QW-NP}^{ET}$  represents the energy transfer rate from the donor QW to the acceptor NP array and  $k_{QW-NP}$  represents the total decay rate of the Ag array decorated donor QW. Here  $k_{QW-NP}^{ET} = k_{QW-NP} - k_{QW}$ . To simulate the quenching efficiency of the donor QW, a large number (500) of electric point dipoles with random positions and orientations were placed in the InGaN layer representing the donor QW and these dipoles were restricted to the central unit cell of a  $5 \times 5$  array of acceptor NPs. The nonradiative and total decay rates of these dipoles are calculated. From this, the quenching efficiency can be calculated *via* the above expression. The mean of this distribution is taken as the value of the quenching efficiency, and its standard error generates the error bar. These simulations were completed by Dr. Cristian Marocico. The simulated data for all seven arrays is also shown in Fig. 5.8 and excellent agreement with the experimental data is achieved.

The QW lifetime is even further reduced when the QD layer is added, as seen in Fig. 5.7. This further reduction in the QW lifetime is evidence of a plasmon-enhanced nonradiative energy transfer from the QW to the QDs. Using Eqn. 5.4 the plasmon enhanced energy transfer efficiency is found to be  $(51 \pm 7) \%$  [25],

$$E_{FRET} = 1 - \frac{\tau_{QW-Array-QD}}{\tau_{QW-Array}} \quad (5.4)$$

This represents a significant enhancement of the energy transfer efficiency. As commented earlier, there is no directly measureable FRET from the QW to the QDs when the NP array is not present, seen in Fig. 5.6 (b). The enhancement of the energy transfer process is large enough for the LSP-FRET to the QD layer to compete with the very efficient quenching of the QW by the NP array and the intrinsic spontaneous emission rate of QW.

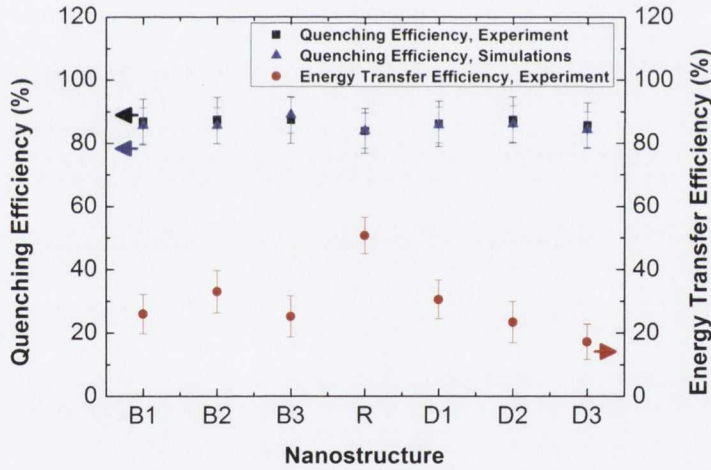


**Figure 5.7:** Normalized decay curves of QW only (green line), QW with nanoring array (black line) and QW with nanoring array and QD layer (red line), at a carrier density of  $5.4 \times 10^{18} \text{ cm}^{-3}$ .

The energy transfer efficiency for all seven arrays is also shown in Fig. 5.8, to allow for both comparison of the structures and comparison with the quenching efficiency. Whilst the quenching efficiency is observed to be relatively static, the energy transfer efficiency shows a much greater variation from structure to structure. Looking firstly the three nanobox geometries, the energy transfer efficiency is approximately 30 % in all cases, and appears to be relatively insensitive to the change in gap from 100 nm (B1) to 160 nm (B3), respectively. Whilst spectral overlap exists between a peak in the absorption spectra of the nanobox arrays and the QW emission spectrum, the level of absorption decreases from B1 to B3, as seen in Fig. 5.3 (a,c,e). However, despite this clear reduction in the absorption at the donor emission wavelength, a static trend in the LSP-FRET efficiency amongst the box arrays can be seen in Fig. 5.8. Therefore, the simulated absorption and scattering spectra alone cannot predict what the level of LSP-FRET will be within the system as the plasmonic array is varied. The energy transfer efficiency across the disc structure is far more sensitive, decreasing from  $(30 \pm 6) \%$  to  $(17 \pm 6) \%$  as the gap is increased from 100 nm



(D1) to 160 nm (D3), respectively. Again, this decrease in the LSP-FRET efficiency could be influenced by the red-shift in the absorption spectra with increasing disc spacing from D1 to D3, as shown in Fig. 5.3 (b,d,f), which would reduce the spectral overlap between the donor QW emission spectrum and the disc arrays absorption spectra going from D1 to D3. However, as commented earlier the absorption and scattering spectra do not directly predict the influence of the array on the energy transfer. As for the nanoring array there is a peak in the absorption spectrum which overlaps with the QW emission. The peak value is similar to Box 2 as seen from Fig. 5.3 (c) and (g). The larger ET efficiency of  $(51 \pm 7) \%$  could be attributed to the much greater extent of the electric field intensity observed for the nanoring array in Fig. 5.4. As a result, the total number of acceptor QDs that are within a region of enhanced field is far higher for the ring array. Therefore, the increased degree of field penetration into the QD layer combined with comparably similar levels of absorption at the donor emission wavelength could contribute to the significant increase in the LSP-FRET efficiency observed for the ring array.



**Figure 5.8:** Measured (black squares) and simulated (blue diamonds) quenching efficiencies of the donor quantum well and the measured energy transfer efficiency (red circles) as a function of nanostructure. Simulated data was provided by Dr. Cristian Marocico.

Therefore, the trends seen in the LSP-FRET efficiency with varying plasmonic array cannot be simply predicted by examining the simulated far-field absorption and scattering spectra alone. It is worthwhile to note that the field intensity enhancement at the excitation wavelength due to the plasmonic arrays can also be simulated using a plane wave source and this enhanced field at the excitation wavelength can play an important role in the ET processes, as it can enhance the effective excitation within the QW. Whilst the simulated absorption and scattering spectra can act as a guide in selecting a plasmonic geometry, a more complex model is required to explain the



LSP-FRET within the system investigated. This is due largely to the fact that the absorption and scattering spectra are generated for a plane wave excitation, whilst the donors in this system are in fact dipoles within the QW. The field generated in the NP arrays by plane wave excitation is distinct from the one generated by dipolar excitation. The difficulty with performing the simulations using a dipole excitation, as mention in chapter 4, is that the field intensity enhancement is highly dependent on the position of the dipole source. Therefore, these simulations are computationally expensive as they would require averaging over very high numbers of QW donor dipoles at many positions to very high numbers of QD acceptor dipoles at many positions.

Next, the change in the QD emission within the system is examined by integrating the TRPL data. As the plasmonic arrays can impact both the absorption and emission properties of the QDs by themselves, this interaction is examined first by measuring on a bulk GaN substrate. Fig. 5.9 shows the QD emission ratio (total emission on the NP array divided by the total emission off the NP array) as a function of the different nanostructures on bulk GaN. It can be seen from Fig. 5.9 that the QD emission is much more sensitive to NP geometry than the QW, the QD emission ratio varying from  $\sim 66\%$  to  $\sim 141\%$  over the structures, compared with the relatively flat quenching efficiency observed in the case of the QW. The sensitivity of the QD emission to changes in the gap between consecutive plasmonic NPs within an array is highest for nanobox arrays. The QD emission is enhanced on structures B1 and B2 by  $\sim 41\%$  and  $\sim 20\%$ , respectively, but for all other structures the QD emission is quenched by the NP arrays. The level of scattering at the acceptor emission wavelength (649 nm) amongst the nanobox arrays decreases as the gap increase from B1 to B3, as seen in Fig. 5.3 (a,c,e). This decrease could account for the decreasing trend of the QD emission seen for the nanobox arrays. The ring array produces the highest direct quenching of the QD emission. As the gap is increased amongst the nanodisc arrays from D1 to D3, the level of absorption decreases, as seen in Fig. 5.3 (b,d,f). This decrease could account for the increasing trend of the QD emission seen for the nanodisc arrays, as the QD emission starts to recover due to lower absorption. This data is then fit with an expression for the QD emission enhancement, given by Eqn. 5.5:

$$\frac{I_{em}^{QD-NP}}{I_{em}^{QD}} = \frac{I_{abs}^{QD-NP}}{I_{abs}^{QD}} \frac{k_{rad}^{QD-NP}}{k_{rad}^{QD}} \frac{\tau_{QD-NP}}{\tau_{QD}} \quad (5.5)$$

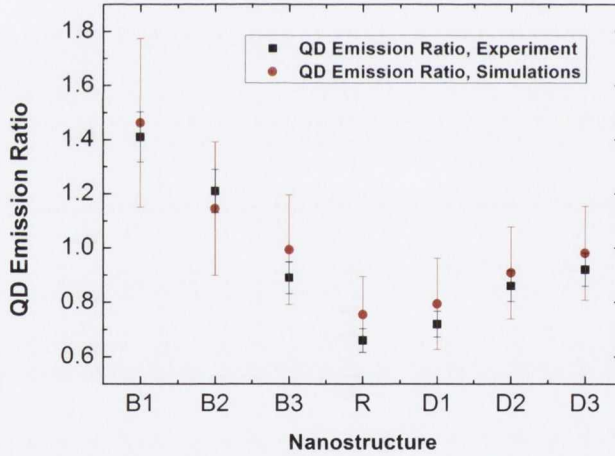
where  $\frac{I_{em}^{QD-NP}}{I_{em}^{QD}}$  is the QD emission ratio on the GaN substrate;

- $\frac{I_{abs}^{QD-NP}}{I_{abs}^{QD}}$  is the absorbed intensity ratio, given by the field intensity factor at the position of the QD acceptor with and without the array at the excitation

frequency,  $\omega_{exc}$ ;

- $\frac{k_{rad}^{QD-NP}}{k_{rad}^{QD}}$  is the radiative decay ratio for the acceptor QDs;
- $\frac{\tau_{QD-NP}}{\tau_{QD}}$  is the lifetime ratio of the acceptor QDs, taken from experiment. To simulate the QD emission ratio on the arrays, a large number (500) random acceptor QD dipoles are dispersed within the PMMA layer and the volume average of the field intensity within a unit cell of height 80 nm is calculated. The number of acceptors used for the simulation were chosen to be the same as the measured concentration of the QDs in the PMMA layer from experiment. These simulations were carried out by Dr. Cristian Marocico.

It can be seen from Fig. 5.9 that there is agreement between the theoretical and the experimental results for all of the box arrays and all of the discs arrays, as well as for the ring array. Therefore, the intrinsic QD-NP array interaction can be explained through both enhanced absorption and scattering processes only, for all of the NP arrays studied.

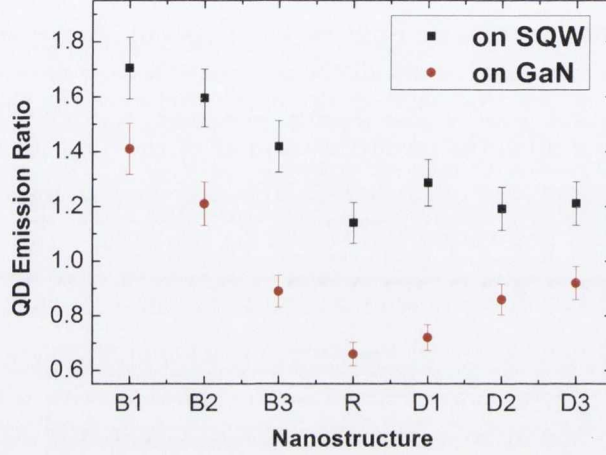


**Figure 5.9:** Experimental QD emission ratios (black squares) and theoretical QD emission ratios (red discs) on bulk GaN as a function of nanostructure. Simulation data provided by Dr. Cristian Marocico.

Next the QD emission on the array decorated QW substrate is examined. Fig. 5.10 shows the QD emission ratio (total emission on the NP array divided by the total emission off the NP array) as a function of the different nanostructures on both the bulk GaN substrate and the SQW substrate. In the case of the QW substrate, the plasmon-mediated FRET from the QW to the QDs has facilitated an overall enhancement of the QD emission on all of the plasmonic arrays. Smallest increase in QD emission ( $\sim 14\%$ ) is observed for the nanoring geometry, even though this geometry shows highest energy transfer efficiency. This is due to the high quenching



efficiency of the QD emission by the nanoring array on the bulk GaN substrate. For arrays B1 and B2, the plasmon-mediated FRET results in further enhancement of the QD emission. In all other cases LSP-FRET allows the QDs to recover from the quenching by the metal arrays and yield an overall enhancement of the QD emission. Therefore, by tuning the NP geometry it is possible to optimise the system for colour conversion, whereby one can benefit from both energy transfer and enhanced scattering mechanisms.



**Figure 5.10:** QD emission ratios on SQW (black squares) and on bulk GaN (red circles) as a function of nanostructure

Leading on from this, a comparison between the ET efficiency obtained from the reduction in the donor QW lifetime to the ET efficiency obtained from the increase in the acceptor QD emission can be made. If, in fact, LSP-FRET is the only mechanism which contributes to the increase in the QD emission on the QW sample, then the trends in the energy transfer efficiency determined by the change in donor lifetime should mirror the trends in the change of the QD emission as a function of nanostructure. Fig. 5.11 shows the increase in the QD emission (QD emission ratio on SQW divided by QD emission ratio on GaN) as a function of nanostructure. This data is then fit with an expression for the total change in QD emission, which includes energy transfer efficiency contribution, given by Eqn. 5.6:

$$\frac{I_{em}^{QD-NB}}{I_{em}^{QD}} = \frac{I_{abs}^{QD-NB}}{I_{abs}^{QD}} \frac{k_{rad}^{QD-NB}}{k_{rad}^{QD}} \frac{\tau_{QD-NB}}{\tau_{QD}} \left[ 1 + \frac{A_{QW}(\omega_{exc})}{A_{QD}(\omega_{exc})} \frac{I_{abs}^{QW}}{I_{abs}^{QD}} \eta_{ET}^{QW-NB-QD} \right] \quad (5.6)$$

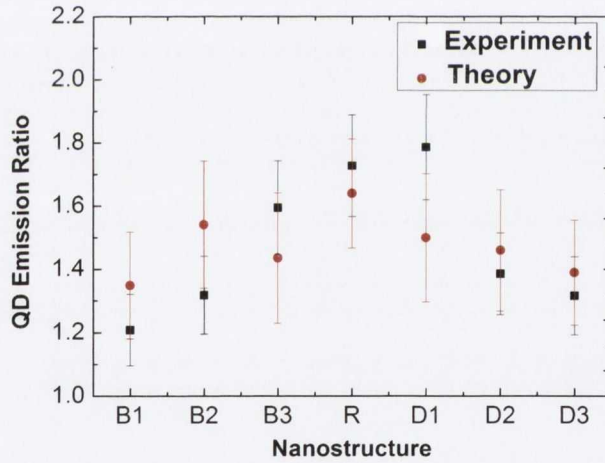
where  $\frac{I_{em}^{QD-NB}}{I_{em}^{QD}}$  is the QD emission ratio on the QW substrate;

- $\frac{I_{abs}^{QD-NB}}{I_{abs}^{QD}}$  is the absorbed intensity ratio, given by the field intensity factor at



the position of the QD acceptor with and without the array at the excitation frequency,  $\omega_{exc}$ ;

- $\frac{k_{rad}^{QD-NB}}{k_{rad}^{QD}}$  is the radiative decay ratio for the acceptor QDs;
- $\frac{\tau_{QD-NB}}{\tau_{QD}}$  is the lifetime ratio of the acceptor QDs, taken from experiment;
- $\frac{A_{QW}(\omega_{exc})}{A_{QD}(\omega_{exc})}$  is the field intensity ratio in the donor QW relative to the acceptor QD;
- $\frac{I_{abs}^{QW}}{I_{abs}^{QD}}$  is the ratio of the intrinsic absorption in the donor QW to the intrinsic absorption in the acceptor QDs, in the absence of the nanobox array, taken from experiment;
- $\eta_{ET}^{QW-NB-QD}$  is the LSP-FRET efficiency from the donor QW to the acceptor QDs, taken from experiment. These simulations were carried out by Dr. Cristian Marocico.

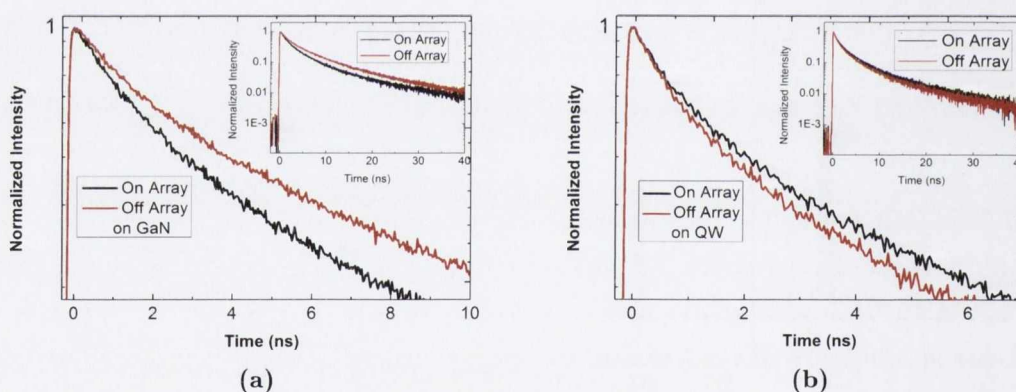


**Figure 5.11:** Experimental QD emission ratios on SQW/GaN (black squares) and theoretical values (red circles) as a function of nanostructure. Simulation data provided by Dr. Cristian Marocico.

We can see from Fig. 5.11 that there is good agreement between the experimental and theoretical results for all of the nanostructures, indicating that the total change in the QD emission from the GaN substrate to the QW substrate is solely due to the LSP-FRET from the QW to the QDs. This study shows that the sensitivity of the QD to the plasmonic arrays once again indicates a trade-off between the LSP-FRET from the QW and the intrinsic QD-NP array interaction; whether that be enhancement or quenching. Therefore, it allows for a discussion regarding optimization of these nanostructure arrays for either an energy transfer or colour tuning system.

By combining what we have seen from Fig. 5.9, Fig. 5.10 and Fig. 5.11, it can be concluded that the ring geometry (R) is best for an energy transfer system; however the box geometry (B1) provides the largest total emission of the QDs for any metal structures studied. Therefore, depending on the specific requirements of a given system, a different nanostructure should be chosen.

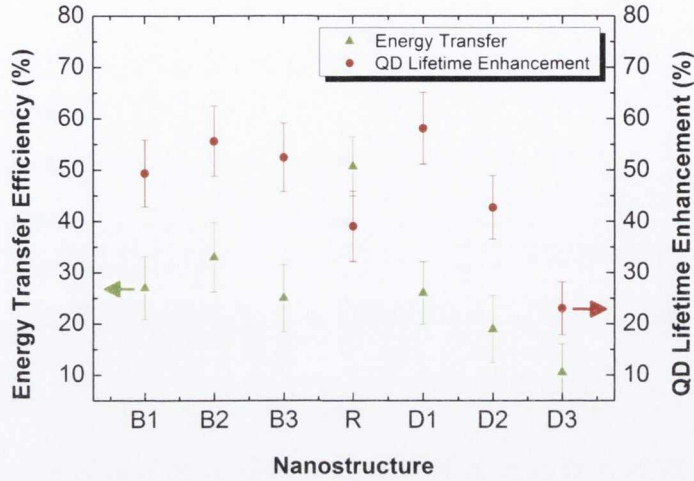
Having characterised the energy transfer system based on the modified QW emission and the modified QD emission, it is also highly relevant to characterise the influence of the NP arrays on the QD lifetime. This can provide evidence for pumping of the QDs by the LSP-FRET as well as a study of the QD emitted intensity. As described earlier, to determine whether the NP arrays cause direct quenching or enhancement of the QD emission, the different nanostructures were built directly onto bulk GaN. Fig. 5.12 (a) shows the QD PL decays on and off the nanoring array on a GaN substrate. On the array the QD PL lifetime is reduced by  $(21 \pm 2) \%$  from 8.1 ns to 6.4 ns. Fig. 5.12 (b) shows the QD lifetime on and off the nanoring array on the QW substrate. Here the QD lifetime on the array is increased by  $(10 \pm 1) \%$  due to pumping via LSP-FRET from the QW.



**Figure 5.12:** The QD PL decay on and off the Ag nanobox array on a GaN bulk layer. (b) QD PL decay on and off of Ag nanobox array on the QW sample. The insets shows the PL decays over a 40 ns range.

Similar analysis of the QD TRPL was completed for all the NP arrays. The overall QD lifetime increase is calculated as the ratio of the change in lifetime on GaN divided by the change in lifetime on the QW. Using the nanoring array as an example; we had a reduction on the NP array of  $(21 \pm 2) \%$  on GaN and an increase of  $(10 \pm 1) \%$  on the MNPs on the QW. Therefore overall QD lifetime increase on the nanoring array is given by  $1.1/0.79 = 1.39$ , representing an overall QD lifetime increase of  $(39 \pm 8) \%$ . Fig. 5.13 shows the overall QD lifetime as a function of nanostructure. An overall increase in the QD lifetime is seen for all structures, providing further evidence from the acceptors that plasmon mediated FRET occurs

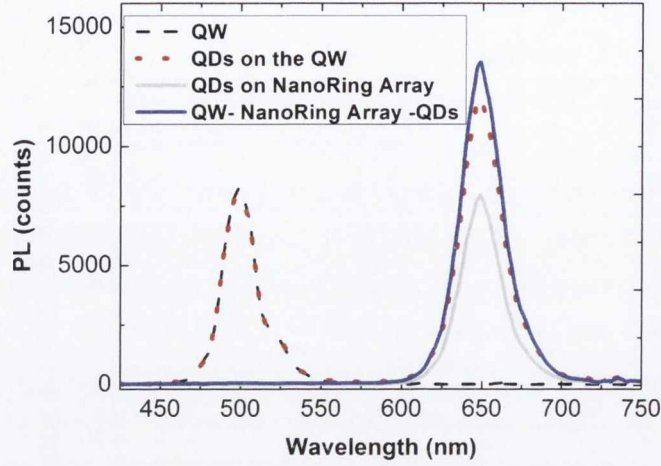
for all NP arrays.



**Figure 5.13:** Energy transfer efficiencies (green triangles) and QD lifetime enhancements (red circles) as a function of nanostructure.

For completeness the PL spectra were also measured. Considering again the nanoring structure for example, Fig. 5.14 shows the PL spectra of the QW by itself, the QW with the QDs without the nanoring array, the QDs on the nanoring on bulk GaN and the QW with the QDs on the nanoring array. From the black and red lines in Fig. 5.14 it can be seen that there is no direct NR energy transfer from the QW to the QDs, as the emission from the QW is the same in both cases. As seen earlier, the QW is quenched dramatically on the NP array, and the QDs are also quite strongly quenched by approximately  $(66 \pm 5) \%$  for this nanoring structure. However on the QW in the presence of the nanoring array, the QD emission recovers and subsequently shows a total emission enhancement of the QDs on the nanoring array by approximately  $(14 \pm 1) \%$ , which is again attributed to the plasmon-enhanced nonradiative energy transfer.





**Figure 5.14:** Direct PL spectra of complete 3-component system.

## 5.4 Conclusion

In conclusion, plasmon-enhanced FRET from an InGaN/GaN QW to a  $\sim 80$  nm layer of QDs embedded in PMMA has been demonstrated using silver NP arrays fabricated by HIL. The GaN barrier was fixed at 3 nm to enable strong near-field coupling between the donor QW and the plasmonic arrays. The arrays were fabricated directly on the SQW and on bulk GaN substrates to allow for independent investigation of the QD-NP array interaction. The QD-NP array interaction can be completely understood by a combination of enhanced absorption and scattering processes due to the presence of the NP arrays. A range of NP array geometries were fabricated to investigate the impact of the various shapes and sizes of the NPs on the strength of NR energy transfer within the system. TRPL and PL spectra measurements demonstrate and quantify the presence of the LSP enhanced FRET from the QW to the QDs *via* the increased local field around the NP arrays. Quenching efficiencies from 84% to 90% are observed from the QW to the different NP array geometries and plasmon-enhanced nonradiative energy transfer efficiencies from 25 % to 51 % were also observed from the QW to the QDs *via* the different NP array geometries. As there is no measureable direct FRET from the QW to the QDs, the NP arrays provide substantial enhancement to facilitate large ET efficiencies from the QW to the QDs, despite the strong presence of quenching of the QW emission to the NP arrays directly. QD lifetime enhancements of almost 60 % were observed and QD emission enhancements of up to 71 % were also seen.

From this study it has been shown that any potential energy transfer or colour tuning application comprising of a plasmon-coupled hybrid QW-QD system can be very sensitive to the shape, size and periodicity of the metallic NP arrays used.

Structures can be designed to optimise FRET, or to benefit from combined FRET and scattering mechanisms for light emitter applications. By using array geometries the NPs absorption and scattering profiles can be tailored to control the relative strengths of any enhanced energy transfer or enhanced emission processes within the system. The trends seen in the LSP-FRET efficiency with varying plasmonic array cannot be simply predicted by examining the simulated far-field absorption and scattering spectra alone, therefore a more complex model is required. It should also be noted that for future device applications the QW can be electrically pumped, not optically pumped as we have demonstrated here. The increase in the FRET efficiency could allow for a thicker GaN capping layer, which will help to overcome potential problems with using thin GaN capping layers, such as used in this exploratory study. These types of structures can be used for colour conversion and light emitting devices which can exploit plasmon enhanced FRET from the QW and enhanced scattering from the metallic NP arrays.

As discussed in chapter 1, thin GaN barriers can dramatically increase the non-radiative losses within QWs and will pose problems for carrier spreading in LEDs [10, 44]. In an attempt to address this issue, in the next chapter QWs with varying GaN barrier thickness will be studied for LSP-FRET *via* plasmonic nanobox arrays.





# 6 Barrier Thickness Dependent Study of LSP Mediated FRET

## 6.1 Introduction

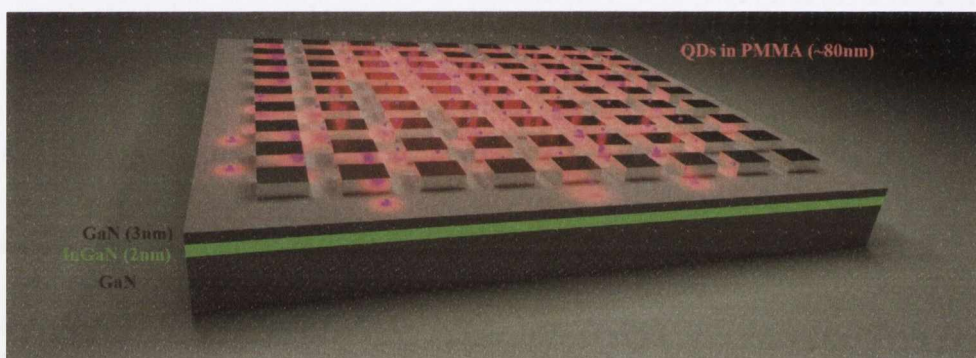
In the previous chapter, LSP-FRET was demonstrated from an InGaN/GaN QW with a GaN barrier thickness of 3 nm to an approximately 80 nm thick layer of acceptor QDs. InGaN/GaN QWs have been promising to explore in terms of optoelectronic devices, such as LEDs [103–105] and light harvesting devices [106, 107]. Whilst the work presented in the previous chapter is significant, as it shows that QWs can nonradiatively pump thicker layers of QDs by utilizing plasmonic elements, having a thin GaN barrier presents several drawbacks. Firstly, thin QW barriers ( $\sim$  few nm thick) dramatically increase the nonradiative losses within QWs [10]. This is effectively a product of the fabrication process and is driven by the quality and purity of the barrier itself. As this barrier thickness increases, the overall quality is improved and therefore the nonradiative losses are decreased. Secondly, if QWs such as these were to be used in devices, thin GaN barriers would reduce the degree of carrier spreading which would obviously not be desirable for LEDs. Growth and device processes could expect the carrier spreading to be sufficient in QWs with a barrier thickness of between 7 nm to 10 nm [44]. In an attempt to solve some of these issues, many studies have focussed on the optimisation of the geometries, such as dry etched nanopillars [11, 12] which would allow a higher number of acceptor QDs to be close enough to benefit from nonradiative energy transfer from the QW, or graded QD systems [14]. However, whilst there were some performance improvements made due to the etching process in such devices, they also provide their own drawbacks, such as fabrication complexity or the need to carefully position emitters. With this in mind, the ability of QWs with thicker barriers to nonradiatively pump thick layers of QDs would be considerably beneficial.

In this chapter three different QW donors, with barrier thicknesses ranging from 3 nm to 7 nm, are used to enable LSP-FRET to a  $\sim$  80 nm layer of acceptor QDs using silver nanobox arrays fabricated by EBL. The impact that the changing barrier thickness has on both the LSP-FRET rate and efficiency will be discussed. Also, the impact that modifying the barrier has on the QD emission will be presented.

TRPL and PL spectral measurements will be used to demonstrate and quantify the LSP-FRET from the QWs to the QDs.

## 6.2 Experimental Methods

A schematic of the complete structure for QW1 is shown in Fig. 6.1. As before, Ag nanobox arrays were fabricated *via* EBL on three different single InGaN QW structures and subsequently covered in a layer of CdSe/ZnS core-shell QDs embedded in a  $\sim 80$  nm thick layer of PMMA. The single QWs used in this chapter were also grown by metal-organic vapour phase epitaxy (MOVPE) on a thick GaN layer on a c-plane sapphire substrate.



**Figure 6.1:** Schematic of 3-component system. Schematic kindly generated by Dr. Cristian Marocco.

In this chapter, the impact of changing the QW barrier thickness on the LSP-FRET process from the QW donor to the QD acceptors will be discussed. In the previous two chapters a QW donor that had a barrier thickness of 3 nm was used, which was specifically selected to allow for strong near-field coupling between the excitons in the QW donor and the plasmonic NPs. However, as mentioned earlier, thin QW barriers can increase nonradiative losses within the QW donor and can be detrimental for carrier spreading across the device area. Having a thicker QW barrier can help to alleviate both of these problems. For this reason, an investigation into how an increase in the QW barrier thickness will modify the LSP-FRET within the QW-QD system is undertaken. The details of the QW structures used in this chapter are shown in Table 6.1. In all of the QW structures in this chapter, the InGaN layer was fixed at a thickness of 2 nm and the QW barrier thickness was increased from 3 nm to 7 nm in steps of 2 nm. It is worthwhile to note at this point, by moving from one QW donor to another, the barrier thickness is not the only thing that changes. Due to small differences in the electro-potential within the QW and the purity of each sample, the peak emission wavelength and full-width-at-half-maximum (FWHM) can change [143]. This is seen clearly in Fig. 6.2. Also, variation



in the the composition of the QW thickness can modify these emission properties. The photoluminescence (PL) spectrum of the three QW donors discussed in this

| Label | InGaN thickness (nm) | Barrier (nm) | Emission wavelength (nm) |
|-------|----------------------|--------------|--------------------------|
| QW1   | 2                    | 3            | 535                      |
| QW2   | 2                    | 5            | 508                      |
| QW3   | 2                    | 7            | 517                      |

Table 6.1: QW specifications

chapter, along with the absorption and emission spectra of the acceptor QDs are shown in Fig. 6.2. Both the broadening and the shift in the QW PL spectra can modify the spectral overlap between the donor QW and the acceptor QDs. It is worthwhile to note that these are both factors can effect the LSP-FRET within the system under study. The QW PL intensity varies slightly for each of the three QW donors, however the normalized QW PL is presented in Fig. 6.2. The nanobox arrays were fabricated using Electron-Beam Lithography (EBL). PMMA is first spun onto the GaN capping layer surface and patterned using a Carl Zeiss Supra electron-beam microscope. Following the development, 5nm of Ti and 35nm of Ag are deposited using a metal evaporation process, and then the arrays are finally created by a lift-off process. The arrays were comprised of nanoboxes of different sizes. The dimensions of the nanobox arrays are presented in Table 6.2. Each array contained units that were arranged in a symmetric two-dimensional square lattice with overall dimensions of between 40  $\mu\text{m}$  x 40  $\mu\text{m}$  to 52  $\mu\text{m}$  x 52  $\mu\text{m}$ .

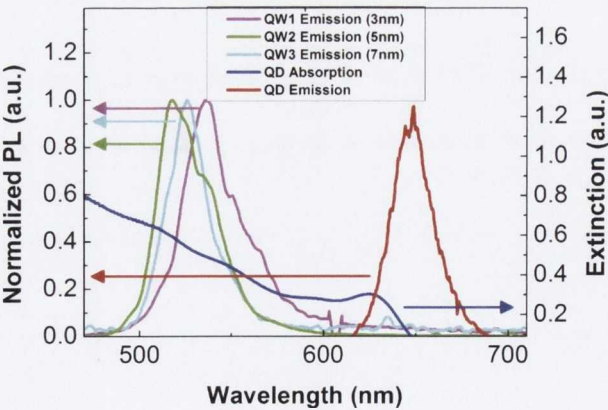


Figure 6.2: PL spectra for all three QW donors and QD acceptor (left hand axis) and acceptor QD absorption (right hand axis).

As in the previous chapter, the QDs are CdSe/ZnS core-shell nanocrystals with a diameter of 6.3 nm and a peak emission wavelength of 649 nm, shown in Fig. 6.2. The QDs are embedded in PMMA by first adding the QDs in toluene to a 2.5 %

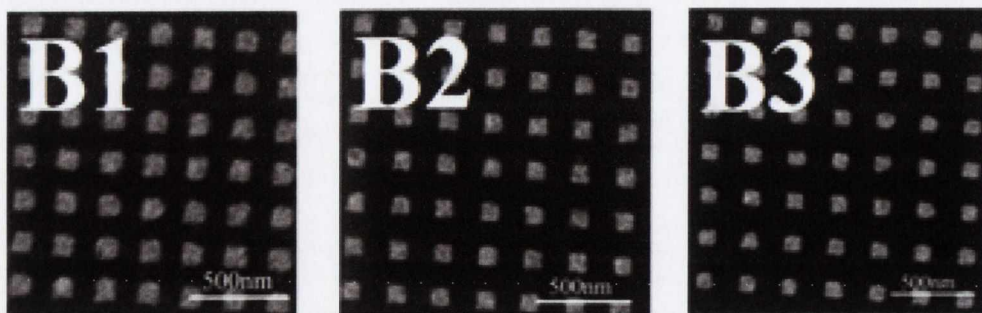


wt. PMMA (also dissolved in toluene) solution. This mixture is then sonicated to ensure the QDs are thoroughly dispersed. The solution is then spun down onto the QW decorated by the NP array to create a layer of QDs in PMMA. The layer has a QD concentration of  $(1.9 \pm 0.1) \times 10^{21} \text{ m}^{-3}$ , measured as described in chapter 3, section 3. The QD layer thickness has been measured with a Dektac6 profilometer. It is found that the thickness of the PMMA layer is increased by  $(19 \pm 5) \text{ nm}$  on the array compared with a  $(60 \pm 5) \text{ nm}$  thickness off the array. The QD concentration used represents approximately 5-6 QDs per unit cell for the nanobox arrays. The deposition of the QD layer completes the hybrid structure, shown in Fig. 6.1.

| Label | Shape | Unit Dimension (nm) | Gap (nm) |
|-------|-------|---------------------|----------|
| B1    | Box   | 100                 | 100      |
| B2    | Box   | 100                 | 130      |
| B3    | Box   | 100                 | 160      |

**Table 6.2:** Details of nanobox arrays fabricated on QW substrates

The emission and energy transfer (ET) processes were characterised using PL spectroscopy and time-resolved photoluminescence (TRPL). The TRPL and PL were performed as previously described in chapter 4, with a brief description supplied here for completeness. For PL measurements the samples were excited at normal incidence using a pulsed 405 nm laser diode focused using a x40 objective lens. The PL spectra were recorded using a fiber-coupled Andor grating spectrometer. The PL decays were measured using a PicoQuant Microtime 200 time-resolved confocal microscope with 90 ps temporal resolution. The dimensions and periodicity of the Ag nanostructures were selected such that each array had overlap of the surface plasmon resonance with the QW donor emission [30, 31]. SEM micrographs of the three nanobox arrays are shown in Fig. 6.3. The images clearly show that there is a large degree of uniformity across the arrays and that the aspect ratio of each individual unit is also well maintained.



**Figure 6.3:** SEM images of B1, B2, B3 arrays (scale bar 500nm)

The nanobox arrays were designed using Lumerical, a finite difference time domain

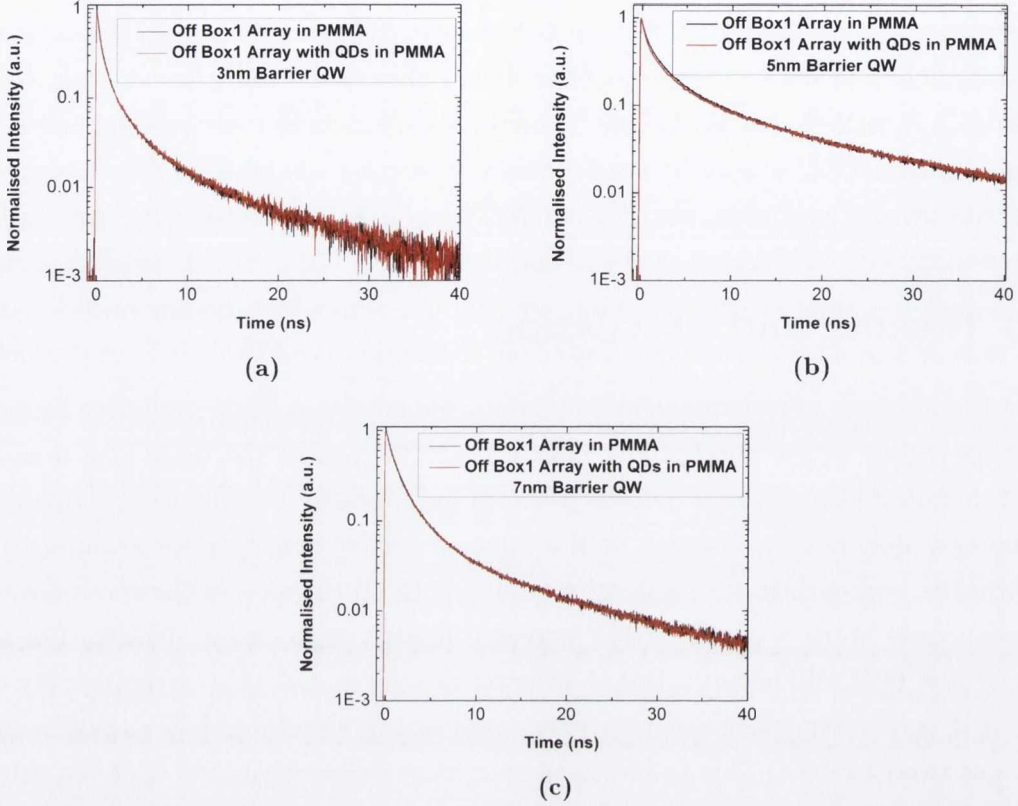
(FDTD) commercial software. The absorption and scattering spectra of the Ag nanobox array are simulated using plane-wave excitation. The simulations took account of the PMMA layer on top of the Ag nanoboxes and the 5 nm Ti layer. The dielectric permittivity of the Ag and Ti materials are included using experimentally measured data [38]. The GaN and PMMA layers are modelled with a constant dielectric permittivity of  $\epsilon_{\text{GaN}} = 5.35$  and  $\epsilon_{\text{PMMA}} = 2.2$ , respectively.

### 6.3 Results and Discussion

As in the previous two chapters, all measurements are taken in the radiative recombination regime of the donor QWs. The average lifetime of the three QW donors as a function injected carrier density is shown in Appendix B. The decay dynamics of the QW donors as a function of the injected carrier density were examined to confirm the appropriate carrier density required. In all three cases the spontaneous emission rates above a certain value increased linearly with carrier density. For all three donor QWs discussed in this chapter data is presented at a carrier density of  $2.7 \times 10^{17} \text{cm}^{-3}$ . The carrier density value used in this chapter is lower than in the previous two chapters. This is due to the fact that the spontaneous emission rates of the three QWs used in this chapter are faster than that of the QW sample used for chapter 4 and chapter 5. In other words the average lifetime of the three QWs used in this chapter is shorter compared to the previous two chapters. As a result a lower carrier density value is selected so that the measurements can be taken at a lifetime value that is higher in order that the fractional error (due to experimental measurement and instrument response) is smaller. This is clearly seen in the average QW lifetimes presented in Appendix. B.

Once again, there was no measureable direct FRET between the QW and the QDs in the absence of the plasmonic nanobox arrays, for all three QW donors. This was confirmed by examining the lifetime of the QW donors before and after the addition of the QD layer, in the absence of the nanobox arrays. The QW PL decay curves with and without the addition of the QD layer in the absence of nanobox 1 array for each of the QW donors is shown in Fig. 6.4. Away from the plasmonic nanoboxes, the lifetime of the QWs were found to be unchanged after the addition of the QDs. This is seen clearly in Fig. 6.4. This is also consistent with the observations seen in chapters 4 and 5.

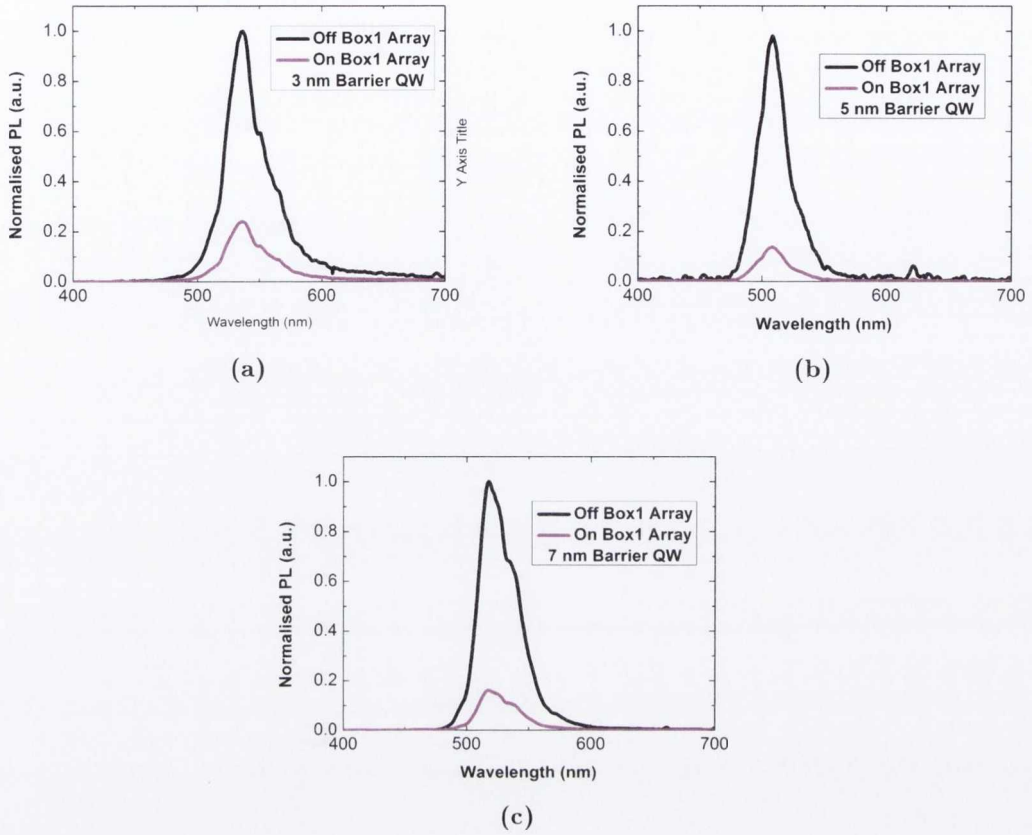




**Figure 6.4:** QW PL decay curves in the absence of Box 1 array with (red curve) and without (black curve) the addition of the QD layer for (a) 3 nm barrier, (b) 5 nm barrier and (c) 7 nm barrier QWs, respectively.

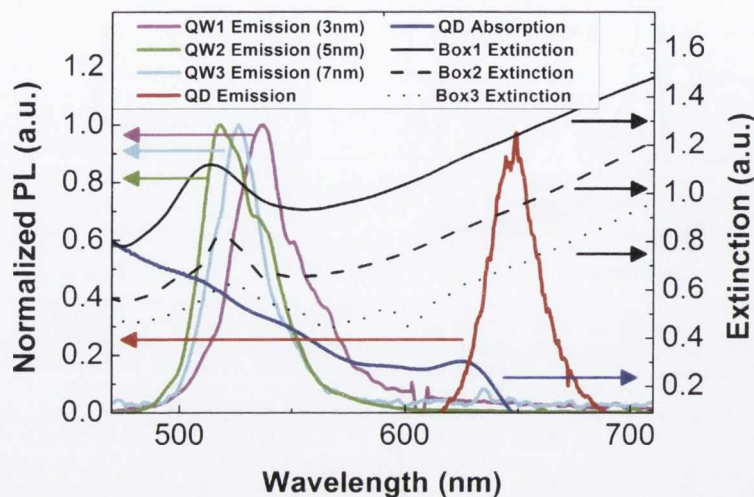
Next, the direct quenching of the donor QW lifetime and emission on the nanobox arrays was examined for each QW donor. Fig. 6.5 shows the QW PL spectra on and off of Box 1 array for each of the three QW samples. It can be seen from Fig. 6.5 that the QW emission is quenched substantially, between 80-90 % on Box 1 array for each of the QW samples. This is consistent with the results seen in chapters 4 and 5 and is relatively unsurprising as there is a peak in the absorption of all three nanobox arrays overlapping with the emission spectra of all three QW donors, as can be seen in Fig. 6.6. It can be seen from Fig. 6.5 that the emission quenching is slightly lower for the 3 nm barrier QW which can be explained by examining the spectral properties of the nanobox arrays, seen in Fig. 6.6. It is worthwhile to note that along with the observed red-shift in the absorption peak as we move from Box1 to Box3 seen in Fig. 6.6, the total magnitude of the absorption for Box1 is in fact higher due to the larger metal filling factor within a unit cell. This explains why the value of the absorption decreases from Box1 to Box3 respectively as the filling factor decreases. The emission spectrum of the 3 nm barrier QW is red-shifted compared to the other two QW samples. This results in less overlap between the emission of the QW and the array absorption which explains the slight decrease in the quenching



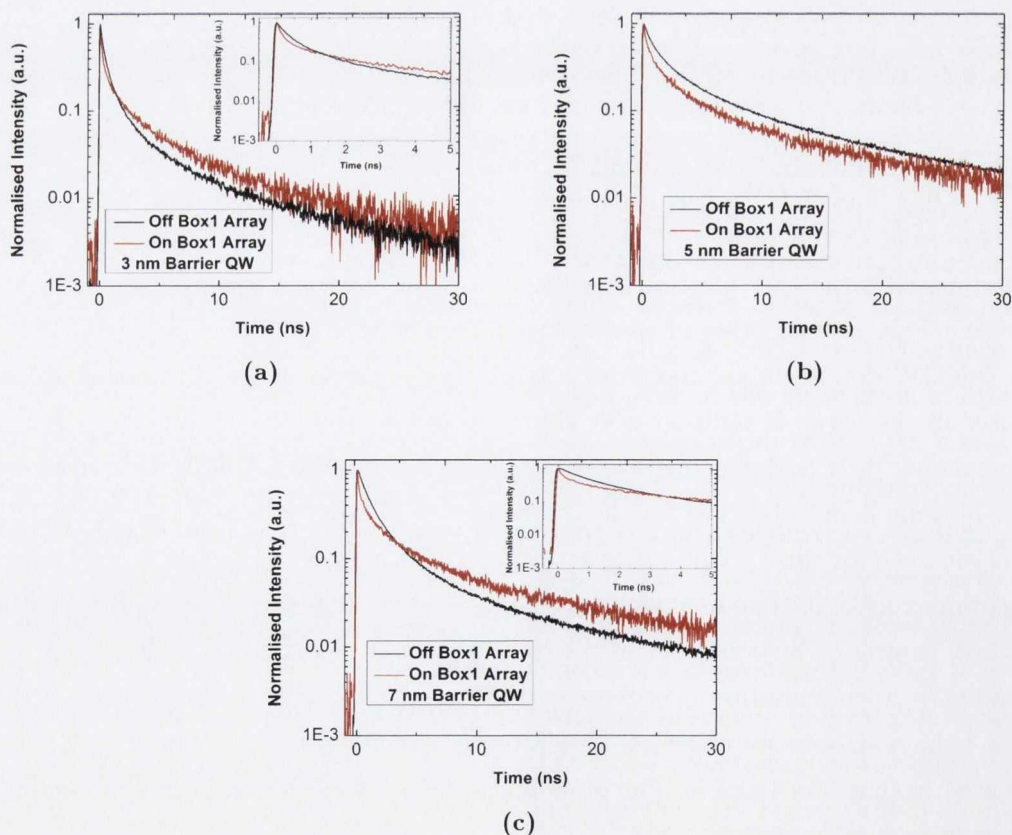


**Figure 6.5:** QW PL spectra off (black line) and on (magenta line) Box 1 array for the (a) 3 nm barrier, (b) 5 nm barrier and (c) 7 nm barrier QW samples, respectively.

for the 3 nm barrier QW. Fig. 6.7 shows the QW PL decays on and off of Box 1 array for each of the three QW samples. It can be seen from Fig. 6.7 that over short timescales the QW lifetime is reduced on nanobox 1 array for each of the QW samples. This is indicative of nonradiative energy transfer (or direct quenching) from the QW donors to the nanobox 1 array. It should be noted that although the lifetime on the array is reduced over short timescales (seen from the insets in Fig. 6.5 (a) and (c)), it is in fact increased over longer timescales. Whilst this crossover of the lifetime is not observed for the 5 nm barrier QW decays presented in Fig. 6.7 (b), it was seen for this QW on other arrays and at other carrier densities. Therefore, this complex QW lifetime behaviour after fabrication of the arrays was observed for each QW sample. This crossover of the lifetime may be driven by an increase in the nonradiative recombination processes within each QW due to fabrication by EBL, as this behaviour was not observed for similar plasmonic array fabricated by HIL, as presented in chapters 4 and 5. The modification of the QW lifetimes in this complex way requires further investigation.



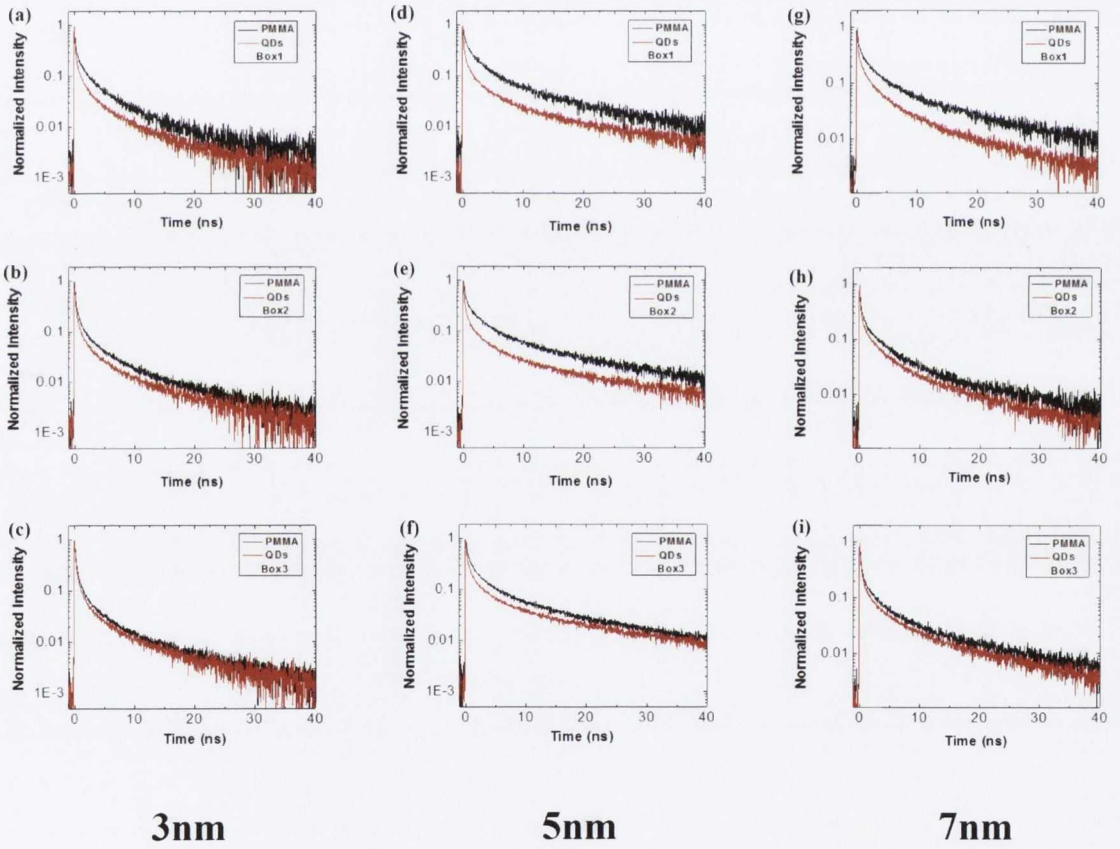
**Figure 6.6:** PL spectra for all three QW donors and QD acceptor (left hand axis) along with the simulated extinction spectra for all three nanobox arrays and acceptor QD absorption (right hand axis). Simulated data provided by Dr. Vasilios Karanikolas.



**Figure 6.7:** QW PL decay curves off (black curve) and on (red curve) Box 1 array, for (a) 3 nm barrier (b) 5 nm barrier and (c) 7 nm barrier QWs, respectively. The insets in (a) and (c) show the decays over the first 5 ns for the 3 nm and 7 nm barrier QWs, respectively.

However, the main focus of this chapter is not on the direct quenching process but on the subsequent LSP-FRET process. As the quenching between a QW donor and a nanobox array has been discussed in detail in both chapter 4 and chapter 5, from this point forward the impact of changing the QW barrier on the LSP-FRET process only will be discussed.

The donor QW PL lifetimes are presented. Fig. 6.8 shows the QW PL lifetimes on the nanobox arrays with and without the addition of the QD layer, for all three QW donors. It can be clearly seen from Fig. 6.8 that the donor lifetime is further reduced after the addition of the acceptor QD layer for all arrays and for all QW donors. This is a significant result as it shows that the LSP-FRET process can compete with both the donor spontaneous emission rate and the direct quenching rate to the nanoboxes for each nanobox array and for each barrier thickness.



**Figure 6.8:** Time-resolved photoluminescence decays for Box1, Box2 and Box3, respectively for QW 1 (a-c), QW 2 (d-f) and QW 3 (g-i).

In order to understand the process further, the LSP-FRET rates need to be examined. The LSP-FRET rate is calculated by comparing the donor QW PL lifetimes before and after the addition of the QD layer. In this case



$$k_{FRET} = k_{QW-Array-QD} - k_{QW-Array} \quad (6.1)$$

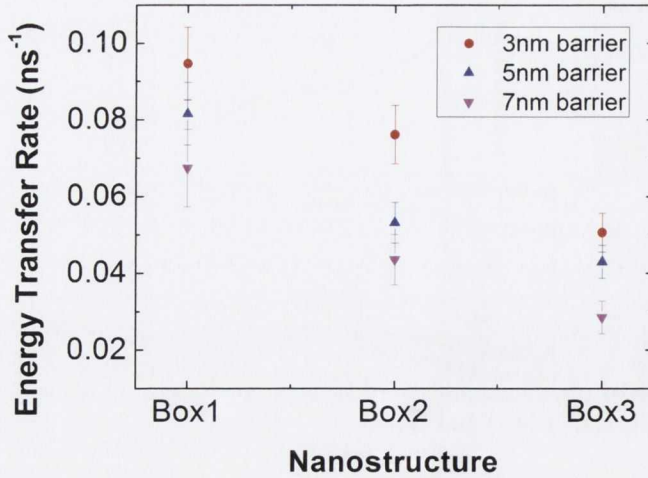
$$= \left( \frac{1}{\tau_{QW-Array-QD}} \right) - \left( \frac{1}{\tau_{QW-Array}} \right)$$

where  $k_{QW-Array-QD}$  is the total donor rate on the array after the addition of the QD layer and  $k_{QW-Array}$  is the total donor rate on the array before the addition of the QD layer. The average QW lifetimes on each of the nanobox arrays before and after the addition of the QD layer for each of the three QW samples are shown in Table 6.3.

|                                     | On Box1 (ns) | On Box2 (ns) | On Box3 (ns) |
|-------------------------------------|--------------|--------------|--------------|
| $\tau_{QW-Array}$ (3 nm Barrier)    | 3.11         | 2.52         | 1.81         |
| $\tau_{QW-Array-QD}$ (3 nm Barrier) | 2.40         | 2.11         | 1.66         |
| $\tau_{QW-Array}$ (5 nm Barrier)    | 4.91         | 3.95         | 4.41         |
| $\tau_{QW-Array-QD}$ (5 nm Barrier) | 3.51         | 3.28         | 3.71         |
| $\tau_{QW-Array}$ (7 nm Barrier)    | 5.22         | 4.70         | 4.21         |
| $\tau_{QW-Array-QD}$ (7 nm Barrier) | 3.85         | 3.91         | 3.76         |

**Table 6.3:** Average QW lifetime on each of the nanobox arrays before and after the addition of the QD layer for each of the three QW samples.

Using Eqn. 6.1 the LSP-FRET rates were calculated by using the lifetime values presented in Table 6.3 . These LSP-FRET rates are presented in Fig. 6.9.



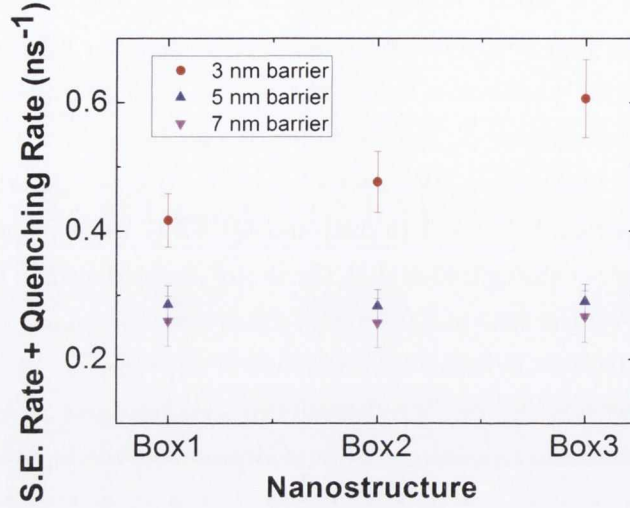
**Figure 6.9:** LSP-FRET rates for all three nanobox arrays on all three QW donors

It can be seen from Fig. 6.9 that the LSP-FRET rates decrease moving from Box 1 to Box 2 to Box 3, respectively. This can be due to the reduction in the spectral

overlap between our QW donor emission spectra and the absorption spectra of the nanoboxes, as seen in Fig. 6.6. This reduction is observed for all three donor QWs. This trend amongst the nanoboxes is also consistent with the observed trend seen for these structures in chapter 5. Furthermore, it can be seen in Fig. 6.9 that the LSP-FRET rates are highest for QW 1 which has the thinnest barrier (3 nm). The rates then steadily reduce for QW 2 (5 nm) and QW 3 (7 nm), respectively. This is a significant result as it demonstrates that the donor-array distance has a direct and measureable impact on the rate of LSP-FRET from the QW to the QDs. The trend in the LSP-FRET rate for the three QW barriers is expected as the donor-plasmon coupling decreases with distance. Therefore, this system once again suggests that the donor-plasmon acts like an enhanced donor dipole which couples to the acceptor dipole.

It has been successfully experimentally demonstrated that LSP-FRET can occur from a donor QW with a thicker barrier (up to 7 nm) to a thick layer of acceptor QDs *via* plasmonic nanobox arrays. This system clearly indicates the possibility to enable FRET between donors and acceptors that would otherwise be too far apart from one another to transfer energy nonradiatively, by using plasmonic arrays in layered geometries.

As mentioned earlier, by moving from one QW donor to another, the barrier thickness is not the only thing that changes. Due to small differences in the electro-potential within the QW and the purity of each sample, the spontaneous emission (S.E.) rate of each of the QW samples also varies [143, 144]. As the LSP-FRET efficiency is effectively a measure of how the LSP-FRET rate competes with both the spontaneous emission rate and the quenching rate to the arrays, it is important to examine these rates before presenting the efficiency. The sum of the spontaneous emission rate and the quenching rate for each nanobox array on each QW sample is shown in Fig. 6.10.



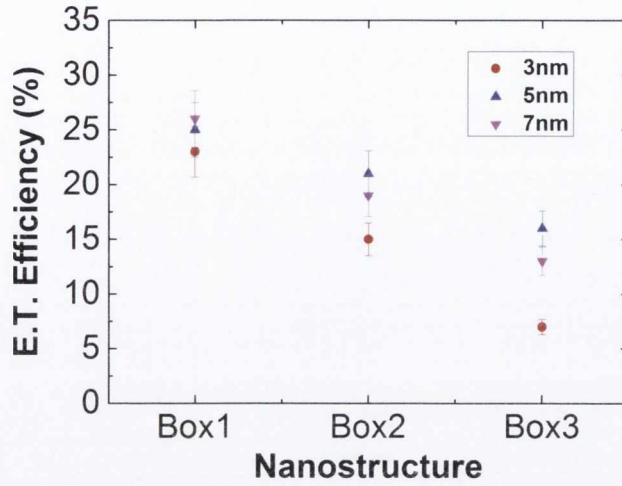
**Figure 6.10:** Sum of spontaneous emission rate and quenching rate for each nanobox array on all three QW samples.

The rates presented in Fig. 6.10 represent the total donor rate on each array before addition of the QD acceptor layer. It can be seen in Fig. 6.10 that the total QW rate (spontaneous emission rate plus quenching rate) is fastest for QW 1 which has a 3 nm barrier. This rate is decreased for both QW 2 (5 nm barrier) and QW 3 (7 nm barrier), respectively. We can see from both Fig. 6.9 and Fig. 6.10 that although the LSP-FRET rate is largest for QW 1 (3 nm barrier), it has to compete with the fastest spontaneous emission and quenching rates. The LSP-FRET efficiency will represent how competitive the FRET process is compared to the underlying decay mechanisms. The LSP-FRET efficiency can be expressed as

$$\eta_{FRET} = \frac{k_{FRET}}{k_{QW} + k_{QW-Array} + k_{FRET}} \quad (6.2)$$

where  $k_{QW}$  is the spontaneous emission decay rate for the bare QW,  $k_{QW-Array}$  is the QW quenching rate for the QW decorated with the Ag nanobox array and  $k_{FRET}$  is the plasmon-coupled QW to QD FRET energy transfer rate. The LSP-FRET efficiency for each nanobox array on each of the three QW samples is presented in Fig. 6.11.



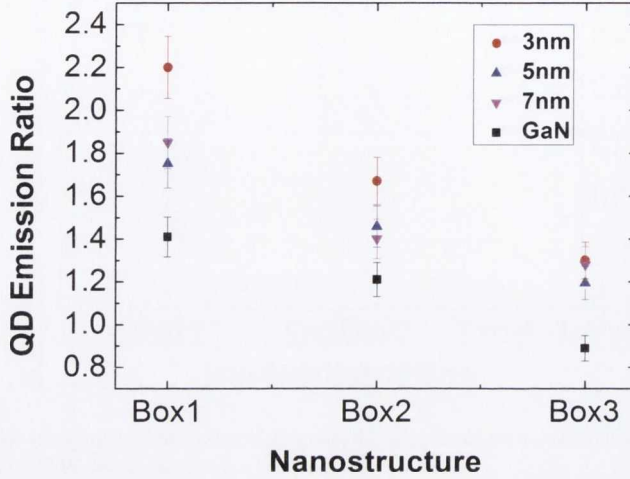


**Figure 6.11:** LSP-FRET efficiency for Box1, Box2 and Box3, respectively on all the QW samples.

It can be seen from Fig. 6.11 that for all QW samples the LSP-FRET efficiency decreases moving from Box 1 to Box 2 to Box 3, respectively. This mirrors the trend observed in the FRET rates seen in Fig. 6.9. It is also consistent with the FRET efficiencies seen in chapter 5 for similar arrays. Also, it can be seen clearly in Fig. 6.11 that the LSP-FRET efficiency is, in fact, lowest for the QW with the thinnest barrier. As discussed earlier, this is due to the fact that the LSP-FRET rate, whilst fastest for QW 1, must compete with the faster spontaneous emission and quenching rates. This therefore reduces the efficiency of the FRET process for the 3 nm barrier QW compared to the other two QW samples. Secondly, when we examine QW 2 and QW 3 more closely, it can be seen in Fig. 6.11 that QW 2 shows the highest FRET efficiency values. This is due to the fact that the FRET rates for QW 2 are higher than for QW 3, whilst their spontaneous emission and quenching rates, seen in Fig. 6.10, are comparable. So once again the trade-off between the LSP-FRET rate and the spontaneous emission and quenching rates explains the efficiency values. Furthermore, examining the efficiency of the 7 nm barrier QW, it can be seen from Fig. 6.11 that a 25 % LSP-FRET efficiency is achieved using Box 1 array. This is a substantial result as it demonstrates that despite fast spontaneous emission and quenching rates, FRET remains competitive over larger distances in a thicker barrier QW. It is worthwhile to note that within the hybrid system studied, it is not possible to determine the precise distance dependence of FRET efficiency between the QW and QDs (following a  $d^{-3}$  or  $d^{-4}$ ) due to the acceptor QDs being randomly distributed within a 3-D volume and therefore having an undefined centre-to-centre distance between the donors and acceptors.

Next, the impact that the LSP-FRET efficiency has on the acceptor QD emission is examined. Fig. 6.12 shows the QD emission ratio (QD emission on the array

divided by QD emission off the array) on each of the QW samples.



**Figure 6.12:** QD emission ratio for Box 1, Box 2 and Box 3 on each of the three QW samples and bulk GaN.

As the nanobox arrays can influence the QD emission by themselves, the QD emission ratio for the three nanobox arrays on bulk GaN is also shown in Fig. 6.12. By using a bulk GaN substrate the contribution to the QD emission that is solely from plasmon enhanced absorption and scattering processes is separated out. It can be seen from the black squares in Fig. 6.12 that the QD emission is enhanced on Box 1 and Box 2 arrays on the GaN by 41 % and 20 %, respectively. However, the QD emission is quenched by approximately 10 % on Box 3 array on the GaN substrate. These observations are consistent with the QD emission values seen in chapter 5 for similar arrays. Therefore, by comparing the QD emission on the GaN substrate to the QD emission on the QW substrates, any further increase in the QD emission on all three QW samples can only be due to the LSP-FRET from the QW directly to the QDs. It can be seen from Fig. 6.12 that the LSP-FRET from the QWs to the QDs results in an increase in the QD emission on all nanobox arrays for all QW samples, relative to the bulk GaN substrate. Once again, this is a significant result as it successfully demonstrates that the nonradiative energy transferred to a thick layer of QDs *via* the nanobox arrays can produce an increase in the light from the acceptor QDs. It is clear from Fig. 6.12 that the QD emission on Box 1 array is always higher than Box 2 and Box 3 arrays, respectively, for each QW sample. Also, Fig. 6.12 shows that the QDs on nanobox 1 array on the 3 nm barrier QW produce the largest total emission, with an increase of 120 % in the QD emission observed. For nanobox 2 array, the QD emission is highest for the 3 nm barrier QW, with the emission being similar for both the 5 nm and 7 nm barrier wells, respectively. On each of the QW samples, the QD emission enhancement for nanobox 3 is similar,



within the experimental error. However, the QDs on the 3 nm barrier QW produce slightly more emission than QDs on either the 5 nm barrier QW or the 7 nm barrier QW, respectively. The variation in the QD emission between the three QW samples is largest for the nanobox 1 array.

To understand the QD emission change in more detail, nanobox 1 is examined more closely. An expression for the total change in the QD emission, identical to the one used in chapter 5, which includes the energy transfer efficiency contribution is given by Eqn. 6.3:

$$\frac{I_{em}^{QD-NB}}{I_{em}^{QD}} = \frac{I_{abs}^{QD-NB}}{I_{abs}^{QD}} \frac{k_{rad}^{QD-NB}}{k_{rad}^{QD}} \frac{\tau_{QD-NB}}{\tau_{QD}} \left[ 1 + \frac{A_{QW}(\omega_{exc})}{A_{QD}(\omega_{exc})} \frac{I_{abs}^{QW}}{I_{abs}^{QD}} \eta_{ET}^{QW-NB-QD} \right] \quad (6.3)$$

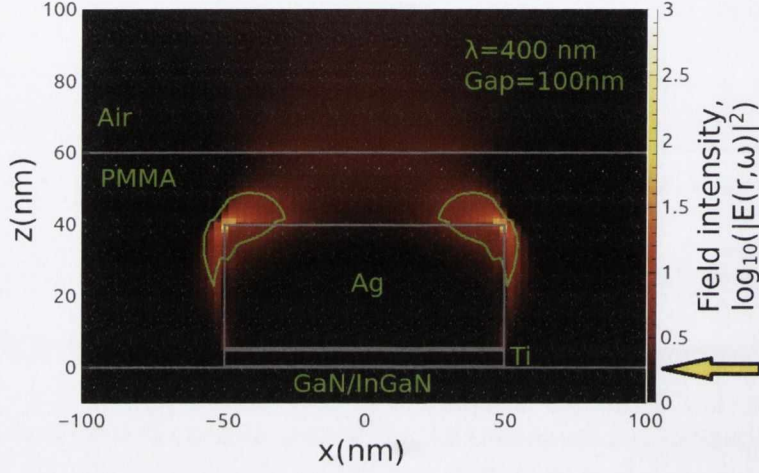
where  $\frac{I_{em}^{QD-NB}}{I_{em}^{QD}}$  is the QD emission ratio on the QW substrate;

- $\frac{I_{abs}^{QD-NB}}{I_{abs}^{QD}}$  is the absorbed intensity ratio, given by the field intensity factor at the position of the QD acceptor with and without the array at the excitation frequency,  $\omega_{exc}$ ;
- $\frac{k_{rad}^{QD-NB}}{k_{rad}^{QD}}$  is the radiative decay ratio for the acceptor QDs;
- $\frac{\tau_{QD-NB}}{\tau_{QD}}$  is the lifetime ratio of the acceptor QDs, taken from experiment;
- $\frac{A_{QW}(\omega_{exc})}{A_{QD}(\omega_{exc})}$  is the field intensity ratio in the donor QW relative to the acceptor QD;
- $\frac{I_{abs}^{QW}}{I_{abs}^{QD}}$  is the ratio of the intrinsic absorption in the donor QW to the intrinsic absorption in the acceptor QDs, in the absence of the nanobox array, taken from experiment;
- $\eta_{ET}^{QW-NB-QD}$  is the LSP-FRET efficiency from the donor QW to the acceptor QDs, taken from experiment. To simulate the QD emission ratio on the arrays, a large number (500) random acceptor QD dipoles are dispersed within the PMMA layer and the volume average of the field intensity within a unit cell of height 80 nm is calculated. Simulations were carried out by Dr. Cristian Marocico.

As indicated by eqn. 6.3, the QD emission ratio on the QW samples is linearly dependent on the energy transfer efficiency,  $\eta_{ET}^{QW-NB-QD}$ . However, it can be seen in Fig. 6.12 that the QD emission ratio is largest for the 3 nm barrier QW, yet the energy transfer efficiency is lowest for the 3 nm barrier QW, as seen in Fig.



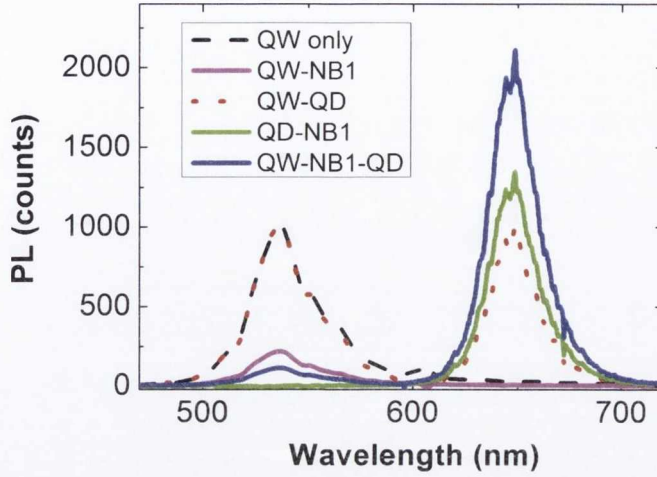
6.11. However, the QW donor field intensity factor,  $A_{QW}(\omega_{exc})$ , which is the field intensity within the QW due to the plasmonic nanobox is expected to decrease as the plasmonic array is moved further from the QW due to the thicker GaN barrier layer. A higher  $A_{QW}(\omega_{exc})$ , in the case of the 3 nm barrier QW, will produce a higher total number of carriers in the QW compared to the 5 nm barrier or 7 nm barrier wells. This can be more easily observed by examining the field generated around nanobox 1 at the excitation wavelength, as seen in Fig. 6.13.



**Figure 6.13:** Map of the field intensity at the excitation wavelength in the x-z plane for nanobox 1 for a plane wave excitation. Simulation data provided by Dr. Vasilios Karanikolas.

It can be seen clearly that as the GaN barrier is increased and the distance between the nanobox and the QW (or InGaN layer, indicated by a yellow arrow) increases, the enhanced field decreases. Therefore, although the efficiency is lower, the increase in the number of QW excitations can result in an increase in the number of excited QDs and can therefore produce more total emission. This can explain why, despite a lower FRET efficiency for the 3 nm barrier QW compared to the 5 nm barrier or 7 nm barrier QWs, the QD emission enhancement is higher.

For completeness the PL spectra were also measured. An example of the PL spectra for the complete 3-component system using nanobox 1 and QW 1 is shown in Fig. 6.14. Fig. 6.14 shows the PL spectra of the QW by itself, the QW with the nanobox array without the QDs, the QW with the QDs without the nanobox array, the QDs on the nanobox array on bulk GaN and the QW with the QDs on the nanobox array. From the black and red lines in Fig. 6.14 it can be seen that there is no evidence of direct radiative or nonradiative energy transfer in the absence of the nanobox array, as the QW emission is the same with or without the addition of the QD layer. The direct quenching of the QW emission by the nanobox array is seen by comparing the black and magenta lines. On the bulk GaN substrate the QD emission is increased by  $\sim 40\%$  on the nanobox array compared to off of the nanobox array (green line). However, in the presence of the nanobox array after the



**Figure 6.14:** PL spectra for 3-component system using nanobox 1 array on QW 1 (3 nm barrier).

addition of the QD layer (blue line), the QW emission is further reduced and the QD emission is increased by  $\sim 120\%$  compared to off the nanobox array, which is again attributed to the LSP-FRET.

## 6.4 Conclusion

In conclusion, LSP-FRET from three InGaN/GaN QWs with different barrier thicknesses to a  $\sim 80\text{nm}$  layer of QDs embedded in PMMA using silver nanobox arrays has been demonstrated. These arrays were fabricated by EBL directly on the SQWs and on bulk GaN substrates to allow for investigation of the QD-nanobox array interaction independently. The QD-nanobox array interaction can be fully understood by a combination of enhanced absorption and scattering processes due to the presence of the nanobox arrays. TRPL and PL spectral measurements demonstrate and quantify the presence of the LSP-FRET from the QWs to the QDs arising from the increased local field around the nanobox arrays. For a given array, the FRET rate is observed to decrease as the QW barrier thickness is increased. This observation indicates that at smaller QW-array distances, the LSP-FRET process is faster and that the rate of FRET decreases as the QW-array distance increases, as expected. This result is consistent with observations of LSP-FRET in other material geometries [134]. The trade-off between the FRET rate and the spontaneous emission and quenching rates within the donor QWs is discussed and the efficiency values are presented. Also, the change in the QD emission due solely to LSP-FRET is can be understood by a combination of the energy transfer efficiency and the donor field enhancement factor. LSP-FRET efficiencies of up to 28 % are observed from the QWs to the QDs. QD emission enhancements of up to 120 % are also seen.

This study clearly demonstrates that LSP-FRET can occur from QWs with thicker barriers (up to 7 nm) to a thick layer of acceptor QDs by utilizing plasmonic arrays. This result provides a very promising outlook on the use of nonradiate pumping for down-conversion based LEDs. It is also worthwhile to note that the QW-QD distance can be systematically increased by the addition of oxide layers on top of the GaN barrier itself or indeed by the introduction of, for example, an AlGaIn layer. The introduction of an AlGaIn buffer layer would be compatible with the growth processes used in the III/V QW material growth and could provide for even smaller incremental changes in the QW-QD distance which could be used to increase the insight within this hybrid system even further.



## 7 Conclusions and Future Work

### 7.1 Carrier Density Dependence of LSP-FRET from a QW to a Layer of QDs

Plasmon-enhanced nonradiative energy transfer has been observed for the first time from an InGaN/GaN SQW to core-shell CdSe/ZnS QDs embedded in a  $\sim 80$  nm host PMMA layer. A Ag nanobox array, fabricated by helium-ion lithography and designed such that the QW emission peak spectrally overlaps with the LSP resonance, was used to enable this LSP enhanced process. No measureable direct FRET from the QW to the QDs was observed, therefore the NP arrays provide substantial enhancement to facilitate large ET efficiencies from the QW to the QDs, despite the strong presence of quenching of the QW emission to the NP arrays. The carrier density dependence within this system was presented to both understand the nature of the donor carriers and to demonstrate that the direct quenching and energy transfer efficiencies were carrier density independent, which is a first step towards implementation in electrically pumped LEDs. Both the QW emission quenching rate and the plasmon-coupled nonradiative energy transfer rate were found to increase with increasing QW carrier density. TRPL and PL spectra measurements were used to quantify the LSP-FRET from the QW to the QDs. Despite strong direct quenching by the metal nanoparticles, a plasmon-coupled energy transfer efficiency of 25 % was observed from the QW directly to the layer of QDs. The carrier density dependence of the nonradiative energy transfer from the QW to the Ag nanobox array and that of the plasmon-enhanced nonradiative energy transfer from the QW to the QD layer are found to be the same as for conventional Förster-like energy transfer. This indicates that secondary effects of the plasmon coupling, such as spectral shifts, do not have a significant effect in the system studied. Furthermore, the plasmon-coupled energy transfer resulted in a 16 % increase of the QD emission.

## 7.2 Nanostructure Dependence of LSP-FRET from a QW to a Layer of QDs

Having observed LSP-FRET from a QW donor to a layer QD acceptors for the first time, chapter 5 demonstrated how the LSP enhanced processes were dependent on the plasmonic array geometries. To do this a range of different Ag plasmonic arrays were fabricated directly onto both a QW and bulk GaN substrate. The plasmonic arrays were shown to impact the QW donor and QD acceptors independently. The QD-NP array interaction could be completely understood by a combination of enhanced absorption and scattering processes due to the presence of the NP arrays. The different arrays were also shown to change the efficiency of the LSP-FRET from the QW to the QDs. Once again, TRPL and PL spectra measurements demonstrated and quantified the presence of the LSP enhanced FRET from the QW to the QDs via the increased local field around the NP arrays. Quenching efficiencies from 84% to 90% were observed from the QW to the different NP array geometries and plasmon-enhanced FRET efficiencies from 25 % to 51 % were observed from the QW directly to the QDs. QD lifetime enhancements of almost 60 % were observed and QD emission enhancements of up to 71 % were also seen. The QD emission enhancement data was fit with an expression which includes the energy transfer efficiency contribution and agreement between the experimental and theoretical results was achieved. This clearly demonstrated that the total change in the QD emission from the GaN substrate to the QW substrate was solely due to the LSP-FRET from the QW to the QDs and was not driven by any other mechanism. The work in chapter 5 successfully showed the versatile role that the plasmonic arrays play within the QW-Array-QD hybrid system to enhance both LSP modified FRET and LSP modified emission processes. Therefore, it could be concluded that depending on the specific requirements of a given system, a different nanostructure should be chosen. Colour switching could be achieved by selecting a plasmonic array that quenches the donor emission strongly along with maintaining LSP-FRET to the acceptor, whilst colour tuning could be achieved by a combination of both LSP enhanced absorption and emission of either the donor or acceptor and enhanced FRET between them.

## 7.3 QW Barrier Thickness Dependence of LSP-FRET from a QW to a Layer of QDs

InGaN/GaN QWs have been promising to explore in terms of opto-electronic devices, such as LEDs [103–105] and light harvesting devices [106, 107]. Whilst the work presented in this thesis showed that QWs can nonradiatively pump thicker



layers of QDs by utilizing plasmonic elements, the first study was demonstrated for a QW with a thin (3 nm) GaN barrier. As discussed in chapter 6, thin QW barriers ( $\sim$  few nm thick) can dramatically increase the nonradiative losses within QWs and can be detrimental for carrier spreading across the device area [10]. Having a thicker QW barrier can help to alleviate both of these problems. Therefore, to remedy these issues, in chapter 6 the impact of changing the QW barrier thickness on the LSP-FRET process from the QW donor to the QD acceptors was discussed. To do this the QW barrier thickness was increased from 3 nm to 7 nm in steps of 2 nm. LSP-FRET was demonstrated using all three InGaN/GaN QWs, with different barrier thicknesses to an  $\sim$  80nm layer of QDs embedded in PMMA decorated with Ag nanobox arrays. These arrays were fabricated by EBL directly on the SQWs and on bulk GaN substrates to allow for independent investigation of the QD-nanobox array interaction. Once again, the QD emission on the plasmonic array can be fully understood by a combination of enhanced absorption and scattering processes due to the presence of the nanobox arrays. For a given array, the FRET rate was observed to decrease as the QW barrier thickness is increased. This observation indicated that at smaller QW-array distances, the LSP-FRET process is faster and that the rate of FRET decreases as the QW-array distance increases, as expected. This result is consistent with observations of LSP-FRET in other material geometries [134]. The change in the QD emission due solely to LSP-FRET arose from a combination of the energy transfer efficiency and donor field enhancement factor at the excitation wavelength. LSP-FRET efficiencies of up to 28 % were observed from the QWs to the QDs, and a LSP-FRET efficiency of 25 % was observed for a QW with a 7 nm barrier. QD emission increases of up to 120 % were also seen. The work presented in chapter 6 clearly demonstrates that LSP-FRET can occur from QWs with thicker barriers (up to 7 nm) to a thick layer of acceptor QDs by utilizing plasmonic arrays.

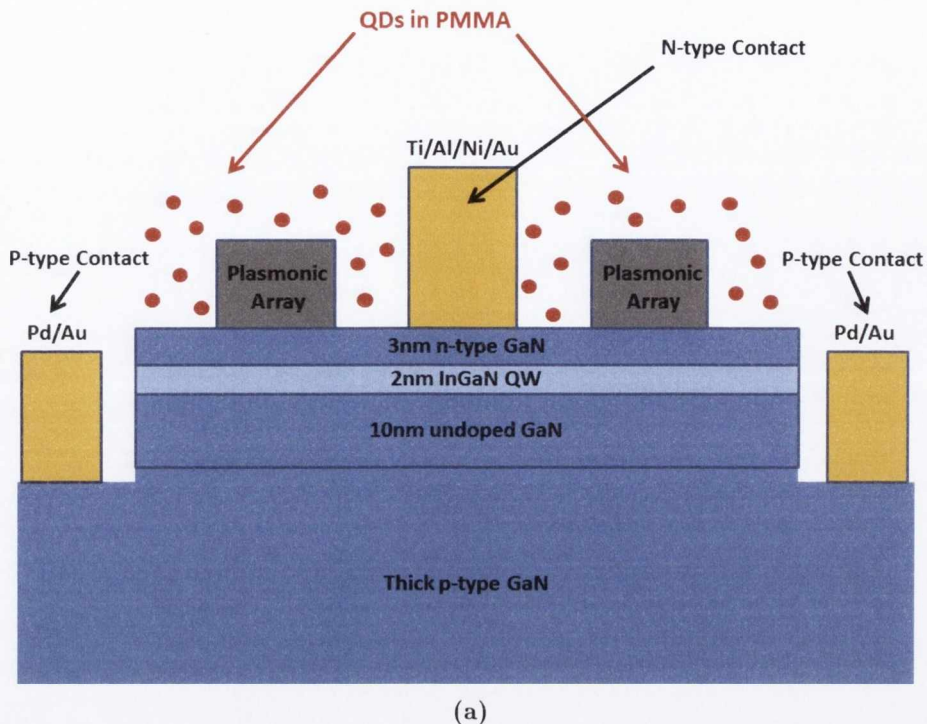
To conclude, it is interesting to compare the total efficiency of nonradiative energy transfer presented in this thesis to its radiative counterpart. Let us consider radiative pumping first. Although complex simulation could calculate to total efficiency of ET from the QW to the QDs *via* radiative pumping, a reasonably accurate estimation can in fact be made by using the known experimental parameters. The internal quantum efficiency of the QW is  $\sim$  85 %. Therefore,  $\sim$  85 % of the generated carriers in the QW are converted into photons. These photons are emitted in all directions and there is no preferential emission direction. Therefore,  $\sim$  50 % are emitted in the upward direction towards the GaN barrier. However, due to total internal reflection at the GaN-air interface, only photons that are emitted within a cone of semi-angle of  $\sim$  30 degrees actually escape from the QW. This cone constitutes only  $\sim$  13 % of the photons emitted in the upward direction. As a result, the external quantum



efficiency becomes  $(0.85 \times 0.5 \times 0.13) \sim 5\%$ . This is consistent with values for the extraction efficiency seen in the literature [145]. Therefore, only  $\sim 5\%$  of the carriers generated in the QW actually escape and can pump the QD layer. Also, it is important to note that for the QD acceptors, the absorption efficiency is less than  $1\%$  in a  $\sim 80$  nm layer. This is precisely why very thick layers (several microns thick) of acceptors are required in LEDs, in order to ensure almost  $100\%$  absorption of the limited number of extracted photons from the QW. By comparison, the work presented in this thesis shows that LSP-FRET efficiencies of  $>50\%$  can be achieved from the QW to the QDs. Therefore more than half of all the generated carriers within the QW actually excite the QD acceptors in only a  $\sim 80$  nm layer. This result provides a very promising outlook on the use of nonradiate pumping for down-conversion based LEDs.

## 7.4 Potential Plasmonic White Light LED Device Design

As mentioned before, all of the investigations undertaken in the hybrid QW-Array-QD system throughout this thesis used light to excite the donor carriers in the QW. However, the practical implementation of this system to create an LED device would require that the donor QW carriers be electrically excited. A promising inverted-type architecture for transferring energy from a QW donor to QD acceptors was proposed by Achermann *et. al.* in 2006 [10]. Fig. 7.1 shows a schematic of the type of design for a white light LED, similar to that used by Achermann, that could be used in the future which would incorporate plasmonic arrays to enhance both the FRET from the donor QW to the acceptor QDs and to subsequently enhance the acceptor QD emission. The design allows for creation of donor carriers by doping of the GaN layers such that there is both a p-type and n-type layer. The n-type contact pad can be made from Ti/Al/Ni/Au and the p-type contact can be made from Pd/Au as in Achermanns paper. The plasmonic arrays must be placed close (within several tens of microns) to the n-type contact pad because within this region sufficient carrier spreading can be expected. Careful positioning of the arrays is therefore of crucial importance for implementing plasmonic elements into the QW-QD electrically contacted system. Additionally, green and/or red emitting QDs could be used in the PMMA layer to tune the overall colour from the system.



**Figure 7.1:** Schematic of electrically contacted QW-Array-QD system which could be a promising design for device application.

## 7.5 Future Work

Looking forward, the hybrid QW-Array-QD system could be developed further to tune the level of both enhanced emission and enhanced FRET mechanisms. For colour tuning applications, this could be done by fabricating arrays which independently facilitate absorption and/or emission enhancement of either the QW or the QDs. Such arrays could be fabricated using HIL. Colour tuning devices could also benefit from enhancement of the FRET process between the QW and the QD by having a level of control over the colour mixing of the entire structure. Optimization of the hybrid system for a colour switching plasmonic device could be achieved by selecting a plasmonic array that quenches the donor emission strongly along with maintaining high levels of LSP-FRET to the acceptor. The nanoring geometry presented in chapter 5 could fulfil both of these requirements but other plasmonic arrays could also be considered.

It would be interesting to examine how thick the QW barrier can be made before FRET within this system no longer competes with the QW spontaneous emission and quenching rates to the plasmonic arrays. The LSP-FRET demonstration with the thicker barrier opens the way for electrically contacted QW donors. In such



thicker barrier QWs the carrier spreading across the device area should be sufficient. One of the main issues with current LEDs is the extraction efficiency from the QW. Whilst QWs have a relatively high internal quantum efficiency, due to total internal reflections at the GaN-air interface the external quantum efficiency is considerably reduced. In this way nonradiative ET possesses a distinct advantage over radiative pumping within the LED. An investigation into the role that the plasmonic array has in such electrically-contacted devices would also be incredibly useful in determining the viability of using FRET in such nonradiatively pumped down-conversion LEDs. If high LSP-FRET efficiencies could be achieved from electrically contacted QW donors to thick layers of QD acceptors, the electricity-to-light efficiency for the total LED could be substantially improved.

More generally, within the range of applications for QWs into the future, the possibility exists to move from electro-optically inefficient silicon to using germanium, whose direct gap transitions are much closer to the optical telecommunications wavelength of  $1.5\mu\text{m}$ . As a result, germanium quantum wells look to be a very promising candidate for future application. QWs have been used extensively in applications for injection lasers [42, 146, 147].

Furthermore, the 3-component systems used throughout this thesis could also be used as a light harvesting device, whereby the QDs become the donors and the QW acts as the acceptor. This could be achieved by selecting QDs at higher energies that have an emission spectrum that overlaps with the QW absorption. The plasmonic arrays would also have to be modified to position their absorption overlapping with the QD donor emission. This would likely require arrays consisting of smaller units than the ones considered in this thesis, but such structures could be made by HIL or colloidal metallic NPs could be explored. It could be interesting to investigate this light harvesting system using both QW acceptors that were electrically contacted and ones that were not electrically contacted. The scope for investigation within the hybrid QW-Array-QD system is considerable. Further investigation into this system for applications in both light emitting and light harvesting devices could yield fruitful results.

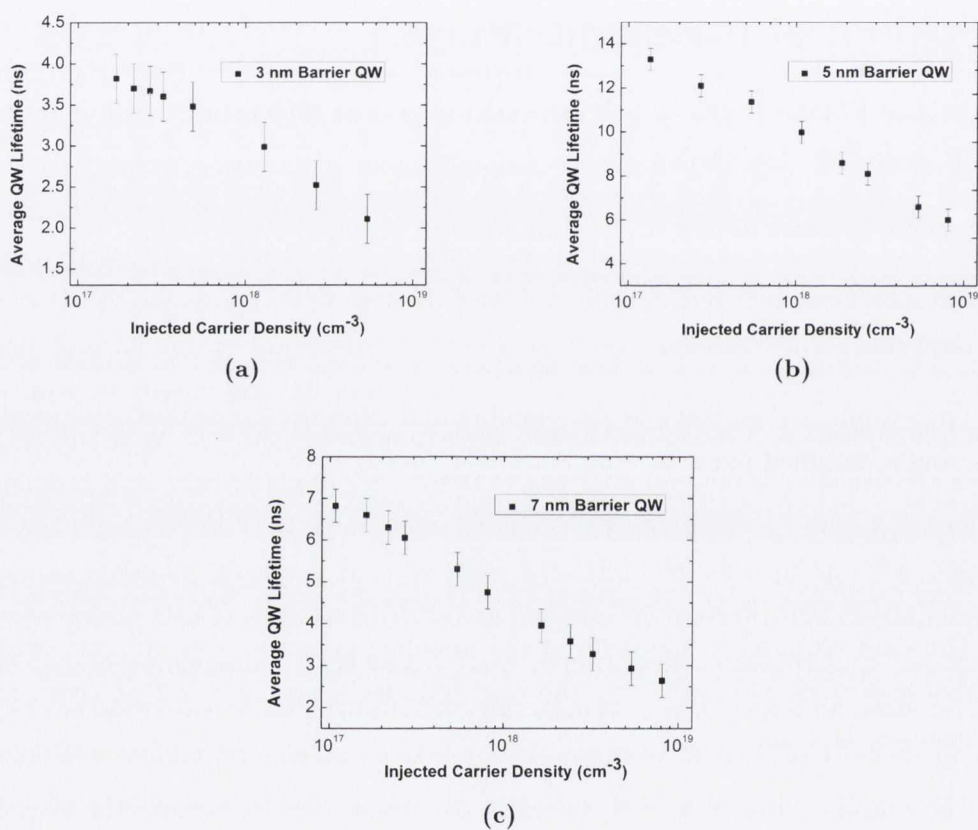


# Appendix A

## Example of sample preparation process for fabrication of plasmonic arrays.

- 60  $\mu\text{L}$  of PMMA 950K-A3 polymer resist is spun at 3000 rpm for approximately 30 seconds on GaN substrate.
- Sample is baked at 180 °C for 3 minutes to promote outgassing.
- 100  $\mu\text{L}$  of e-spacer (conducting polymer) is spun down on to the substrate at 1500 rpm for 30 seconds.
- The sample is then placed in the chamber and exposure procedure is performed using a designed pattern.
- The exposures are performed at an accelerating voltage of 30 kV with a current of  $\sim 1.7$  pA.
- The dose required to fabricate the nanobox arrays is  $\sim 6 \mu\text{C}/\text{cm}^2$ , whilst the dose required to fabricate the ring and disc arrays is  $\sim 7.2 \mu\text{C}/\text{cm}^2$ , at a step size of 4 nm.
- The sample is then removed, rinsed in deionised water to remove the e-spacer and then developed in MIBK:IPA 1:3 solution for 45 seconds.
- The sample is then rinsed in IPA for 1 minute and dried under nitrogen flow.
- The metal is then deposited using an evaporation process.
- Finally, lift-off is performed by immersing the sample in acetone for 10-15 minutes with very slight sonication to promote clean removal of residual metal.

# Appendix B



**Figure 7.2:** Average QW lifetime as a function of injected carrier density for QW samples with (a) 3 nm, (b) 5 nm and (c) 7 nm GaN barriers.

# References

- [1] J. Hansen, M. Sato, R. Ruedy, A. Lacis, and V. Oinas, "Global warming in the twenty-first century: an alternative scenario," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 97, no. 18, pp. 9875–80, 2000.
- [2] J. Houghton, *Global Warming: The complete briefing*. Cambridge University Press, 2009.
- [3] S. Solomon, K. H. Rosenlof, R. W. Portmann, J. S. Daniel, S. M. Davis, T. J. Sanford, and G. Plattner, "Contributions of stratospheric water vapor to decadal changes in the rate of global warming," *Science*, vol. 327, no. 5970, pp. 1219–1223, 2010.
- [4] S. Luque, A., & Hegedus, *Handbook of photovoltaic science and engineering (2nd ed.)*. 2011.
- [5] E. Schubert, *Light-Emitting Diodes*. Cambridge University, 2006.
- [6] H. V. Demir, S. Nizamoglu, T. Erdem, E. Mutlugun, N. Gaponik, and A. Eyichmuller, "Quantum dot integrated LEDs using photonic and excitonic color conversion," *Nano Today*, vol. 6, no. 6, pp. 632–647, 2011.
- [7] A. Shaw, A. Bradley, J. Donegan, and J. Lunney, "GaN Resonant Cavity Light-Emitting Diodes for Plastic Optical Fiber Applications," *IEEE Photonics Technology Letters*, vol. 16, no. 9, pp. 2006–2008, 2004.
- [8] T. Fujii, Y. Gao, R. Sharma, E. L. Hu, S. P. DenBaars, and S. Nakamura, "Increase in the extraction efficiency of GaN-based light-emitting diodes via surface roughening," *Applied Physics Letters*, vol. 84, no. 6, pp. 855–857, 2004.
- [9] M. Achermann, M. a. Petruska, S. Kos, D. L. Smith, D. D. Koleske, and V. I. Klimov, "Energy-transfer pumping of semiconductor nanocrystals using an epitaxial quantum well," *Nature*, vol. 429, no. 6992, pp. 642–646, 2004.
- [10] M. Achermann, M. A. Petruska, D. D. Koleske, M. H. Crawford, and V. I. Klimov, "Nanocrystal-based light-emitting diodes utilizing high-efficiency non-



- radiative energy transfer for color conversion,” *Nano Letters*, vol. 6, no. 7, pp. 1396–1400, 2006.
- [11] S. Nizamoglu, B. Guzelturk, D. W. Jeon, I. H. Lee, and H. V. Demir, “Efficient nonradiative energy transfer from InGaN/GaN nanopillars to CdSe/ZnS core/shell nanocrystals,” *Applied Physics Letters*, vol. 98, no. 16, 2011.
- [12] F. Zhang, J. Liu, G. You, C. Zhang, S. E. Mohny, M. J. Park, J. S. Kwak, Y. Wang, D. D. Koleske, and J. Xu, “Nonradiative energy transfer between colloidal quantum dot-phosphors and nanopillar nitride LEDs,” *Optics Express*, vol. 20, no. S2, p. A333, 2012.
- [13] B. Guzelturk, S. Nizamoglu, D. W. Jeon, I. H. Lee, and H. V. Demir, “Strong nonradiative energy transfer from the nanopillars of quantum wells to quantum dots: Efficient excitonic color conversion for light emitting diodes,” *Conference on Lasers and Electro-Optics 2012*, p. CW1L.1, 2012.
- [14] S. Nizamoglu, P. Ludwig Hernandez-Martinez, E. Mutlugun, D. Ugur Karatay, and H. Volkan Demir, “Excitonic enhancement of nonradiative energy transfer from a quantum well in the optical near field of energy gradient quantum dots,” *Applied Physics Letters*, vol. 100, no. 24, pp. 2010–2014, 2012.
- [15] S. Nizamoglu, O. Akin, and H. V. Demir, “Quantum efficiency enhancement in nanocrystals using nonradiative energy transfer with optimized donor-acceptor ratio for hybrid LEDs,” *Applied Physics Letters*, vol. 94, no. 24, pp. 1–4, 2009.
- [16] A. Neogi, C. W. Lee, H. Everitt, T. Kuroda, A. Tackeuchi, and E. Yablonovitch, “Enhancement of spontaneous recombination rate in a quantum well by resonant surface plasmon coupling,” *Physical Review B*, vol. 66, no. 15, p. 153305, 2002.
- [17] K. Okamoto, I. Niki, A. Shvarts, Y. Narukawa, T. Mukai, and A. Scherer, “Surface-plasmon-enhanced light emitters based on InGaN quantum wells,” *Nature materials*, vol. 3, no. 9, pp. 601–5, 2004.
- [18] J. Henson, E. Dimakis, J. DiMaria, R. Li, S. Minissale, L. Dal Negro, T. D. Moustakas, and R. Paiella, “Enhanced near-green light emission from InGaN quantum wells by use of tunable plasmonic resonances in silver nanoparticle arrays,” *Optics Express*, vol. 18, no. 20, pp. 21322–21329, 2010.
- [19] G. Lozano, D. J. Louwers, S. R. Rodríguez, S. Murai, O. T. Jansen, M. A. Verschuuren, and J. Gómez Rivas, “Plasmonics for solid-state lighting: enhanced excitation and directional emission of highly efficient light sources,” *Light: Science & Applications*, vol. 2, no. 5, p. e66, 2013.

- 
- [20] M. K. Kwon, J. Y. Kim, B. H. Kim, I. K. Park, C. Y. Cho, C. C. Byeon, and S. J. Park, "Surface-plasmon-enhanced light-emitting diodes," *Advanced Materials*, vol. 20, no. 7, pp. 1253–1257, 2008.
- [21] A. Kumar, R. Srivastava, P. Tyagi, D. Mehta, and M. Kamalasanan, "Efficiency enhancement of organic light emitting diode via surface energy transfer between exciton and surface plasmon," *Organic Electronics*, vol. 13, no. 1, pp. 159–165, 2012.
- [22] P. P. Pompa, L. Martiradonna, a. D. Torre, F. D. Sala, L. Manna, M. De Vittorio, F. Calabi, R. Cingolani, and R. Rinaldi, "Metal-enhanced fluorescence of colloidal nanocrystals with nanoscale control," *Nature nanotechnology*, vol. 1, no. 2, pp. 126–130, 2006.
- [23] K. Tanaka, E. Plum, J. Y. Ou, T. Uchino, and N. I. Zheludev, "Multifold enhancement of quantum dot luminescence in plasmonic metamaterials," *Physical Review Letters*, vol. 105, no. 22, pp. 1–4, 2010.
- [24] V. K. Komarala, Y. P. Rakovich, A. L. Bradley, S. J. Byrne, Y. K. Gun'ko, N. Gaponik, and A. Eychmuller, "Off-resonance surface plasmon enhanced spontaneous emission from CdTe quantum dots," *Applied Physics Letters*, vol. 89, no. 25, pp. 2004–2007, 2006.
- [25] S. M. Sadeghi, B. Hood, A. Nejat, R. G. West, and A. Hatef, "Excitation intensity dependence of plasmonic enhancement of energy transfer between quantum dots," *Journal of Physics D: Applied Physics*, vol. 47, p. 165302, 2014.
- [26] S. M. Sadeghi, A. Hatef, A. Nejat, Q. Campbell, and M. Meunier, "Plasmonic emission enhancement of colloidal quantum dots in the presence of bimetallic nanoparticles," *Journal of Applied Physics*, vol. 115, no. 13, 2014.
- [27] P. Anger, P. Bharadwaj, and L. Novotny, "Enhancement and quenching of single-molecule fluorescence," *Physical Review Letters*, vol. 96, no. 11, pp. 3–6, 2006.
- [28] J. I. Gersten and A. Nitzan, "Accelerated energy transfer between molecules near a solid particle," *Chemical Physics Letters*, vol. 104, no. 1, pp. 31–37, 1984.
- [29] X. M. Hua, J. I. Gersten, and A. Nitzan, "Theory of energy transfer between molecules near solid state particles," *The Journal of Chemical Physics*, vol. 83, no. 7, pp. 3650–3659, 1985.



- 
- [30] V. K. Komarala, A. L. Bradley, Y. P. Rakovich, S. J. Byrne, Y. K. Gun'ko, and A. L. Rogach, "Surface plasmon enhanced Forster resonance energy transfer between the CdTe quantum dots," *Applied Physics Letters*, vol. 93, no. 12, pp. 2006–2009, 2008.
- [31] J. Zhang, Y. Fu, M. H. Chowdhury, and J. R. Lakowicz, "Metal-enhanced single-molecule fluorescence on silver particle monomer and dimer: Coupling effect between metal particles," *Nano Letters*, vol. 7, no. 7, pp. 2101–2107, 2007.
- [32] M. Lessard-Viger, M. Rioux, L. Rainville, and D. Boudreau, "FRET Enhancement in Multilayer Core - Shell Nanoparticles," *Nano Lett.*, vol. 9, pp. 3066–3071, 2009.
- [33] V. Faessler, C. Hrelescu, A. A. Lutich, L. Osinkina, S. Mayilo, F. Jäckel, and J. Feldmann, "Accelerating fluorescence resonance energy transfer with plasmonic nanoresonators," *Chemical Physics Letters*, vol. 508, no. 1-3, pp. 67–70, 2011.
- [34] M. Lunz, V. A. Gerard, Y. K. Gun'ko, V. Lesnyak, N. Gaponik, A. S. Sussha, A. L. Rogach, and A. L. Bradley, "Surface plasmon enhanced energy transfer between donor and acceptor CdTe nanocrystal quantum dot monolayers," *Nano Letters*, vol. 11, no. 8, pp. 3341–3345, 2011.
- [35] X. Zhang, C. A. Marocico, M. Lunz, V. A. Gerard, Y. K. Gun'ko, V. Lesnyak, N. Gaponik, A. S. Sussha, A. L. Rogach, and A. L. Bradley, "Experimental and Theoretical Investigation of the Distance Dependence of Localized Surface Plasmon Coupled Forster Resonance Energy Transfer," *ACS nano*, vol. 8, no. 2, pp. 1273–1283, 2014.
- [36] P. Andrew and W. L. Barnes, "Energy Transfer Across a Metal Film Mediated by Surface Plasmon Polaritons," vol. 306, no. November, pp. 1002–1005, 2004.
- [37] X. Zhao, P. Wang, and B. Li, "Surface plasmon enhanced energy transfer in metal-semiconductor hybrid nanostructures," *Nanoscale*, vol. 3, no. 8, pp. 3056–9, 2011.
- [38] A. O. Govorov, J. Lee, and N. A. Kotov, "Theory of plasmon-enhanced Forster energy transfer in optically excited semiconductor and metal nanoparticles," *Physical Review B - Condensed Matter and Materials Physics*, vol. 76, no. 12, pp. 1–16, 2007.
- [39] X. Zhang, *Localised Surface Plasmon Mediated Energy Transfer in Quantum Dot Systems*. Phd thesis, Trinity College Dublin, 2014.



- 
- [40] C. A. Marocico, X. Zhang, and A. L. Bradley, "A theoretical investigation of the influence of gold nanosphere size on the decay and energy transfer rates and efficiencies of quantum emitters," *The Journal of Chemical Physics*, vol. 144, no. 2, p. 024108, 2016.
- [41] P. L. Hernandez-Martinez, A. O. Govorov, and H. V. Demir, "Generalized theory of Forster-type nonradiative energy transfer in nanostructures with mixed dimensionality," *Journal of Physical Chemistry C*, vol. 117, no. 19, pp. 10203–10212, 2013.
- [42] Gaponenko S., *Introduction to Nanophotonics*. Cambridge University Press, 2005.
- [43] T. Ozel, P. L. Hernandez-Martinez, E. Mutlugun, O. Akin, S. Nizamoglu, I. O. Ozel, Q. Zhang, Q. Xiong, and H. V. Demir, "Observation of selective plasmon-exciton coupling in nonradiative energy transfer: Donor-selective versus acceptor-selective plexcitons," *Nano Letters*, vol. 13, no. 7, pp. 3065–3072, 2013.
- [44] G. Liu, J. Zhang, C. K. Tan, and N. Tansu, "Efficiency-droop suppression by using large-bandgap AlGaInN thin barrier layers in InGaN quantum-well light-emitting diodes," *IEEE Photonics Journal*, vol. 5, no. 2, 2013.
- [45] R. Clegg, *Fret and Flim Techniques 1*. 1 ed., 2009.
- [46] C. S. Van Der Meer B.W., Coker G., *Resonance energy transfer: theory and data*. New York: Vch, 1994.
- [47] A. J. Nozik, "Relaxation Dynamics in Semiconductors," *Renewable Energy*, pp. 193–231, 2001.
- [48] V. Klimov and D. McBranch, "Femtosecond 1P-to- 1S Electron Relaxation in Strongly Confined Semiconductor Nanocrystals," *Physical Review Letters*, vol. 80, no. 18, pp. 4028–4031, 1998.
- [49] V. Klimov, D. W. McBranch, C. A. Leatherdale, and M. G. Bawendi, "Electron and hole relaxation pathways in semiconductor quantum dots," *Physical Review B*, vol. 60, no. 19, pp. 13740–13749, 1999.
- [50] P. Guyot-Sionnest, M. Shim, C. Matrangola, and M. Hines, "Intraband relaxation in CdSe quantum dots," *Physical Review B*, vol. 60, no. 4, pp. R2181–R2184, 1999.
- [51] R. Clegg, *Reviews in Fluorescence*. Springer, 2006.

- 
- [52] L. Stryer and R. P. Haugland, "Energy transfer: a spectroscopic ruler," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 58, no. 2, pp. 719–726, 1967.
- [53] S. Empedocles, D. Norris, and M. Bawendi, "Photoluminescence Spectroscopy of Single CdSe Nanocrystallite Quantum Dots," *Physical Review Letters*, vol. 77, no. 18, pp. 3873–3876, 1996.
- [54] J. R. Lakowicz, *Principles of fluorescence spectroscopy. 2nd edition*. Springer, 2007.
- [55] D. Dexter, "A Theory of Sensitized Luminescence in Solids," *The Journal of Chemical Physics*, vol. 21, no. 836, 1953.
- [56] D. L. Andrews, "A unified theory of radiative and radiationless molecular energy transfer," *Chemical Physics*, vol. 135, no. 2, pp. 195–201, 1989.
- [57] P. F. Barbara, T. J. Meyer, and M. A. Ratner, "Contemporary Issues in Electron Transfer Research," *The Journal of Physical Chemistry*, vol. 100, no. 31, pp. 13148–13168, 1996.
- [58] D. D. Adams, L. Brus, C. Chidsey, S. Creager, C. Creutz, C. Kagan, P. Kamat, O. Marya Lieberman, S. Lindsay, and R. Marcus, "Charge transfer on the nanoscale: current status," *The Journal of Physical Chemistry B*, vol. 107, no. 28, pp. 6668–6697, 2003.
- [59] C. S. Yun, A. Javier, T. Jennings, M. Fisher, S. Hira, S. Peterson, B. Hopkins, N. O. Reich, and G. F. Strouse, "Nanometal surface energy transfer in optical rulers, breaking the FRET barrier," *Journal of the American Chemical Society*, vol. 127, no. 9, pp. 3115–3119, 2005.
- [60] C. Kagan, C. Murray, and M. Bawendi, "Long-range resonance transfer of electronic excitations in close-packed CdSe quantum-dot solids," *Physical Review B*, vol. 54, no. 12, pp. 8633–8643, 1996.
- [61] C. B. Murray, C. R. Kagan, and M. G. Bawendi, "Synthesis and characterization of monodisperse and close-packed nanocrystal assemblies," *Annu. Rev. Mater. Sci.*, pp. 545–610, 2000.
- [62] B. O. Dabbousi, C. B. Murray, M. F. Rubner, and M. G. Bawendi, "Langmuir-blodgett Manipulation of Size-selected Cdse Nanocrystallites," *Chemistry of Materials*, vol. 6, no. 2, pp. 216–219, 1994.
- [63] L. N. N. Bimberg D., Grundmann M., *Quantum dot heterostructures*. John Wiley & Sons, 1999.

- [64] X. Peng, M. C. Schlamp, A. V. Kadavanich, and A. P. Alivisatos, "Epitaxial Growth of Highly Luminescent CdSe / CdS Core / Shell Nanocrystals with Photostability and Electronic Accessibility," *Journal of American Chemical Society*, vol. 7863, no. 25, pp. 7019–7029, 1997.
- [65] C. Kagan, C. Murray, M. Nirmal, and M. Bawendi, "Electronic energy transfer in CdSe quantum dot solids.," *Physical Review Letters*, vol. 76, no. 9, pp. 1517–1520, 1996.
- [66] S. A. Crooker, J. A. Hollingsworth, S. Tretiak, and V. I. Klimov, "Spectrally Resolved Dynamics of Energy Transfer in Quantum-Dot Assemblies: Towards Engineered Energy Flows in Artificial Materials," *Physical Review Letters*, vol. 89, no. 18, p. 186802, 2002.
- [67] M. Lunz, A. L. Bradley, W. Y. Chen, V. A. Gerard, S. J. Byrne, Y. K. Gun'Ko, V. Lesnyak, and N. Gaponik, "Influence of quantum dot concentration on Forster resonant energy transfer in monodispersed nanocrystal quantum dot monolayers," *Physical Review B - Condensed Matter and Materials Physics*, vol. 81, no. 20, pp. 1–10, 2010.
- [68] A. A. Mamedov, A. Belov, M. Giersig, N. N. Mamedova, and N. A. Kotov, "Nanorainbows: Graded semiconductor films from quantum dots [2]," *Journal of the American Chemical Society*, vol. 123, no. 31, pp. 7738–7739, 2001.
- [69] G. Allan and C. Delerue, "Energy transfer between semiconductor nanocrystals: Validity of Forster's theory," *Physical Review B - Condensed Matter and Materials Physics*, vol. 75, no. 19, pp. 1–8, 2007.
- [70] C. Curutchet, A. Franceschetti, A. Zunger, and G. D. Scholes, "Examining Forster energy for semiconductor nanocrystalline quantum dot donors and acceptors," *Journal of Physical Chemistry C*, vol. 112, no. 35, pp. 13336–13341, 2008.
- [71] T. Franzl, T. A. Klar, S. Schietinger, A. L. Rogach, and J. Feldmann, "Exciton recycling in graded gap nanocrystal structures," *Nano Letters*, vol. 4, no. 9, pp. 1599–1603, 2004.
- [72] I. L. Medintz, K. E. Sapsford, A. R. Clapp, T. Pons, S. Higashiya, J. T. Welch, and H. Mattoussi, "Designer variable repeat length polypeptides as scaffolds for surface immobilization of quantum dots," *Journal of Physical Chemistry B*, vol. 110, no. 22, pp. 10683–10690, 2006.



- [73] A. R. Clapp, I. L. Medintz, J. M. Mauro, B. R. Fisher, M. G. Bawendi, and H. Mattoussi, "Fluorescence resonance energy transfer between quantum dot donors and dye-labeled protein acceptors," *Journal of the American Chemical Society*, vol. 126, no. 1, pp. 301–310, 2004.
- [74] A. R. Clapp, I. L. Medintz, and H. Mattoussi, "Forster resonance energy transfer investigations using quantum-dot fluorophores," *ChemPhysChem*, vol. 7, no. 1, pp. 47–57, 2006.
- [75] Z. Chen, S. Berciaud, C. Nuckolls, T. F. Heinz, and L. E. Brus, "Energy transfer from individual semiconductor nanocrystals to graphene," *ACS Nano*, vol. 4, no. 5, pp. 2964–2968, 2010.
- [76] A. M. Dennis and G. Bao, "Quantum dot-fluorescent protein pairs as novel fluorescence resonance energy transfer probes," *Nano Letters*, vol. 8, no. 5, pp. 1439–1445, 2008.
- [77] K. A. Willets and R. P. Van Duyne, "Localized Surface Plasmon Resonance Spectroscopy and Sensing," *Phys. Chem.*, vol. 58, pp. 267–297, 2007.
- [78] O. Kulakovich, N. Strekal, A. Yaroshevich, S. Maskevich, S. Gaponenko, I. Nabiev, U. Woggon, and M. Artemyev, "Enhanced Luminescence of CdSe Quantum Dots on Gold Colloids," *Nano Letters*, vol. 2, no. 12, pp. 1449–1452, 2002.
- [79] Y. Wang, T. Yang, M. T. Tuominen, and M. Achermann, "Radiative rate enhancements in ensembles of hybrid metal-semiconductor nanostructures," *Physical Review Letters*, vol. 102, no. 16, pp. 1–4, 2009.
- [80] J. L. Stokes, Y. Yu, Z. H. Yuan, J. R. Pugh, M. Lopez-Garcia, N. Ahmad, and M. J. Cryan, "Analysis and design of a cross dipole nanoantenna for fluorescence-sensing applications," *J. Opt. Soc. Am.*, vol. 31, no. 2, pp. 302–310, 2014.
- [81] J. L. Stokes, A. Sarua, J. R. Pugh, N. Dorh, J. W. Munns, P. G. Bassindale, N. Ahmad, A. J. Orr-Ewing, and Cryan M. J., "Purcell enhancement and focusing effects in plasmonic nanoantenna arrays," vol. 32, no. 10, pp. 2158–2163, 2015.
- [82] I. Medintz and N. Hildebrandt, *FRET-Forster Resonance Energy Transfer: From Theory to Applications*. John Wiley & Sons, 2013.
- [83] T. Forster, "Energiewanderung und Fluoreszenz," *Annalen der Physik*, vol. 2, no. 6, pp. 55–75, 1948.

- [84] R. S. Knox, "Forster resonance excitation transfer theory: not just a formula," *Journal of Biomedical Optics*, vol. 17, no. 1, p. 011003, 2012.
- [85] R. G. West and S. M. Sadeghi, "Enhancement of Energy Transfer between Quantum Dots : The Impact of Metallic Nanoparticle Sizes Enhancement of Energy Transfer between Quantum Dots : The Impact of Metallic Nanoparticle Sizes," *The Journal of Physical Chemistry C*, vol. 116, no. 38, pp. 20496–20503 (7 pages), 2012.
- [86] X. R. Su, W. Zhang, L. Zhou, X. N. Peng, D. W. Pang, S. D. Liu, Z. K. Zhou, and Q. Q. Wang, "Multipole-plasmon-enhanced forster energy transfer between semiconductor quantum dots via dual-resonance nanoantenna effects," *Applied Physics Letters*, vol. 96, no. 4, pp. 2008–2011, 2010.
- [87] J. de Torres, P. Ferrand, G. Colas Des Francs, and J. Wenger, "Coupling Emitters and Silver Nanowires to Achieve Long-Range Plasmon-Mediated Fluorescence Energy Transfer," *ACS Nano*, p. acsnano.6b00287, 2016.
- [88] S. Bidault, A. Devilez, P. Ghenuche, B. Stout, N. Bonod, and J. Wenger, "Competition between Förster resonance energy transfer and donor photodynamics in plasmonic dimer nanoantennas," *ACS Photonics*, p. acsphotonics.6b00148, 2016.
- [89] S. M. Sadeghi, a. Nejat, and R. G. West, "Inhibition of plasmonically enhanced interdot energy transfer in quantum dot solids via photo-oxidation," *Journal of Applied Physics*, vol. 112, no. 10, 2012.
- [90] Y. Shen, J. Malicka, S. D. Auria, and J. R. Lakowicz, "Effects of Metallic Silver Particles on Resonance Energy Transfer Between Fluorophores Bound to DNA," vol. 13, no. 1, 2003.
- [91] J. Zhang, Y. Fu, and J. R. Lakowicz, "Enhanced Forster Resonance Energy Transfer ( FRET ) on a Single Metal Particle," pp. 50–56, 2007.
- [92] M. Lessard-Viger, D. Brouard, and D. Boudreau, "Plasmon-enhanced resonance energy transfer from a conjugated polymer to fluorescent multilayer core-shell nanoparticles: A photophysical study," *Journal of Physical Chemistry C*, vol. 115, no. 7, pp. 2974–2981, 2011.
- [93] C. H. Wang, C. W. Chen, Y. T. Chen, C. M. Wei, Y. F. Chen, C. W. Lai, M. L. Ho, P. T. Chou, and M. Hofmann, "Surface plasmon enhanced energy transfer between type I CdSe/ZnS and type II CdSe/ZnTe quantum dots," *Applied Physics Letters*, vol. 96, no. 7, pp. 0–3, 2010.



- 
- [94] L. Zhao, T. Ming, L. Shao, H. Chen, and J. Wang, "Plasmon-Controlled Forster Resonance Energy Transfer," *The Journal of Physical Chemistry C*, vol. 116, no. 14, p. 120328120034006, 2012.
- [95] R. Wargnier, A. V. Baranov, V. G. Maslov, V. Stsiapura, M. Artemyev, M. Pluot, A. Sukhanova, and I. Nabiev, "Energy Transfer in Aqueous Solutions of Oppositely Charged CdSe/ZnS Core/Shell Quantum Dots and in Quantum Dot-Nanogold Assemblies," *Nano lett.*, vol. 4, no. 3, pp. 451–457, 2004.
- [96] T. Pons, I. L. Medintz, K. E. Sapsford, S. Higashiya, A. F. Grimes, D. S. English, and H. Mattoussi, "On the quenching of semiconductor quantum dot photoluminescence by proximal gold nanoparticles," *Nano Letters*, vol. 7, no. 10, pp. 3157–3164, 2007.
- [97] A. O. Govorov, G. W. Bryant, W. Zhang, T. Skeini, J. Lee, N. A. Kotov, J. M. Slocik, and R. R. Naik, "Exciton Plasmon Interaction and Hybrid Excitons in Semiconductor Metal Nanoparticle Assemblies," *Nano Letters*, vol. 6, no. 5, pp. 984–994, 2006.
- [98] T. Ozel, S. Nizamoglu, M. A. Sefunc, O. Samarskaya, I. O. Ozel, E. Mutlugun, V. Lesnyak, N. Gaponik, A. Eychmuller, S. V. Gaponenko, and H. V. Demir, "Anisotropic emission from multilayered plasmon resonator nanocomposites of isotropic semiconductor quantum dots," *ACS Nano*, vol. 5, no. 2, pp. 1328–1334, 2011.
- [99] D. V. Guzatov, S. V. Vaschenko, V. V. Stankevich, A. Y. Lunevich, Y. F. Glukhov, and S. V. Gaponenko, "Plasmonic enhancement of molecular fluorescence near silver nanoparticles: Theory, modeling, and experiment," *Journal of Physical Chemistry C*, vol. 116, no. 19, pp. 10723–10733, 2012.
- [100] P. Viste, J. Plain, R. Jaffiol, A. Vial, P. M. Adam, and P. Royer, "Enhancement and quenching regimes in metal-semiconductor hybrid optical nanosources," *ACS Nano*, vol. 4, no. 2, pp. 759–764, 2010.
- [101] D. A. B. Miller and T. B. Laboratories, "Optical Physics of Quantum Wells," *Quantum Dynamics of Simple Systems*, pp. 239–266, 1996.
- [102] D. A. B. Miller, "Device Requirement for Optical Interconnects to Silicon Chips," *Proc. of IEEE Special Issue on Silicon Photonics*, vol. 97, no. 7, pp. 1166–1185, 2009.



- [103] T. Mukai, M. Yamada, Nakamura, and Shuji, "Characteristics of InGaN-Based UV / Blue / Green / Amber / Red Light-Emitting Diodes," *Journal of Applied Physics*, vol. 38, no. 7, pp. 3976–3981, 1999.
- [104] S. Nakamura, M. Senoii, N. Iwasa, S. ichi Nagahama, T. Yamada, and T. Mukai, "Superbright green InGaN single-quantum-well-structure light-emitting diodes," *Japanese Journal of Applied Physics, Part 2: Letters*, vol. 34, no. 10 B, 1995.
- [105] R. A. Arif, H. Zhao, Y. K. Ee, and N. Tansu, "Spontaneous emission and characteristics of staggered InGaN quantum-well light-emitting diodes," *IEEE Journal of Quantum Electronics*, vol. 44, no. 6, pp. 573–580, 2008.
- [106] O. Jani, I. Ferguson, C. Honsberg, and S. Kurtz, "Design and characterization of GaNInGa solar cells," *Applied Physics Letters*, vol. 91, no. 13, pp. 13–16, 2007.
- [107] D. H. Lien, Y. H. Hsiao, S. G. Yang, M. L. Tsai, T. C. Wei, S. C. Lee, and J. H. He, "Harsh photovoltaics using InGaN/GaN multiple quantum well schemes," *Nano Energy*, vol. 11, pp. 104–109, 2015.
- [108] H. S. Chen, D. M. Yeh, C. F. Lu, C. F. Huang, W. Y. Shiao, and J. J. Huang, "White Light Generation With CdSe-ZnS Nanocrystals Coated on an InGaN-GaN Quantum-Well Blue / Green Two-Wavelength Light-Emitting Diode," *IEEE Photonics Technology Letters*, vol. 18, no. 13, pp. 1430–1432, 2006.
- [109] S. Nizamoglu, T. Ozel, E. Sari, and H. V. Demir, "White light generation using CdSe/ZnS core-shell nanocrystals hybridized with InGaN/GaN light emitting diodes," *Nanotechnology*, vol. 18, no. 6, p. 065709, 2007.
- [110] He G., "Warm-white light-emitting diodes integrated with colloidal quantum dots for high luminous efficacy and color rendering: comment," *Optics Letters*, vol. 36, no. 15, p. 2851, 2011.
- [111] A. H. Mueller, M. A. Petruska, M. Achermann, D. J. Werder, E. A. Akhador, D. D. Koleske, M. A. Hoffbauer, and V. I. Klimov, "Multicolor light-emitting diodes based on semiconductor nanocrystals encapsulated in GaN charge injection layers," *Nano Letters*, vol. 5, no. 6, pp. 1039–1044, 2005.
- [112] H. V. Demir, S. Nizamoglu, E. Mutlugun, T. Ozel, S. Sapra, N. Gaponik, and A. Eychmüller, "Tuning shades of white light with multi-color quantum-dot-quantum-well emitters based on onion-like CdSe-ZnS heteronanocrystals," *Nanotechnology*, vol. 19, no. 33, p. 335203, 2008.

- [113] D. Basko, G. C. L. Rocca, F. Bassani, and V. M. Agranovich, "Forster energy transfer from a semiconductor quantum well to an organic material overlayer," *The European Physical Journal B - Condensed Matter and Complex Systems*, vol. 8, no. 3, pp. 353–362, 1999.
- [114] H. A. Atwater and A. Polman, "Plasmonics for improved photovoltaic devices," *Nature materials*, vol. 9, no. 3, pp. 205–213, 2010.
- [115] M. A. Hines and P. Guyot-Sionnest, "Synthesis and characterization of strongly luminescing ZnS- Capped CdSe nanocrystals," *Journal of Physical Chemistry*, vol. 100, no. 2, pp. 468–471, 1996.
- [116] N. Gaponik, D. V. Talapin, A. L. Rogach, K. Hoppe, V. Shevchenko, A. Kornowski, A. Eychmüller, H. Weller, and E. V. Shevchenko, "Thiol-Capping of CdTe Nanocrystals : An Alternative to Organometallic Synthetic Routes Thiol-Capping of CdTe Nanocrystals : An Alternative to Organometallic Synthetic Routes," pp. 7177–7185, 2002.
- [117] W. C. W. Chan, D. J. Maxwell, X. Gao, R. E. Bailey, M. Han, and S. Nie, "Luminescent quantum dots for multiplexed biological detection and imaging," *Current Opinion in Biotechnology*, vol. 13, no. 1, pp. 40–46, 2002.
- [118] P. Reiss and A. Pron, "Highly Luminescent CdSe / ZnSe Core / Shell Nanocrystals of Low Size Dispersion," *Nano*, pp. 21–24, 2010.
- [119] A. L. Rogach, T. Franzl, T. A. Klar, J. Feldmann, N. Gaponik, V. Lesnyak, A. Shavel, A. Eychmüller, Y. P. Rakovich, and J. F. Donegan, "Aqueous Synthesis of Thiol-Capped CdTe Nanocrystals: State-of-the-Art," *The Journal of Physical Chemistry C*, vol. 111, no. 40, pp. 14628–14637, 2007.
- [120] C. Wang, X. Gao, and X. Su, "In vitro and in vivo imaging with quantum dots," *Analytical and Bioanalytical Chemistry*, vol. 397, no. 4, pp. 1397–1415, 2010.
- [121] R. C. Somers, M. G. Bawendi, and D. G. Nocera, "CdSe nanocrystal based chem-/bio- sensors," *Chemical Society reviews*, vol. 36, no. 4, pp. 579–591, 2007.
- [122] C. C. Tu and L. Y. Lin, "High efficiency photodetectors fabricated by electrostatic layer-by-layer self-assembly of CdTe quantum dots," *Applied Physics Letters*, vol. 93, no. 16, 2008.
- [123] A. Rogach, *Semiconductor Nanocrystal Quantum Dots: Synthesis, Assembly, Spectroscopy and Applications*. Springer, 2008.



- 
- [124] M. Lunz, *Forster Resonant Energy Transfer in Nanocrystal Quantum Dot Structures*. PhD thesis, Trinity College Dublin, 2010.
- [125] C. Weisbuch and B. Vinter, *Quantum Semiconductor Structure: Fundamentals and Applications*. Academic Press, 1991.
- [126] P. Gibart, “Metal organic vapour phase epitaxy of GaN and lateral overgrowth,” *Reports on Progress in Physics*, vol. 67, no. 5, pp. 667–715, 2004.
- [127] Peter S. Zory, *Quantum Well Lasers*. Academic Press, 1993.
- [128] W. W. Chow and S. W. Koch, *Semiconductor-laser fundamentals: physics of the gain materials*, vol. 32. Springer Science & Business Media, 2013.
- [129] A. E. Grigorescu and C. W. Hagen, “Resists for sub-20-nm electron beam lithography with a focus on HSQ: state of the art,” *Nanotechnology*, vol. 20, no. 29, p. 31, 2009.
- [130] L. Ren, “Proximity effect in electron beam lithography,” *Proceedings. 7th International Conference on Solid-State and Integrated Circuits Technology, 2004.*, vol. 1, pp. 579–582, 2004.
- [131] T. H. P. Chang, “Proximity effect in electron-beam lithography,” *Journal of Vacuum Science and Technology*, vol. 12, no. 6, p. 1271, 1975.
- [132] B. W. Ward, J. A. Notte, and N. P. Economou, “Helium ion microscope: A new tool for nanoscale microscopy and metrology,” *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures*, vol. 24, no. 6, p. 2871, 2006.
- [133] J. Notte, B. Ward, N. Economou, R. Hill, R. Percival, L. Farkas, and S. McVey, “An introduction to the helium ion microscope,” *AIP Conference Proceedings*, vol. 931, no. April, pp. 489–496, 2007.
- [134] X. Zhang, C. A. Marocico, M. Lunz, V. A. Gerard, Y. K. Gun’ko, V. Lesnyak, N. Gaponik, A. S. Sussha, A. L. Rogach, and A. L. Bradley, “Wavelength, concentration, and distance dependence of nonradiative energy transfer to a plane of gold nanoparticles,” *ACS Nano*, vol. 6, no. 10, pp. 9283–9290, 2012.
- [135] E. Palik, *Handbook of Optical Constants of Solids*, vol. 39. Academic Press, 1985.
- [136] Š. Kos, M. Achermann, V. I. Klimov, and D. L. Smith, “Different regimes of Forster-type energy transfer between an epitaxial quantum well and a proximal



- monolayer of semiconductor nanocrystals,” *Physical Review B - Condensed Matter and Materials Physics*, vol. 71, no. 20, pp. 1–8, 2005.
- [137] Y. Li, R. Zhang, Z. Xie, B. Liu, P. Chen, G. Zhang, T. Tao, Z. Zhuang, L. Zhi, T. Gan, and Y. Zheng, “Investigation of surface plasmon coupling with the quantum well for reducing efficiency droop in GaN-based light emitting diodes,” *Journal of Applied Physics*, vol. 114, no. 11, 2013.
- [138] Y. J. Lee, C. H. Chiu, C. C. Ke, P. C. Lin, T. C. Lu, H. C. Kuo, and S. C. Wang, “Study of the excitation power dependent internal quantum efficiency in InGaN/GaN LEDs grown on patterned sapphire substrate,” *IEEE Journal on Selected Topics in Quantum Electronics*, vol. 15, no. 4, pp. 1137–1143, 2009.
- [139] H. Wang, Z. Ji, S. Qu, G. Wang, Y. Jiang, B. Liu, X. Xu, and H. Mino, “Influence of excitation power and temperature on photoluminescence in In-GaN/GaN multiple quantum wells,” *Optics Express*, vol. 20, no. 4, p. 3932, 2012.
- [140] T. L. Jennings, M. P. Singh, and G. F. Strouse, “Fluorescent lifetime quenching near  $d = 1.5$  nm gold nanoparticles: Probing NSET validity,” *Journal of the American Chemical Society*, vol. 128, no. 16, pp. 5462–5467, 2006.
- [141] M. Sukharev, N. Freifeld, and A. Nitzan, “Numerical calculations of radiative and non-radiative relaxation of molecules near metal particles,” *Journal of Physical Chemistry C*, vol. 118, no. 20, pp. 10545–10551, 2014.
- [142] M. P. Singh and G. F. Strouse, “Involvement of the LSPR spectral overlap for energy transfer between a dye and Au nanoparticle,” *Journal of the American Chemical Society*, vol. 132, no. 27, pp. 9383–9391, 2010.
- [143] A. Hangleiter, J. S. Im, H. Kollmer, S. Heppel, J. Off, and F. Scholz, “The role of piezoelectric fields in GaN-based quantum wells,” *Internet Journal Nitride Semiconductor Research*, vol. 15, no. 1998, pp. 1–8, 1999.
- [144] T. Takeuchi, C. Wetzel, S. Yamaguchi, H. Sakai, I. Akasaki, Y. Kaneko, S. Nakagawa, Y. Yamaoka, and N. Yamada, “Determination of piezoelectric fields in strained GaInN quantum wells using the quantum-confined Stark effect,” *Applied Physics Letters*, vol. 73, no. 12, pp. 1691–1693, 1998.
- [145] W. L. Barnes, “Electromagnetic Crystals for Surface Plasmon Polaritons and the Extraction of Light from Emissive Devices,” *Journal of Lightwave technology*, vol. 17, no. 11, pp. 2170–2182, 1999.
- [146] P. Zory, *Quantum Well Lasers*. Academic Press, 1993.

- [147] Chow W. W. and Koch S. W., *Semiconductor-Laser Fundamentals*. Springer-Verlang Berlin Heidelberg, 1 ed., 1999.