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Hybrid Semiconductor Quantum Dot/Quantum Well & Metal Nanoparticle Structures

A PhD Thesis

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PhD
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Abstract

Non-radiative energy transfer is an energy transfer mechanism based on dipole-dipole interactions. It has come to the fore in biomedical imaging and sensing, as well as light emitting and harvesting applications. Utilising non-radiative energy transfer in hybrid semiconductor quantum dot and quantum well systems is just one avenue of exploration for improving the efficiency of said light emitting/harvesting devices. Combining these hybrid systems with metal nanoparticles that display surface plasmon resonances can improve the efficiency, rate, and effective distance of the non-radiative energy transfer. Thus, in this work the surface plasmon-mediated non-radiative energy transfer interaction between pairs of quantum dots, and between quantum dots and quantum wells is investigated both to increase fundamental understanding of the system and with a view towards viable device applications.

The temperature dependence of the photoluminescence spectra and average photoluminescence decay rate of CdTe quantum dot monolayers of different sizes as a function of concentration is investigated in the range 77 K to 296 K. It is shown that a simple three level analytic model involving bright and dark exciton states can only describe the data at the low end of the temperature range and is unable to satisfactorily fit the data over the full temperature range. An extended model which includes external trap states is necessary to fit the data above approximately 150 K. Parameters for the model are obtained using both temporal and spectral data. The model indicates that the efficiency of interaction with trap states increases as the QD monolayer concentration increases, which is likely due to an increase in the density of available traps or formation of new traps.

The temperature dependence of non-radiative energy transfer in various quantum dots systems is investigated over the same temperature range as for the quantum dot monolayers. Firstly, the temperature dependence of the non-radiative energy transfer between quantum dots and Au nanoparticles is considered. Two different quantum dots are used that have emission wavelengths on and off the surface plasmon resonance. The energy transfer rate was shown to increase with temperature and it is highest for the on resonance quantum dot case. The experimental data can be explained to a reasonable degree with an analytic model involving bright and dark states which can both interact with a trap state. The energy transfer rate between separated bilayers of quantum dots is also observed

to increase with increasing temperature, however the model requires adjustment to fit all the features observed in the experimental data. This raises questions relating to the role of the dark state and exciton recycling in the energy transfer process. An anomalous trend is seen in the surface plasmon-mediated energy transfer in a quantum dot-Au nanoparticle-quantum dot trilayer system. Here the surface plasmon-mediated energy transfer rate decreases with increasing temperature, in contrast to both the direct quantum dot to quantum dot energy transfer and the quantum dot to Au nanoparticle energy transfer.

Ag nanoparticles in the form of colloids and ordered arrays are used to demonstrate surface plasmon-mediated non-radiative energy transfer from quantum dots in a PMMA layer to quantum wells with different barrier thicknesses. This is the first demonstration of surface plasmon-mediated non-radiative energy transfer from quantum dots to quantum wells. Surface plasmon-mediated energy transfer efficiencies of up to approximately 25% are observed. Utilising the colloids the distance dependence of the surface plasmon-mediated energy transfer is found to follow the same d^{-4} dependence as the direct quantum dot to quantum well energy transfer. In the surface plasmon-mediated case there is some evidence for an increase in the characteristic distance of the interaction, thus indicating that it follows a Förster-like model with the Ag-quantum dot acting as an enhanced donor dipole. The ordered Ag arrays display plasmon-mediated energy transfer efficiencies up to 17% and are found to be highly tunable, with the ability to go from a situation of overall quenching of the quantum well emission to enhancement by altering the geometry of the structure.

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List of Abbreviations and Acronyms

AFM Atomic force microscopy	NB Nanobox
AgNPs Silver nanoparticles	ND Nanodisc
AuNPs Gold nanoparticles	NP Nanoparticle
EBL Electron beam lithography	NRET Non-radiative energy transfer
ET Energy transfer	NSET Nanometal surface energy transfer
FDTD Finite-difference time-domain	PE Polyelectrolyte
FRET Förster resonance energy transfer	PL Photoluminescence
FWHM Full width half maximum	QD Quantum dot
LED Light emitting diode	QW Quantum well
LSPs Localised surface plasmons	R_0 Förster Radius
LSPR Localised surface plasmon resonance	SEM Scanning electron microscopy
MNPs Metal nanoparticles	

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Chapter 1

Motivation

Solar energy and other renewable and sustainable energy sources will play a key role in battling global warming. 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 [1]. Increased demand for solar energy requires better device performance and efficiency coupled with low cost. One route being pursued is the use of solution processed quantum dot (QD) photovoltaics due to the low cost, ease of processing, and large area coverage [2]. QDs provide the capability to harvest sunlight over the full visible region and into the infrared [3]. It is also possible to increase harvesting efficiencies due to multiple exciton generation [4]. More relevant to this thesis, QDs can be utilised to enable energy transfer (ET) of excitation energy to other species in close proximity [5, 6] via non-radiative mechanisms such as Förster resonance energy transfer (FRET) [7]. Dye sensitised solar cells incorporating QDs and FRET have been recently reported [6, 8], providing a proof of concept that QD based solar cells using FRET are possible.

Having QDs behave as FRET donors and acceptors has gained incredible interest in recent years because they can play an important role in optoelectronic devices, such as the aforementioned light harvesting structures [9, 10], and also in light emitting devices [11–14]. Additionally QDs have potential uses in a wide variety of bioanalysis applications [15], as well as imaging [16, 17], sensing [18–21], a display [22] applications.

Combining quantum wells (QWs) with QDs paves the way for further device im-

plementation such as tunable solid state lighting and electrically pumped nanoscale lasers [11,23,24]. However, QDs have poor carrier transport properties and require additional charge transport layers for device implementation [25]. One way to overcome this obstacle would be harnessing non-radiative ET between QD and QWs. This would be advantageous for both light harvesting and LED applications as it will combine the excellent optical properties of QDs with electrical properties of QWs.

Most current commercial white light generating solid-state devices utilise high-energy photons emitted from QWs which are then absorbed and re-emitted at a lower frequency/energy by a (YAG) phosphor [26]. However, this method has several disadvantages: There are significant losses associated with the emission of the high-energy photon, its subsequent extraction from the QW (due to total internal reflection), and the absorption and re-emission by the phosphor. The completed structure is not-tunable and allows no opportunity for adjusting white light quality or colour tuning for a particular phosphor.

QDs have been put forward in several publications [11,14,27–29] as alternatives to phosphor because of their widely tunable emission, therefore providing precise control over the white light quality [23,30,31]. They also have high absorption in the blue/high energy part of the spectrum, hence reducing some of the losses associated with the absorption of the high-energy photon generated in the QW. Utilising QDs present their own challenges, such as the poor charge transport properties mentioned above, and they can have reduced quantum efficiencies compared with phosphors. Again, non-radiative ET (NRET) shows promise in circumventing these issues. Enhancement of the quantum efficiency of up to 17% has been observed for optimised donor-acceptor ratios [32]. Also, non-radiatively pumping the QDs with the QW will reduce losses associated with total internal reflection in the QW. Overall single-step ET such as that provided by NRET has the potential to be more efficient than the lossy, multi-step radiative pumping.

QDs also have broad absorption bands which makes them an attractive option for light harvesting devices [3,5,33–35]. They can extend the wavelength range of solar cell devices into the infrared [2,3,36,37], and efficiently funnel the absorbed energy to other parts of the device using NRET [9,38].

One notable disadvantage to FRET based devices is the inherent distance dependence of this non-radiative process. Due to the dipole-dipole nature of the interaction FRET follows a d^{-6} distance dependence for isolated donor-acceptor pairs, this becomes d^{-4} in planar structures. In practice this leads to a very limited length scale of approximately 10 nm for single donor-acceptor pairs. Hence, extensive work is ongoing in an effort to increase interaction distances [39]. Considerable attention in this area has been given to interactions between QDs and metal nanoparticles (MNPs). MNPs can display localized surface plasmons (LSPs), collective oscillations of electrons between a metal surface and a dielectric [40]. Optical properties of fluorophores close to MNPs can be influenced by ET to the MNPs and by the field enhancement due to LSPs. This can lead to situations of fluorescence quenching [41] and metal enhanced fluorescence [42–44]. Modification of the emission can occur as the result of various processes; ET to the MNP, scattering or absorption by the MNP, changes in the radiative/non-radiative decay rate of the donor, or modification of the excitation rate of the donor due to the presence of the MNP. In addition, ET from a fluorophore to a MNP has exhibited longer interaction distances than traditional ET pairs [45]. Theoretical studies of LSP coupled ET have also been investigated; specifically of interest in this case are studies predicting enhancement of direct FRET between a donor and acceptor in proximity to a metallic nanoparticle or nano-structure [46, 47]. The enhancement of the ET rate, efficiency, and range has been experimentally verified for different geometries with a variety of emitters and MNPs [48–58]. Extensive studies of QD-MNP-QD interactions have been undertaken previously [59] showing that LSP coupled FRET with QDs has the same dipole-dipole (d^{-4}) behaviour as conventional FRET with a strongly coupled donor-plasmon system that can be considered as enhanced dipole, Section 2.3.2 will provide details on some of the wide ranging material systems and hybrid structures previously studied in the area of LSP-mediated NRET.

In order to delve deeper into the fundamental understanding of this QD-MNP system it would be prudent to undertake temperature dependent measurements. Previous studies investigating the temperature dependence of QDs have revealed the importance of considering the dark exciton state in order to explain the behaviour of QD lifetimes at lower temperatures. The dark state is long lived and weakly emitting due to spin transition rules. It lies below the nearest optically active state (bright exciton)

in energy. However, much of the work to date has focused on temperatures below 150 K; this is because above this temperature non-radiative recombination becomes increasingly prevalent and thermal quenching of the photoluminescence (PL) intensity is non-negligible, leading to greater complexity. In addition, to the author's knowledge, there have been no published investigations of the temperature dependence of ET in QD-MNP systems. This is of fundamental interest for considering surface plasmon mediated ET, the main interest focusing on whether the QD-MNP interaction can still be consistent with a dipole-dipole mechanism and if the influence of bright and dark states is different for this hybrid system. Therefore, a few of the aims of this thesis are to investigate the temperature dependent photoluminescent properties of QDs without ignoring temperatures above 150 K, investigating the temperature dependence of ET between QDs in this range and finally to investigate the temperature dependence of surface plasmon coupled ET.

MNPs have also attracted a lot of attention for enhancing light harvesting [60, 61] as sub-wavelength scattering elements to trap propagating waves into thin semiconductor layers and as sub-wavelength antennas where the plasmonic near-field can be coupled to the semiconductor, thereby increasing its effective absorption cross section. QDs and plasmonics are exciting prospects individually for light harvesting solutions. Combining them could lead to new technologies in photovoltaics. Enhanced absorption and emission of QDs using plasmonics has been demonstrated with a view towards photovoltaics [61, 62]. LSP enhanced FRET between QDs has been widely reported [53–55, 57], and recently plasmon-enhanced QD emission from an ≈ 80 nm thick layer of QDs via ET from QWs utilising arrays of Ag nanoparticles has been demonstrated [63]. NRET from QDs to QWs [64], from QDs to 2D nanoplatelets [65], and transition metal dichalcogenides [66] are all promising results. However, plasmon mediated ET from QDs into QWs has yet to be demonstrated. This thesis aims to rectify this and to show that plasmon-mediated ET from QDs to QWs is viable for further development as a light harvesting technology.

Therefore, in this thesis **Chapter 2** will focus on introducing general topics, such as the optical properties of QDs and QWs. The basics of FRET theory, as well as discussing LSPs and their impact on fluorophores and FRET. The temperature dependent

properties of QDs are presented as well as an analytic theory suitable to describe their behaviour.

Sample preparation and characterisation will be the focus of **Chapter 3**. It will include details on the materials and techniques used to create the samples. Description of the analysis of the samples using absorption, photoluminescence, and time resolved photoluminescence. Using these techniques we can extract important parameters, such as the concentration, quantum yield, and Förster radius.

The temperature dependent luminescence properties of QD monolayers will be investigated in **Chapter 4**. In particular, the role of concentration will be the focus with regard to the importance of considering thermally activated carrier trapping.

The temperature dependence of ET in QD systems will be presented in **Chapter 5**. Firstly an extension of the analytic model to describe temperature dependent behaviour will be introduced to fit ET between QDs and Au nanoparticles (fluorescence quenching). Following this, QD to QD ET will be studied, culminating in measuring the temperature dependence of surface plasmon mediated ET.

In **Chapter 6** surface plasmon-mediated ET from a QD to a QW will be investigated by monitoring the decay lifetime of a layer of QDs mixed with Ag nanoparticles deposited above the quantum well. The dependence of ET efficiency on QW barrier thickness will be investigated, thus giving a FRET distance dependence study. Additionally arrays of Ag nanoparticles will be fabricated in order to achieve greater control over the sample, leading to better tunability in this system and observe acceptor emission enhancement.

Conclusions and a summary are presented in **Chapter 7**, as well as some outlook on future work.

Chapter 2

Background

2.1 Quantum Dots

Semiconductor QDs are semiconductor material with spatial confinement in three dimensions. This confinement is possible as an electron's de Broglie wavelength, λ_e , is more than one order of magnitude larger than the lattice constant of many crystals, allowing spatial confinement of electrons while keeping the crystal lattice structure relatively unperturbed. To illustrate this, consider the de Broglie wavelength; assuming the effective mass seen in real crystals and using room temperature ($k_B T = 26.7$ meV) as a measure of the electrons kinetic energy, this gives the de Broglie wavelength as [40]

$$\lambda_e = \frac{h}{\sqrt{2m_e^* k_B T}} \quad (2.1)$$

For example in CdTe the effective electron mass, $m_e^* = 0.1m_0$, giving $\lambda_e = 23$ nm but the lattice constant is $a_L = 0.647$ nm.

Due to quantum confinement, the electronic structure of the QDs is described by discrete energy levels [40], 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 a 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 two species, leading to the formation of the 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 will change depending on the material. $a_B^* = \frac{m\epsilon_r}{\mu}a_0$ 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 in the strong confinement limit ($r \ll a_B^*$) can be estimated using the following [40]

$$E_g^{QD} = E_g^{Bulk} + \frac{\hbar^2\pi^2}{2r^2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right) - 1.786\frac{e^2}{\epsilon r} - 0.248E_{Ry}^* \quad (2.2)$$

Where the first term, E_g^{Bulk} , is the bandgap energy of the bulk solid. The second term is the "particle in a box" term; next is the electron-hole coulomb attraction. r is the radius of the QD, m_e , m_h are the electron and hole effective masses, ϵ is the dielectric constant of the semiconductor. The last term is a spatial correlation term where E_{Ry}^* is the Rydberg energy for the electron hole pair. The electrons and holes tend to reside near one another to maximise their Coulombic interaction, additionally to maximise dielectric stabilisation they tend to reside near the centre of the QD. The band gap therefore increases with decreasing radius of the QD enabling the emission spectra to be tuned with size.

In addition to this attractive possibility of tunable emission wavelengths, the QDs have a broad absorption range which enables free selection of excitation wavelength and multiple QDs of varying size 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 [67–71], giving them a further advantage in many areas over traditional molecular dyes.

These properties make QDs of great interest in applications such as bio-sensing and biomedical imaging [18, 72], photodetectors [73] and, as has already been mentioned in Chapter 1, in LEDs and photovoltaic devices.

2.1.1 Optical Properties of QDs

Absorption of a photon by a QD occurs if the photon energy exceeds the band gap energy. Due to quantum confinement effects *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) [74]. The excess energy can then be re-emitted as light through PL. Rapid excitation and de-excitation resulting in photoluminescence is known as *fluorescence*. The emission rates (usually denoted k_r) are of the order 10^8 Hz which means that fluorescence lifetimes are typically around 10 ns ($1/k_r$) for QDs [40]. The lifetime (τ) of a species is defined as the average time between excitation and return to the ground state. Time dependent PL decays of single QDs should be monoexponential, reflecting only the intrinsic exciton recombination rate. However due to the fact that QDs in solution are an ensemble of various sizes, and also due to defects multi-exponential decays are observed.

Normalised absorption and emission spectra of ensembles of different sizes of CdTe QDs are shown in Figure 2.1a and Figure 2.1b respectively. Each ensemble has a size distribution of 7-10%. One can clearly see the relatively sharp first absorption peak and the *red* shift of both this peak and the emission peak wavelengths with *increasing* size. One can also see that the spectra are quite broad, all with FWHM (full width at half maximum) around 40-60 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 [40]. In addition, since these spectra are measured for a QD ensemble in solution there will be inhomogeneous broadening due to finite size distribution, and variations in stoichiometry and charge as well as other factors [40]. In the ensemble spectra shown it is the inhomogeneous broadening that dominates.

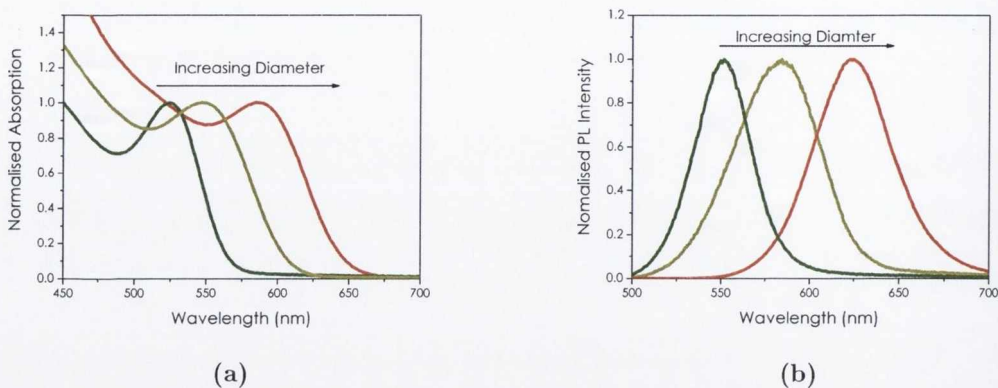


Figure 2.1: (a) Absorption spectra of CdTe QDs in water with diameter increasing from left to right. (b) Photoluminescence spectra of the same samples shown in (a) for an excitation wavelength of 400nm.

Looking closely at the absorption and emission peak wavelengths it can be seen that emission peaks always occurs at higher wavelengths, 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 is called internal conversion. The decay resulting 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 [75].

The Quantum Yield (QY) of a fluorophore describes the probability that an absorbed photon has of being re-emitted.

$$\text{QY} = \frac{\text{emitted photons}}{\text{absorbed photons}} = \frac{k_r}{k_r + k_{nr}} \quad (2.3)$$

Here k_r refers to the radiative decay rate from the excited state and k_{nr} refers to the combined decay rate for **all** non-radiative processes, not just NRET, if present. The QY can be determined for QD samples by comparison with luminescence standards of known QY, this will be described in Section 3.2.2. The QY is also referred to as the quantum efficiency as it can be used to compare emission efficiency of different

materials if excited under the same conditions.

2.2 Förster Resonance Energy Transfer

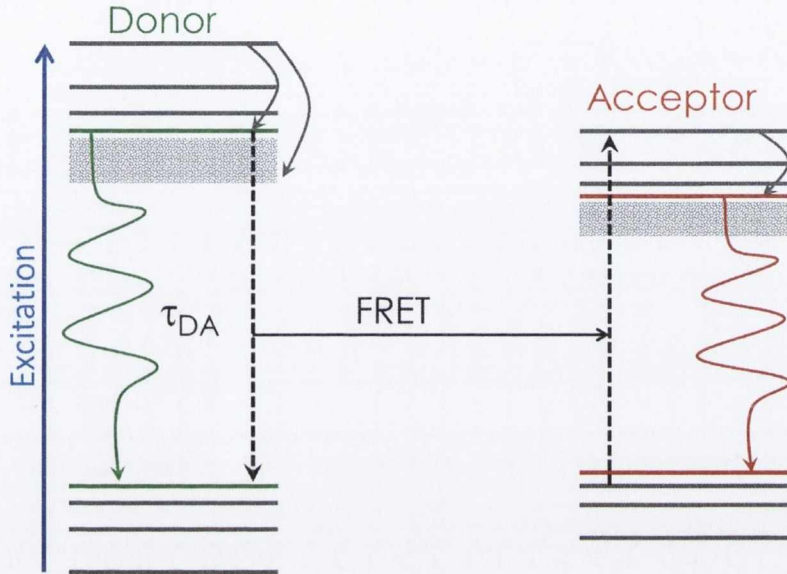


Figure 2.2: Schematic showing a standard FRET process. The excited donor species can relax via emission of a photon and/or transfer energy non-radiatively to the acceptor.

FRET occurs between a fluorescent donor species in an excited state and an acceptor, which need not be fluorescent, in the ground state. ET occurs non-radiatively, and is a result of dipole-dipole interactions between the donor and acceptor species [75]. Exposing the donor to light of an appropriate frequency effectively produces an oscillating dipole. This may then resonate with a dipole in the acceptor, hence the resonant dipole-dipole interaction facilitates a transfer of energy between the two species.

This is shown schematically in Figure 2.2. Here, a donor species is excited from its ground state to some vibrational level of the excited state (blue line). This then relaxes to the lowest vibrational level of the excited state or is lost to defects (shaded regions) via interactions with phonons (grey lines). From this excited state the donor can relax to the ground state via an emission of a photon (green line). If there is an acceptor species in close proximity to the donor, and if that acceptor has available states in resonance with the donor (black dashed lines) FRET can occur (black line). The

acceptor can then subsequently relax to the lowest excited state and emit a photon (red line).

The opening up of additional decay channels for the donor species will increase the decay rate ($k = 1/\tau$). This can be observed experimentally by observing a decrease in the lifetime of the donor species. This lifetime decrease is the main signature of FRET in a system. Other characteristic signatures of FRET experimentally are PL quenching of the donor species coupled with PL enhancement of the acceptor species.

2.2.1 Basic Förster / FRET Theory

The rate of energy transfer depends on:

- The extent of spectral overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor.
- The quantum yield of the donor.
- The relative orientation of the donor and acceptor dipoles.
- The distance between the species.

The rate of ET with respect to the donor-acceptor distance, $k_{DA}(r)$ is given by [75, 76]

$$k_{DA}(r) = \frac{1}{\tau_D} \left(\frac{R_0}{r} \right)^6 \quad (2.4)$$

where r is the donor-acceptor distance, R_0 is the distance at which FRET is 50% efficient, and $\tau_D = (k_r + k_{nr})^{-1}$ is the decay time of the donor without any acceptor present. R_0 is the characteristic distance of the interaction, called the Förster distance or the Förster radius. k_r is the radiative rate and k_{nr} is the rate due to all non-radiative sources other than FRET, examples of which would be internal conversion and trapping of excitons in surface defect states. In terms of the four dependencies mentioned above the FRET rate can be written as [75]

$$k_{DA}(r) = \frac{Q_D \kappa^2}{\tau_D r^6} \left(\frac{9000(\ln 10)}{128\pi^5 N n^4} \right) J(\lambda) \quad (2.5)$$

where Q_D is the QY of the donor in the absence of an acceptor, n is the refractive index of the medium, N is Avogadro's number, $J(\lambda)$ expresses the degree of spectral overlap between the donor emission and the acceptor absorption. τ_D is defined as above and κ^2 is a factor describing the relative orientation in space of the transition dipoles of the donor and acceptor [75].

It is usually assumed that the value of κ^2 is equal to 2/3 due to random orientation of the donor and acceptor [75].

The overlap integral, $J(\lambda)$ is given by

$$J(\lambda) = \int_0^\infty I_D(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda \quad (2.6)$$

$I_D(\lambda)$ is the corrected PL intensity (total intensity normalised to unity) of the donor in the wavelength range λ to $\lambda + \Delta\lambda$; this is dimensionless. $\epsilon_A(\lambda)$ is the extinction coefficient of the acceptor at a wavelength λ , which is usually in units of $\text{M}^{-1} \text{cm}^{-1}$. Since λ is in nm, $J(\lambda)$ has units of $\text{M}^{-1} \text{cm}^{-1} \text{nm}^4$.

From Equation (2.4) and Equation (2.5) one obtains

$$R_0^6 = \frac{9000(\ln 10 \kappa^2 Q_D)}{128\pi^5 N n^4} J(\lambda) \quad (2.7)$$

Since many of the terms are physical constants it is convenient to group these together to have a simpler expression for R_0 .

$$R_0 = 0.0211 \left(\frac{\kappa^2 Q_D}{n^4} \cdot J(\lambda) \right)^{1/6} \quad (2.8)$$

This gives R_0 in nm [77].

Once the value of R_0 is known then the ET rate can be easily calculated using Equation (2.4). The efficiency of the energy transfer, E , is the fraction of the absorbed

photons which have their energy transferred to the acceptor. This is given by

$$E = \frac{k_{ET}(r)}{k_r + k_{nr} + k_{ET}(r)} \quad (2.9)$$

The transfer efficiency is typically measured using PL intensities or lifetimes of the donor both with the acceptor (I_{DA} and τ_{DA}) and in absence of it (I_D and τ_D) [75]:

$$E = 1 - \frac{I_{DA}}{I_D} \quad (2.10)$$

$$E = 1 - \frac{\tau_{DA}}{\tau_D} \quad (2.11)$$

where $\tau_{DA}^{-1} = k_r + k_{nr} + k_{ET}$ and $\tau_D^{-1} = k_r + k_{nr}$. Simply substituting these relations into Equation (2.11) one can rearrange to obtain Equation (2.9). The ET rate can also be extracted from these measured parameters as $k_{ET} = \tau_{DA}^{-1} - \tau_D^{-1}$

Equation (2.9) can be rewritten using Equation (2.4) to obtain an equation for efficiency in terms of distances only.

$$E = \frac{R_0^6}{R_0^6 + r^6} \quad (2.12)$$

or

$$E = \frac{1}{1 + (r/R_0)^6} \quad (2.13)$$

This is illustrated in Figure 2.3. As can be seen, the efficiency is strongly dependent on the distance between donor and acceptor, this has led to FRET being used as a "spectroscopic ruler" to determine distances between biomolecules [78].

The above rate equations are derived for a single donor-acceptor pair. If a donor can interact with several acceptors, denoted i , then the FRET rate, k_{ET} , of this one donor is the sum of all FRET rates, k_i , with respect to energy transfer to the i th acceptor which is at a distance r_i from the donor

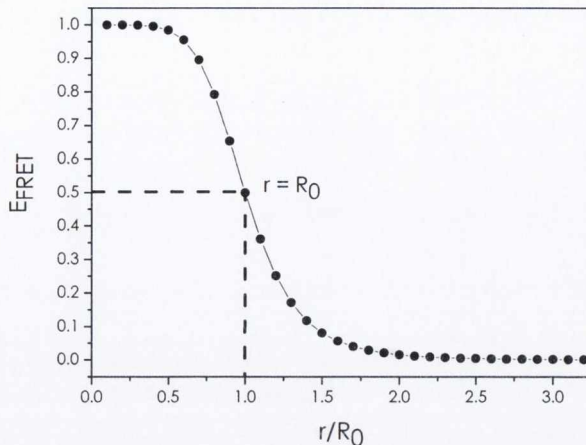


Figure 2.3: Energy transfer efficiency as a function of r/R_0 based on Equation (2.13)

$$k_{ET} = \sum_i k_i = \tau_D^{-1} \cdot \sum_i \left(\frac{R_0}{r_i} \right)^6 \quad (2.14)$$

This shows that with increasing numbers of acceptors around a donor the ET rate becomes faster and therefore more likely. Substituting Equation (2.14) into Equation (2.9) one obtains

$$E_{ET} = \frac{\sum_i (R_0/r_i)^6}{1 + \sum_i (R_0/r_i)^6} \Rightarrow \frac{1}{1 + [\sum_i (R_0/r_i)^6]^{-1}} \quad (2.15)$$

2.2.2 FRET in a Separated Layer Structure

Analytical expressions for FRET between donor and acceptors in separated layers can also be obtained [79]. The sum in Equation (2.14) can be converted to the surface integral below

$$k_{ET} = \tau_D^{-1} \cdot c_{Acc} \cdot \int_0^\infty \left(\frac{R_0}{r} \right)^6 dS \quad (2.16)$$

One can extend the limit of integration to infinity as the range of FRET decreases rapidly with donor-acceptor separation. Carrying out the integration yields [77, 80]

$$k_{ET} = \frac{c_{Acc}\pi R_0^6}{2R_{ex}^4 \tau_D} \quad (2.17)$$

The typical r^{-6} dependence of single donor-acceptor pairs is replaced by a r^{-4} .

Using Equation (2.9), FRET efficiency is given by

$$E_{ET} = \frac{1}{1 + \frac{2R_{ex}^4}{c_{Acc}\pi R_0^6}} \quad (2.18)$$

The above equations were developed originally for molecular systems, however, it has been shown that ET in QD systems can be described well with a Förster-like theory [80–83].

2.2.3 Other Energy Transfer Mechanisms

It is important to distinguish FRET from other possible ET mechanisms, such as Dexter electron exchange [84], charge transfer [85,86], or radiative transfer [87]. When a donor is excited, energy transfer can occur via radiative or non-radiative routes. NRET is a one step process



where D^* and A^* are the excited states of the donor and acceptor, while D and A are the ground states. The energy transfer process can be envisioned as absorption by the acceptor of the near-field time-dependent electric field disturbance by a classically oscillating electric dipole of the donor [88].

In a radiative process however, an emitted photon from a donor is reabsorbed by an acceptor. This has a relatively long range, falling off as r^{-2} [89], it is a two step process with a real photon mediating the transfer of energy,



Dexter transfer is a process which occurs as a result of an electron exchange mechanism, this requires an overlap of the wavefunctions of the donor and acceptor, meaning it is very short range, < 1 nm [90]. The Dexter transfer rate, k_{DET} , decreases exponentially with distance, d

$$k_{DET} = K \cdot J_{DT} \cdot e^{-2d/L} \tag{2.21}$$

where K is a constant related to specific orbital interactions, J_{DT} is the spectral overlap which is similar to what is found in FRET, but does not depend on the acceptor extinction coefficient, L is the sum of the van der Waals radii of the donor and acceptor.

Charge transfer [91] is similar to Dexter in that it requires orbital overlap, the energy transfer range in this case is generally < 2 nm. This mechanism requires an electron or hole donor and acceptor, but does not require any spectral overlap (contrary to both Dexter transfer and FRET). The charge transfer rate k_{CET} also decreases with distance, d , exponentially as

$$k_{CET} = K_0 \cdot e^{-\beta d} \tag{2.22}$$

where β characterises the energy transfer, and K_0 is a pre-exponential factor.

In this work the centre-to-centre distances between donor and acceptors is larger than 2 nm, therefore Dexter or charge transfer can be excluded. Even in highly concentrated monolayer samples, the minimum separation is larger than the diameter of the QDs, as they are further separated by interpenetrating ligands, which adds approximately 0.5 nm to the separation.

2.3 Surface Plasmons

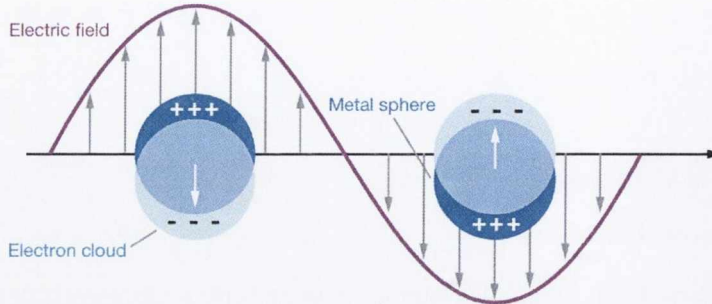


Figure 2.4: Schematic of LSPs from Willets *et al.* [92].

Surface plasmons are collective oscillations of electrons at the interface of two materials where there is a change in sign of the real part of the dielectric function across the interface, i.e. between a metal and a dielectric [40]. They can be localised surface plasmons (LSPs) on the surfaces of metal nanoparticles (MNPs) or can be propagating surface plasmons on planar structures. LSPs display a resonance behaviour and exhibit enhanced near-field amplitude at the resonance wavelength. This is highly localised at the nanoparticle (NP) surface and decays rapidly into the dielectric. The large electric field enhancement is why MNPs are currently such an intense research area.

Optical properties of fluorophores close to a MNP are influenced by ET to the particle and by the field enhancement due to the LSPs. These two processes have different distance dependences [93], emission quenching due to ET [41,94] to the metal dominates at small metal-fluorophore separations. However, at larger distances PL enhancements can be observed [42,43,95–97]. Specifically relevant to this work plasmonic structures have been shown to enhance the the emission properties of both QDs [42, 43, 53, 98] and QWs [99–104]. The enhanced emission can arise due to increased absorption under optical pumping in resonance with the MNPs, increased radiative recombination rates and/or scattering by the plasmonic nanostructures.

The large field enhancements observed with LSPs can also be used to enhance the FRET efficiency between two species, effectively increasing the range of the FRET interaction. This is advantageous for QD systems as due to their relatively large size the FRET efficiency is limited as it is such a short range interaction, falling off as d^{-4} in separated layer structures, and as d^{-6} for single donor-acceptor pairs.

Govorov *et al.* [105] completed theoretical calculations of surface plasmon-mediated FRET, predicting that the strongest enhancement of the FRET rate will be observed for a metal nanoparticle between the donor and acceptor species. This study fuelled much experimental work by this group, leading to the first demonstration of plasmon enhanced FRET within mixed monolayers of QDs [53]. Additionally, it was shown that the FRET efficiency between separated donor and acceptor bilayers was increased upon the introduction of gold nanoparticles (AuNPs). Extensive concentration, distance, and wavelength dependence studies have also been carried out within this group leading to the conclusion that the LSP coupled FRET has the same dipole-dipole behaviour as conventional FRET and that a strongly coupled donor-plasmon system can be considered as an enhanced dipole [59].

2.3.1 Localised Surface Plasmon Quenching

The quenching effect by MNPs has been widely studied, MNPs can act as efficient energy acceptors for donor organic dyes [19, 106–111], QDs [41, 112–115], or fluorescent proteins [116]. Distance dependent quenching has been studied using varying length polypeptide [41], and DNA strands [106], as well as varying silica shell thickness [110]. The spectral overlap of the LSP resonance and the emission spectrum of the fluorophore is an important factor in the quenching efficiency by the MNP; this has been studied by varying molecular dye or QD emission or by changing the MNP size or shape or type [111, 117, 118]. A complete study of the wavelength, concentration, and distance dependence of QD quenching to a plane of AuNPs was a focus of previous work within this group [56] showing that while the observed trends can be fitted with a model for FRET between two planes there is only good agreement with extracted and calculated Förster radii values for QDs that have emission wavelengths close to the LSP peak. Much better agreement is obtained for off-resonance wavelengths with the characteristic distance, d_0 , extracted from a nanometal surface energy transfer (NSET) model [106, 117] suggesting that the NSET model is a useful phenomenological method of analysing emission quenching due to non radiative energy transfer to a plane of MNPs.

2.3.2 Localised Surface Plasmon-Mediated Energy Transfer

Modification of FRET between two molecules via LSP supported by MNPs was theoretically proposed in the 1980s [46,119]. Enhancement of FRET depends strongly on the distance to the MNP, as well as the shape and angular orientation of the molecules with respect to the MNP. This enhancement of FRET can push the limit of distance well beyond the traditional sub 10 nm, out to 70 nm and beyond, which would make FRET much more viable for application purposes. As mentioned above Govorov *et al.* proposed the optimum geometry for LSP mediated FRET. The strongest enhancement of the FRET rate is observed when the MNP is sandwiched between the donor-acceptor pair [105]. 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 (Au nanospheres in this case), the emission wavelength and the QY [120]. Small nanospheres can greatly enhance the quenching rate by the Au, which leads to strong reduction in emission of the emitter, as the size of the nanosphere is increased it acts as an antenna, increasing the emission. The LSP resonance proves important when considering the wavelength dependence of the efficiency of quenching by the Au, exhibiting a peak close the LSP resonance of the nanosphere. For ET between a donor and acceptor mediated by the Au nanosphere it is found that the ET efficiency is much more sensitive to the donor-Au distance than to the acceptor-Au distance. In fact in the small nanosphere limit the donor-acceptor interaction mediated by the Au is essentially dipole-dipole (d^{-6}), with the strength of the interaction enhanced compared to free-space. This is an indication that the coupling between the donor and the Au nanosphere creates an enhanced donor dipole.

A multitude of experimental investigations with various geometries and emitters have demonstrated the enhancement of ET via MNPs. Lakowicz *et al.* showed that the presence of Ag island films near their donor-acceptor pairs increased the Förster radius from 3.5 nm to 16.6 nm [121]. Zhang *et al.* reported a 60% increase in the Förster radius between oligonucleotide donor-acceptor pairs bound to a single MNP [48], the rate constant of FRET in this case was 21 times faster for the bound pair compared to the unbound. Tuning the distance between the FRET pair and the MNP allows for optimisation of the enhancement. Lessard-Viger *et al.* studied FRET from a conjugated polymer to a fluorescent multilayer core-shell NP, observing a 50% increase

in the Förster distance coupled with an 173 times increase in the FRET-rate [52]. In addition to single MNP LSP enhancement, reports include metal plasmonic resonators [49]. Reports on layered structures such as spin coated donor ZnO NPs and acceptor CdSe/ZnS QDs enhanced with silver prisms [50]; mixed layers of CdSe QDs with silica coated AgNPs [122]; CdSe/ZnS and CdSe/ZnTe QDs with AuNPs [123]; mixed CdTe QD layers above a layer of AuNPs [53]; a sandwich structure of donor CdTe QDs, AuNPs, and acceptor CdTe QDs [54] mirroring the optimum structure proposed by Govorov *et al.* Investigations into varying NP size [124], concentration [55], and distance [57] are also prevalent. Nanoapertures of Au have been demonstrated to significantly enhance the FRET rate demonstrating that the FRET rate depends on the local density of states, thus opening up the opportunity to control single emitter fluorescence via nanophotonic methods [58]

FRET can also be switched on and off by varying the spectral position of the LSP resonance relative to the donor emission [51]. Selective coupling to the donor or acceptor is possible by changing the order of QD and Au nanosphere layers in a multilayer stack [125]. 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 PL quenching or enhancement can be observed [41, 94, 105, 126–128].

Extensive studies on LSP mediated FRET was a focus of previous work in this group [53–55, 57, 57]. It was clear that the signatures of LSP coupled FRET depend strongly on the position of the intermediate AuNP layer and on the concentration of the Au NPs. The largest rates and efficiencies are observed for the higher AuNP concentrations, smallest donor-Au NP and acceptor-AuNP separations, however this is more sensitive for the donor-AuNP separation [57]. The distance dependence of the LSP coupled FRET efficiency has the same d^{-4} form as conventional FRET. The independence of the Förster radius on the acceptor-AuNP 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, which is in agreement with theoretical work also demonstrated within this group [120].

2.4 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 Figure 2.5. 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 [40, 129].

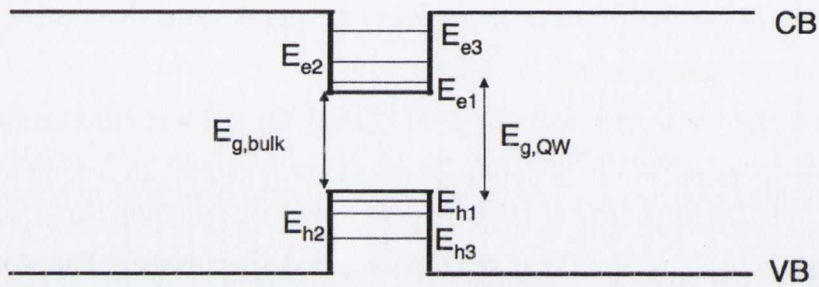


Figure 2.5: Band Diagram for a QW showing the Conduction Band (CB) and Valence Band (VB)

QWs 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 [40]. This leads to a manifestation of many more excitonic properties at higher temperatures. QWs also show strong sensitivity of their absorption spectra to applied electric fields. This has been demonstrated for Ge-Si QWs, which allows for the possibility of integrating with existing CMOS technology to go from electro-optically inefficient silicon to Ge, whose direct gap transitions much more readily fall in the vicinity of $1.5 \mu\text{m}$, the optical communications wavelength. Germanium QWs look to be a very promising candidate for such an application.

QWs have been used extensively in applications for lasers [40, 130, 131]. Electron - hole gases of lower dimensionalities feature a narrow spread in velocities at finite temperatures because of finite density of states at the bottom of the lowest quantum subband. This reduces the emission line spreading and can reduce the dependence of the threshold current on temperature.

Hybrid semiconductor structures of QDs and QWs can play a large role in optoelectronic devices for photovoltaics [36, 64, 132], white light generation [27, 30, 133], and colour conversion [23, 134–136]. Specifically InGaN/GaN QWs have been a promising avenue for solar cells [137–139].

2.5 Light Harvesting

QDs also look promising for developing photovoltaics; half the sun’s power lies in the infrared and utilizing Pb based QDs, for example PbS and PbSe, provides the capability to collect sunlight over the full visible spectrum, and into the infrared. Koleilat *et al.* [2] reported a 46% external quantum efficiency in the infrared and 70% across the visible using PbSe which was attributed to diffusion of electrons and holes through the PbSe QD solid. McDonald *et al.* [3] demonstrated the ability control the spectral response of the photocurrent, with peaks in the photocurrent spectra matching closely to the absorption peaks of PbS nanocrystals. Utilizing QDs for solar cells is a large and diverse research field [33], this work will focus on the area of non-radiative energy transfer (NRET) of energy absorbed by QDs [6, 8, 140].

NRET has been demonstrated in a large range of material systems, with potential for LED [14, 32, 141–145], and light harvesting [9, 10, 34–37, 64, 146–149] applications. However, as mentioned previously QDs possess excellent optical properties such as broadband absorption with narrow and tunable emission profiles which gives them a distinct advantage over organic dyes [150, 151]. Studies of NRET from QDs to other semiconductor materials shows promise for potential technologies. Lu *et al.* [132] demonstrated NRET from PbS QDs to InGaAs QWs with an efficiency of 30%. They proposed a solar cell design utilizing NRET and postulated an efficiency of approximately 19% assuming unity QY for the QDs. Further work by that group [146] demonstrated NRET from PbS QDs to Si nanowires with efficiencies in the range of 15–38%, and showed that the photocurrent due to NRET can be 3 times that due to direct light absorption in the Si nanowires for excitation near the QD absorption peak. Chanyawadee *et al.* [36, 37] micro-patterned hybrid QD-GaAs based p-i-n devices bringing QDs into close proximity with the intrinsic region of the p-i-n heterostructures thereby bene-

fitting from efficient NRET from the QDs and the close proximity of the QDs to the active layers helped circumvent their low carrier transfer efficiency. A six-fold increase of the photocurrent conversion efficiency for a patterned device with CdSe/CdS QDs and a GaAs multi-QW stack [36], and a three-fold increase for CdTe QDs and bulk GaAs device [37] is observed. Dye-sensitised solar cells with QD antennas and using NRET have been demonstrated [6,8] with NRET efficiencies up to 70%. It is important to note that NRET does not preclude radiative transfer (emission and re-absorption) from occurring, and it was found that an additional 12% radiative transfer contributed to an overall 82% internal quantum efficiency [6]. Nizamoglu *et al.* [64] found NRET efficiencies of nearly 70% from CdSe/ZnS QDs to InGaN QWs with a center-to-center separation of ≈ 3.8 nm, thus highlighting that the strong distance dependence means that NRET suffers from a limited length scale.

It is possible to combat this limited length scale with complex nanopillar architectures [147], graded nanocrystal layers [10,148,149], or buried QD nanostructures [132], and micro-patterning of a p-i-n device, [36,37], as mentioned above. These methods introduce additional design complexity, and another method to circumvent the limited length scales takes advantage of LSPs from metal MNPs.

Plasmon-mediated NRET has been used to extend the range of the non-radiative interaction, the enhancement of the NRET rate, efficiency, and range has been established for different geometries with a variety of emitters and metallic structures, as has already been mentioned [48–58]. Within this group, enhancement of the QD emission of a thick (≈ 80 nm) layer of QDs via ET from QWs utilising arrays of Ag NPs has been observed [63]. This enhancement from such a thick layer is highly promising for device applications. Plasmonic MNPs have also been utilised to enhance photovoltaic devices [60,152]. MNPs can be used as sub-wavelength scattering elements to trap propagating waves into a thin semiconductor layer. MNPs are also useful as sub-wavelength antennas where the plasmonic near-field can be coupled to the semiconductor, thereby increasing its effective absorption cross section. AgNPs have been shown to improve the efficiency of wafer-based Si solar cells, particularly in the near infrared where Si is a poor absorber [153]. Lee *et al.* [154] demonstrated an overall increase of the photocurrent by a factor of seven, most obviously observed at the plasmon resonance of

the annealed Au films. Mubeen *et al.* [155] showed that when combining AuNPs with TiO_2 the photoconductance is found to track the absorption spectrum of the AuNPs, with additional photoconductances of up to 30%. The photo response following the plasmon resonance is widely observed for Ag and Au [156,157], however these precious metals can be costly. Utilising larger particles could prove more economical as the shown by Yu *et al.* [157], for larger particles the Au content can be reduced by an order of magnitude with only a 20% drop in the photocurrent. Cost benefits for plasmonics in solar extend beyond the cost of the metals themselves. The light trapping and concentration possibilities of plasmonics lead to new solar-cell designs with smaller semiconductor thicknesses, and thus reduced material costs [152]. Not only will this reduce the physical thickness of Si needed for devices while remaining optically thick, it could see a movement towards other materials which have larger absorption of the solar spectrum. Having thin layers of materials reduces dark current losses and increases cell efficiency, and obviously reduces the distance for carriers to travel before arriving at a junction. This could allow for the use of semiconductors with low minority carrier diffusion lengths or ones possessing significant defect densities. Increasing the pool of potentially useful semiconductor materials to more abundant and possibly inexpensive materials can only be advantageous.

Therefore, QDs and plasmonics are exciting prospects individually for light harvesting solutions. Combining them could lead to new technologies in photovoltaics. Enhanced absorption and emission of QDs using plasmonics has been demonstrated with a view towards photovoltaics [61,158]. However challenges still exist; QDs, while having excellent optical properties, possess poor electrical properties requiring additional charge transport layers [25], therefore coupling to a system such as a QW would be highly advantageous in terms of device applications. Radiative transfer of this energy is inherently lossy, therefore single-step ET, such as that provided by NRET, is a preferred route for transferring the energy absorbed in the QD to the QW as it has the potential to be more efficient. This still faces the limitations on distance due to the dipole-dipole nature of the ET. Therefore in a light harvesting system the plasmonic element would not only be used as a solar concentrator but could perform a second important role in enhancing the ET between the QD layer and the QW.

Demonstrations of NRET from QDs to QWs [64], and more recently from QDs to 2D nanoplatelets [65], and transition metal dichalcogenides [66], show promise for developing this technology. However, plasmon-mediated NRET from a high energy QD (2.75 eV / 450 nm in this case) into a QW has yet to be demonstrated. The work presented in Chapter 6 aims to rectify this and provide a proof of concept that plasmon-mediated NRET from QDs to QWs is viable as a light harvesting solution.

2.6 Temperature Dependent PL of Quantum Dots

Investigations into the temperature dependence of QD lifetimes have revealed the importance of considering fine structure in the exciton state, namely a splitting into a dark and bright exciton state, to explain the observed behaviour at lower temperatures. The dark state is long lived and weakly emitting due to spin transition rules. It lies below the nearest optically active state (bright exciton) in energy. At very low temperatures the thermal energy can be less than the bright-dark energy splitting, $k_B T < \Delta E$. This led Crooker *et al.* [159] to postulate that excitons would be largely frozen into the dark state with no decay channels available, thus, providing an intrinsic upper limit to the exciton lifetime. Many studies have investigated the temperature dependence of the photoluminescence properties of QDs for example; in solution [160], in a polystyrene matrix [161], embedded into a glass substrate [162], as well as single core-shell QDs [163]. An analytic three level model consisting of a ground state and the bright and dark states has been used extensively to fit experimental QD decay rates from as low as 2 K up to generally 140 K in a variety of QD systems [160, 163, 164]. At room temperature the fine structure of the exciton states are thermally mixed giving rise to an effective lifetime resulting from the mixing of the bright and dark states. Temperature dependent measurements in conjunction with this model has allowed for the extraction of bright and dark exciton lifetimes, as well as the bright-dark energy splitting. Bright and dark states in QDs were theoretically studied by Efros *et al.* [165] and the bright-dark splitting was found to be inversely dependent on size. Experimental studies investigating the size dependence of this splitting in various QDs [160, 166–168] has revealed that the temperature dependence of QD lifetimes

in the very low temperature range (< 20 K) is due to coupling between the dark exciton and acoustic phonon mode. Recently nano-engineering of the bright-dark splitting has become possible using advanced synthesis techniques in CdSe/CdS heterostructures. These include varying the number of CdS shells on a CdSe core [169] and changing the width of a nanorod shell of CdS around a spherical core of CdSe [170]. Increasing the activation energy of non-radiative processes such as Auger recombination has also been achieved in CdSe/CdS core/thick shell colloidal nanocrystals and could pave the way for 100% QY structures at room temperature [171].

For all the advances in CdSe based studies the literature is comparatively lacking in investigation analysis of water soluble CdTe QDs, which will be the focus of this work. Additionally, as mentioned above, much of the work to date has focused on temperatures below 150 K; this is because above this temperature non-radiative recombination becomes increasingly prevalent and thermal quenching of the PL intensity is non-negligible, leading to greater complexity. An extension to this model that simultaneously considers both the exciton bright-dark splitting and carrier trapping was introduced to model temperature dependent decay rates of PbS QDs in the 10 K to 296 K range [162]. Both the simple three level model, and the extension to include traps is presented in the next section. In Chapter 4 the model is used to show that accounting for thermally activated carrier trapping is essential when considering the temperature dependent decay rate of QDs above 150 K, and that interactions with these traps become more pronounced as the concentration of QDs is increased.

2.6.1 Analytic Model

Analytic expressions for the decay rates as a function of temperature can be derived using a model consisting of a ground state, $|g\rangle$, and two excited states: a lower energy dark exciton state, $|ketDx\rangle$, and a higher energy bright exciton state, $|Br\rangle$. A schematic of this model is shown in Figure 2.6 where k_{Dx} (k_{Br}) is the radiative decay rate for the dark (bright) state, and ΔE is the bright-dark energy splitting. The rate equations for the number of excitons in the model is given by [164]

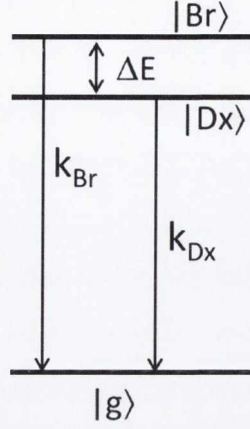


Figure 2.6: Schematic of the analytic model with ground state, $|g\rangle$, dark state, $|Dx\rangle$ with decay rate k_{Dx} , and the bright state, $|Br\rangle$, with decay rate k_{Br} . ΔE is the bright dark splitting energy.

$$\frac{dN_{Br}}{dT} = -k_{Br}N_{Br} - k_{rel}N_{Br} + k_{rel}\exp(-\Delta E/k_B T)N_{Dx} \quad (2.23)$$

$$\frac{dN_{Dx}}{dT} = -k_{Dx}N_{Dx} + k_{rel}N_{Br} - k_{rel}\exp(-\Delta E/k_B T)N_{Dx} \quad (2.24)$$

where N_{Br} and N_{Dx} give the population for the bright and dark state, respectively, and T is the temperature. k_{rel} is the relaxation rate from the bright state to the dark state. Relaxation rates between bright and dark states have been found to be of the order of fractions of ps^{-1} for CdTe QDs [172], which is orders of magnitudes faster than the PL decay times studied here.

The rate equation for the total number of excitons, N , is then

$$\frac{dN}{dT} = -k_{Br}N_{Br} - k_{Dx}N_{Dx} = -Nk(T) \quad (2.25)$$

The population of the bright and dark states gives the total number of excitons ($N_{Br} + N_{Dx} = N$). Assuming a Boltzmann distribution of excitons between $|Br\rangle$ and $|Dx\rangle$ on the basis of a statistical ensemble of QDs [159, 162, 164] then $N_{Br}/N_{Dx} = \exp(-\Delta E/k_B T)$. $k(T)$ is the overall decay rate. Solving Equation (2.25) yields

$$\begin{aligned}
 k(T) &= \frac{k_{Br}N_{Br} + k_{Dx}N_{Dx}}{N_{Br} + N_{Dx}} \\
 &= \frac{k_{Br}\frac{N_{Br}}{N_{Dx}} + k_{Dx}}{1 + \frac{N_{Br}}{N_{Dx}}} \\
 &= \frac{k_{Dx} + k_{Br}\exp(-\Delta E/k_B T)}{1 + \exp(-\Delta E/k_B T)}
 \end{aligned} \tag{2.26}$$

The above model does not consider external traps which are known to strongly influence the PL emission of QDs at higher temperatures. To consider the role of such trapping in more detail the basic three level model can be extended by introducing an external trap state, $|Trap\rangle$, in addition to the bright and dark states, see Figure 2.7.

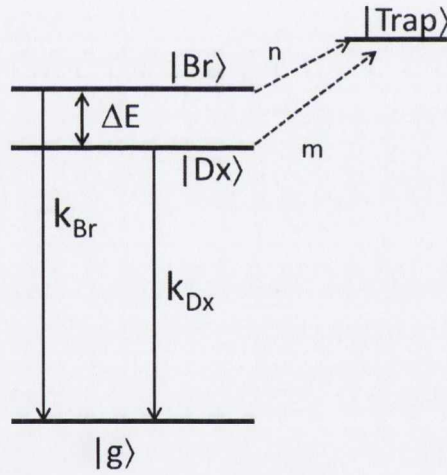


Figure 2.7: Schematic of the analytic model with ground state, $|g\rangle$, dark state, $|Dx\rangle$ with decay rate k_{Dx} , and the bright state, $|Br\rangle$, with decay rate k_{Br} . Additionally, there is an external trap state, $|Trap\rangle$. n and m are the number of phonons that will be required to interact with the trap state for the bright and dark state, respectively. ΔE is the bright dark splitting energy.

In this case the rate equation becomes

$$\frac{dN}{dT} = -(k_{Br} + \kappa_{Br,n})N_{Br} - (k_{Dx} + \kappa_{Dx,m})N_{Dx} = -Nk(T) \tag{2.27}$$

where $\kappa_{Br,n}$ and $\kappa_{Dx,m}$ represent non-radiative relaxation from the bright and dark states to the trap states involving an absorption of n and m phonons with an energy E_{ph} . They can be described as [162]

$$\kappa_{Br,n} = k_0 [\exp(E_{ph}/k_B T)]^{-n} \quad (2.28)$$

$$\kappa_{Dx,m} = k_0 [\exp(E_{ph}/k_B T)]^{-m} \quad (2.29)$$

where k_0 is a rate constant characterizing the efficiency of the thermally induced non-radiative relaxation to trap states, m and n refer to the number of phonons required for carrier escape from the dark and bright state, respectively. Solving Equation (2.27) in the same manner as for equation (2.26) leads to

$$k(T) = \frac{k_{Dx} + \kappa_{Dx,m} + (k_{Br} + \kappa_{Br,m}) \exp(-\Delta E/k_B T)}{1 + \exp(-\Delta E/k_B T)} \quad (2.30)$$

substituting in Equation (2.28) and Equation (2.29) gives

$$k(T) = \frac{ak_{Br} + k_{Dx} + k_0 [a(b-1)^{-n} + (b-1)^{-m}]}{1 + a} \quad (2.31)$$

where $a = \exp(-\Delta E/k_B T)$ and $b = \exp(E_{ph}/k_B T)$, additionally $\Delta E = (m - n)E_{ph}$.

The phonon energy, E_{ph} can be attributed to the average LO phonon energy, E_{LO} , which can be calculated from fitting the temperature dependence of the measured steady-state PL. With decreasing temperature there is an observed blue shift in the peak value of the PL emission, a narrowing of the full width at half maximum (FWHM), and an increasing integrated PL intensity. The common approach for fitting the peak shift and FWHM is to use expressions originally used to describe the temperature dependence of the band-gap and excitonic peak broadening in bulk semiconductors [161, 162, 173]. Firstly the dependence of the FWHM change on temperature can be described as follows

$$\text{FWHM}(T) = \Gamma_{inh} + \sigma T + \Gamma_{LO} [\exp(E_{LO}/k_B T) - 1]^{-1} \quad (2.32)$$

where Γ_{inh} is the temperature independent inhomogeneous broadening (due to QD size, shape, etc), σ is an exciton-acoustic phonon coupling constant, and Γ_{LO} represents the exciton-LO phonons coupling coefficient.

To further confirm the average value of E_{LO} the peak PL energy as a function of temperature can be fitted with an equation first proposed by O'Donnell and Chen [174].

$$E_g(T) = E_g(0) - S \langle E_{LO} \rangle [\coth(\langle E_{LO} \rangle / 2k_B T) - 1] \quad (2.33)$$

in which S is a dimensionless coupling constant known as the Huang-Rhys parameter, $\langle E_{LO} \rangle$ is the average phonon energy and $E_g(0)$ is the energy gap at 0 K.

This peak energy dependence can also be fitted with the Varshni equation [175]

$$E_g(T) = E_g(0) - \alpha \frac{T^2}{T + \beta} \quad (2.34)$$

α is the temperature coefficient, the value of β is close to the Debye temperature of the material.

Fitting the temperature dependences of the steady state PL with the equations above confirms that the QD samples used in these studies display typically observed behaviour and it allows the extraction of a value for E_{LO} to be used in the fitting of the temperature dependence of the decay rate.

2.7 Summary

This chapter provided a glimpse into the extensive work already undertaken with QDs, QWs, MNPs supporting surface plasmons, and NRET, as well as providing some basic theory that will be utilised throughout this thesis. Open questions still exist that this work aims to address. In Chapter 4 the analytic model including trap states to describe

the temperature dependent behaviour of QDs will be applied to CdTe nanocrystals for the first time. It is important to understand the behaviour of QD monolayers, and the impact of carrier trapping in these monolayers before applying the extended model to systems where ET is present, which will be the focus of Chapter 5. Chapter 6 will aim to demonstrate plasmon-mediated NRET from QDs to QWs for the first time. This will be a further step towards commercially viable QD and plasmonic based photovoltaic devices. The next chapter, however, will focus on the sample preparation and characterisation.

Chapter 3

Sample Preparation and Characterisation

Structures for the temperature dependent studies were built up using the Layer-by-Layer (LbL) technique [176,177] which is based on sequential self-assembly of oppositely charged species onto a surface due to electrostatic forces. This deposition technique allows one to develop complex structures on the nanoscale simply by immersion of a sample into solutions containing the different charged species, thus removing the need for highly specialised and expensive equipment. LbL is also very versatile and has already been investigated as a useful tool for biomedical applications [178,179], sensors and detectors [73,180,181], as well as photovoltaic devices [34,182,183]. Due to the possibility of nanometre control, it is also widely used in investigations into energy transfer processes [12,184,185].

For the light harvesting QD-QW energy transfer study samples were prepared using a spin coating technique. QDs and Ag NP samples, dissolved in toluene, were dispersed within a poly(methyl methacrylate) (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 ET study.

3.1 Sample Preparation

3.1.1 Materials and Sample Description: Hydrophilic Samples

The samples referred to in this section are used to investigate the temperature dependent properties of the PL and ET covered in Chapters 4 and 5. They are all water soluble and prepared using the LbL technique.

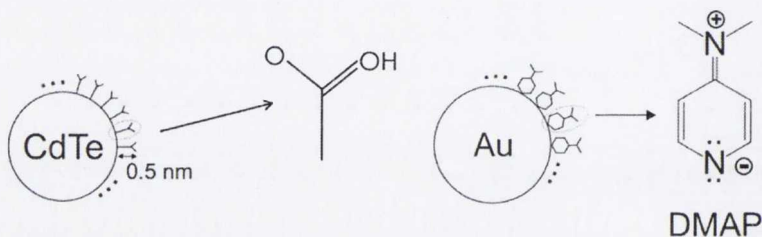


Figure 3.1: Schematic of the COOH stabilised QDs and the DMAP stabilised Au NPs

Polyelectrolyte (PE) layers were initially deposited onto quartz substrates to ensure a uniform and homogeneous charged surface was established before depositing any QDs. Four bilayers (one bilayer refers to the deposition of a pair of positive and negative PE layers) were initially deposited. These initial layers will be herein referred to as PE underlayers or PE buffer layers, to avoid confusion later when PE layers are also used as a varying spacer between different QDs and metal particle layers. The PEs used in this study consisted of positively charged poly(diallyldimethylammonium chloride) (PDDA) and of negatively charged poly(Sodium 4-styrene sulfate) (PSS), and were provided by Sigma Aldrich. The PSS is in powder form and has a molecular weight of approximately 70,000 g/M, the PDDA is in a 20% w/w solution with a molecular weight of 100,000 to 200,000 g/M in water. Usually these polymers tend to spread out in order to minimise the electrostatic forces affecting them, and so they tend to be very long and thus form very thin layers. In order to combat this NaCl is added to solutions of the PE. When this dissociates, the Na^+ and Cl^- ions screen the charge on the polymer, allowing it to curl up and form thicker layers [186]. Millipore water with a resistance of $18.2 \text{ M } \Omega/\text{cm}^2$ was used throughout all sample preparation. All water mentioned in this thesis will be assumed to be Millipore water unless otherwise stated. The PDDA solutions were simply decanted into a smaller glass vial without alteration

and this was then used as a stock solution. A PSS stock solution was made up by dissolving 554 mg of PSS powder in 10 mL of water. The solutions used for deposition were made up from stock as follows: 170 μL of stock PDDA solution was diluted in 0.2 mL of NaCl and 5.8 mL of water, and 560 μL of stock PSS solution was diluted in 0.2 mL of NaCl and 5.3 mL of water. Note that the NaCl solution was prepared by dissolving 1.75g of NaCl in 10 mL of water.

The colloidal QDs stabilised with carboxylic acid (COOH) were obtained commercially from PlasmaChem, this ligand imparts a negative charge. AuNPs were provided by Andrey Rogach from City University of Hong Kong, they are stabilised with 4-dimethylaminopyridine (DMAP), this ligand imparts a positive charge. A schematic of both QDs and AuNPs is shown in Figure 3.1.

3.1.2 Description of Layer-by-Layer Method

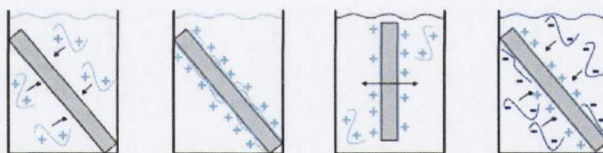


Figure 3.2: Schematic of the LbL deposition method showing the initial adsorption, rinsing, and second adsorption steps.

The LbL method involves sequential adsorption of oppositely charged polyelectrolytes via immersion of a sample substrate in solutions for a set time, thus building up alternating positive and negative charged layers, this is shown schematically in Figure 3.2. Rinsing with water between adsorption steps removes excess solution and removes any particles that are not tightly bound to the surface, therefore leaving only a monolayer of the charged species on the surface. The water rinsing step is important to ensure that monolayers are formed rather than multilayers, it also helps prevent contamination of the positively charged solution with the negatively charged one, and vice versa. After deposition of the first layer the next oppositely charged layer will be electrostatically bound to it. The different layers can be then be built up in this manner by sequential

immersion of the substrate.



Figure 3.3: Schematic of the structures used in the temperature dependent studies. (a) Monolayer of either donor or acceptor QDs with varying concentrations. (b) Separated bilayer of AuNPs and a densely packed monolayer of either donor or acceptor QDs with a 3 nm PE spacer layer. (c) Separated bilayer of donor and acceptor layers (densely packed) with a 3 nm PE spacer layer (d) Schematic of the full trilayer sample.

Since the ligands stabilising the QDs and AuNPs impart a surface charge they can be deposited onto the PE buffers by ensuring the charge of the last PE layer is opposite to that of the QD/AuNP. Throughout this thesis various types of samples are used. QD monolayers with varying concentration, achieved through varying the immersion time of the substrate in the QD solution, shown in Figure 3.3a. QD-Au separated bilayers, achieved by depositing a monolayer of AuNPs onto the PE buffer before depositing a PE spacer layer and then depositing the QDs, shown in Figure 3.3b. QD-QD separated bilayers are deposited in a similar way, the acceptor QD is deposited on top of the PE buffer, a PE spacer layer is placed on top and the donor QD is deposited on top, schematic shown in Figure 3.3c. The full trilayer structure is created by sandwiching AuNPs between the donor and acceptor QDs, see Figure 3.3d.

3.1.3 Materials and Sample Description: Hydrophobic Samples

The samples described in this section are used to investigate the surface plasmon-mediated NRET between QDs and QWs, referred to as the light harvesting system. Single QW samples were received from Tyndall, where they were prepared by MOVPE [187]. A GaN buffer layer was grown onto a sapphire substrate. Onto the buffer was grown a layer of 2 nm InGaN QW followed by GaN capping layers of various thickness; 3 nm, 5 nm, and 7 nm.

Hydrophobic AgNPs with average particle size of 6-7 nm were obtained in powdered form from PlasmaChem. These were dissolved in toluene at a concentration of 10 mg/4 mL, this is then used as a stock solution. CdSeS/ZnS QDs were purchased from Sigma Aldrich with a concentration of 1 mg/mL in toluene, this was used as purchased as a stock solution. The diameter is quoted at (6.0 ± 0.5) nm and the centre emission wavelength is 450 nm.

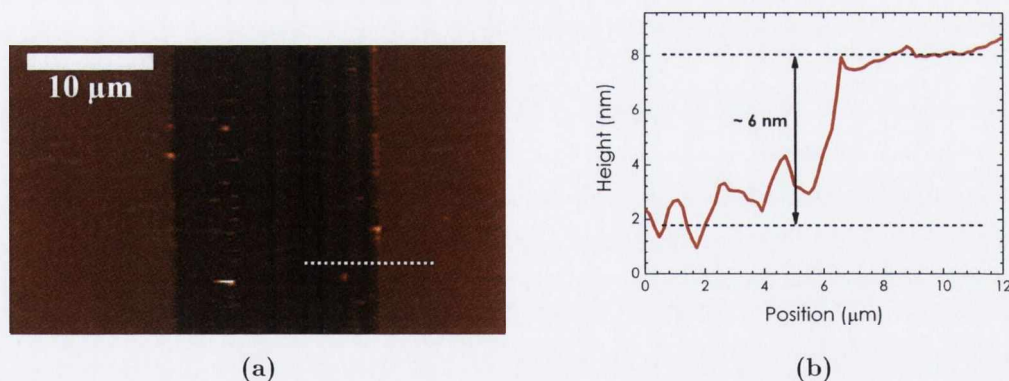


Figure 3.4: AFM of a cut in the QD PMMA layer (b) Measurement of the step height of the layer. AFM measurements were carried out by Robbie O'Connell.

PMMA with a molecular weight of 996,000 g/M was purchased from Sigma and a solution of 0.1% w/w in toluene was prepared. The QDs and AgNPs were dispersed in these PMMA solutions before being spun onto the QWs and a GaN substrate for reference. This 0.1% solution with QDs dispersed in it produces a layer (6 ± 1) nm thick, this was confirmed with AFM (see Figure 3.4). A schematic of the sample is shown in Figure 3.5.

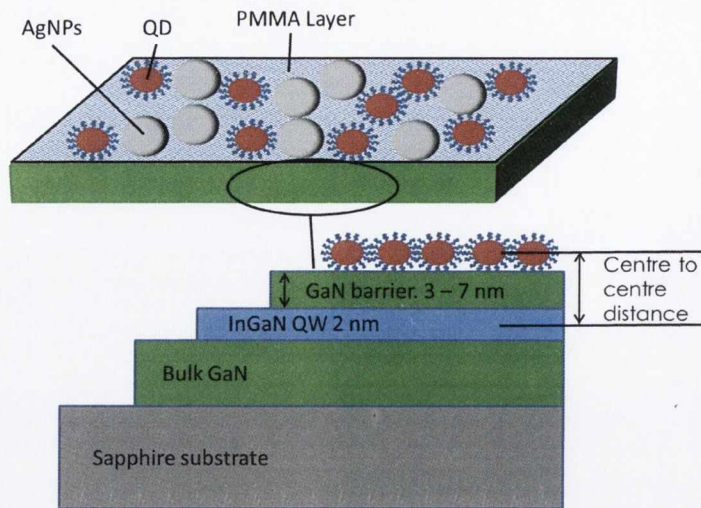


Figure 3.5: Schematic of the QD AgNP sample showing the mixed layer of QDs and AgNPs and the centre-to-centre distance.

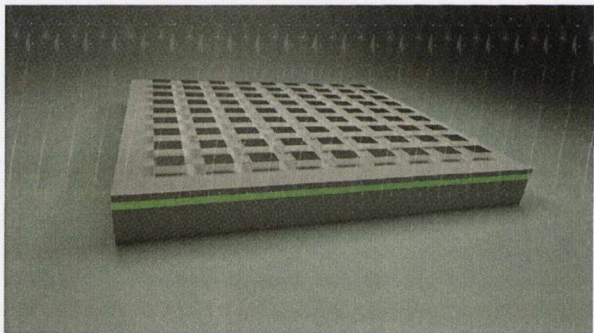


Figure 3.6: Schematic of the nanobox arrays. The green strip indicates the InGaN active layer of the QW. Figure generated by Dr. Cristian Marocico.

Arrays of nanoboxes and nanodiscs were fabricated using electron beam lithography (EBL) by Luke Higgins [188]. A focused beam of electrons is used to draw a pattern of boxes or discs in an electron sensitive resist layer. The resist layer in this case is a 100 nm thick layer of PMMA, this is modified by the electron beam by causing the long chained PMMA to break up into shorter chains. These shorter chained regions are then soluble in methyl-isobutylketone (MIBK), thereby allowing for the removal of these regions within the resist. After this development process metal is then deposited everywhere by metal evaporation. The remaining resist is removed by a lift off process in acetone, taking the metal from unexposed regions off with it. Therefore, only metal from areas that were exposed by the electron beam remain.

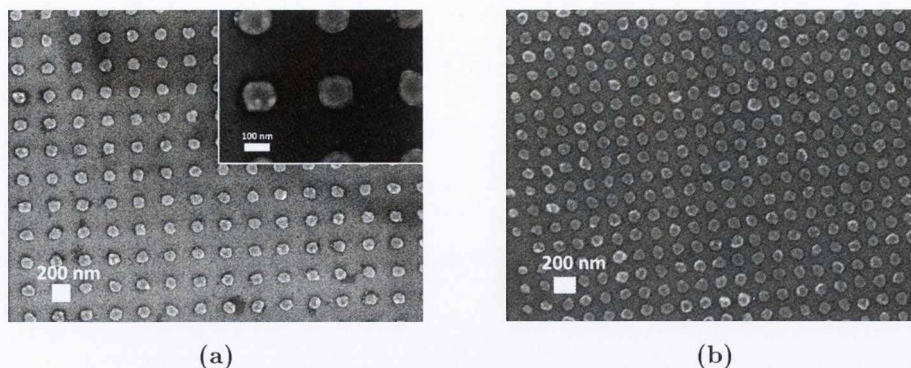


Figure 3.7: (a) SEM of the nanoboxes, inset is a zoomed image. (b) SEM of the nanodiscs. These images were taken by Luke Higgins

The arrays used in this work consist of nanoboxes and nanodiscs arranged in a two dimensional square lattice of 200×200 units. The dimensions of the individual nanoboxes are $100 \text{ nm} \times 100 \text{ nm}$ with a spacing of 200 nm . The nanodiscs have a diameter of 90 nm with a spacing of 80 nm . A schematic of the nanobox array is shown in Figure 3.6. After the development step 5 nm of Ti and 35 nm of Ag is deposited for both structures. The titanium is used as an adhesion layer. SEM images of the nanoboxes and nanodiscs are shown in Figure 3.7. QDs in the same 0.1% PMMA solution as above were spun onto these arrays built on both a GaN substrate and a 3 nm barrier QW.

For more information on the sample preparation see step by step sample recipes are presented in Appendix A.

3.2 Sample Characterisation

3.2.1 Absorption

Absorption spectra of the samples provides information about the concentration of the QDs or MNPs deposited. The measurements were carried out on a Cary 50 UV-Vis Spectrophotometer. The spectra of the QDs/MNPs (both in solution and in layers) were recorded between 300 nm and 800 nm with a resolution of 1 nm . For calculating the thickness of PE layers, the measurements were taken down to 200 nm as the

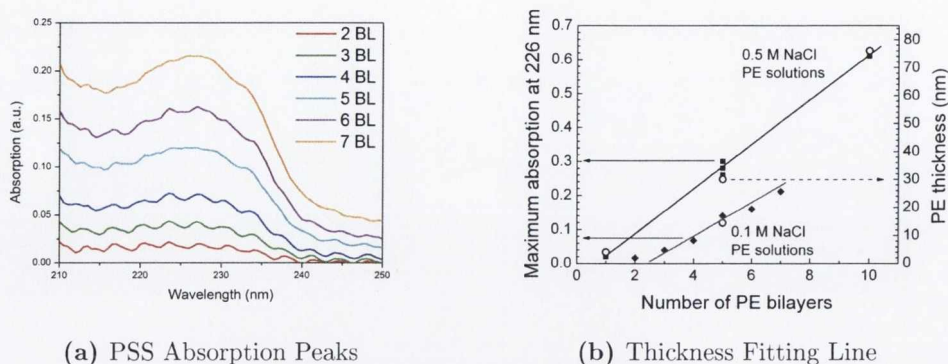


Figure 3.8: (a) PE absorption spectra for different numbers of PE layers. (b) Thickness Fitting Line showing the peak absorption value at 226 nm for the absorption spectra as well as the thickness measured by XRD. This XRD measurements were carried out by Robert Gunning and the Absorption data is reproduced from reference [77].

absorption peak of PSS occurs at approximately 226 nm. By monitoring this peak one can determine the thickness. Since only the PSS absorption peak is monitored it is only possible to measure the thickness of bilayers and not individual monolayers. Absorption of a material is characterised by the Lambert-Beer Law:

$$A(\lambda) = \epsilon(\lambda) \cdot l \cdot c \quad (3.1)$$

Where $\epsilon(\lambda)$ is the extinction coefficient of the sample, l is the length of the path of light and c is the concentration of the material in the sample. If l and $\epsilon(\lambda)$ are known for the material being investigated then the concentration can be determined by measuring the absorption. Similarly, if the concentration and extinction coefficient are known then the thickness of the material can be determined. At the very least, a thickness comparison can be made between different samples of the same material (therefore same $\epsilon(\lambda)$).

To determine the absolute values of the PE bilayer thickness, a few samples with different number of bilayers were analysed with X-Ray Diffraction [77] These results could then be compared with absorption measurements for the PE layers. In particular by comparing the values of the absorption at the characteristic peak of PSS (226 nm) in Figure 3.8a to the XRD measurements in Figure 3.8b one can see that they both follow the same linear trend. It is therefore possible to monitor the change in thickness from the absorption measurements. The fitting curve in Figure 3.8b shows two different concentrations of salt (0.5 M and 0.1 M). This shows that, as mentioned above, the

greater the concentration of salt the thicker the layers that are formed. An average thickness of 3 nm per bilayer was determined for the 0.1 M NaCl concentration used in these experiments. It must be noted when using this method that the first few PE buffer bilayers tend to be thinner than the others [186] as they do not form complete layers. Therefore a few bilayers should always be deposited to ensure that the PE buffer is uniform. Note that due to this five bilayers tend to form PE layers of about 14 nm in thickness.

The thickness of the samples was estimated from previous absorption and XRD measurements on increasing numbers of PE bilayers [77].

Quantum Dot Concentration & Size

The diameter of colloidal QDs, d_{QD} , can be determined from the centre wavelength of the first absorption peak, λ_A in nm. For CdTe QDs this sizing curve is [70, 189]

$$d_{QD} = (9.1827 \times 10^{-7})\lambda_A^3 - (1.7147 \times 10^{-3})\lambda_A^2 + 1.0064\lambda_A - 194.84 \text{ nm} \quad (3.2)$$

The extinction coefficient of QDs, ϵ_{QD} with units of $M^{-1} \text{ cm}^{-1}$, can be determined from the diameter of CdTe QDs by [70]

$$\epsilon_{QD} = 10043(d_{QD})^{2.12} \quad (3.3)$$

Knowing the extinction coefficient of the QDs the molar concentration of the dots in solution, c_{sol} , can be easily determined from the Lambert-Beer law as the length of the light path, l , is simply the width of a standard cuvette, 1 cm.

From the solution spectra of donor QDs shown in Figure 3.9 a diameter of 2.2 ± 0.2 nm was obtained. The absorption value for the first absorption peak is 0.157 ± 0.002 at 494 ± 2 nm. The extinction coefficient is then calculated as $\epsilon_{Don}(\lambda_{peak}) = (5.18 \pm 0.03) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. One can now determine c_{sol} for the QD solution shown in Figure 3.9 using Equation (3.1), a value of $(5.02 \pm 0.02) \times 10^{-6} \text{ M}$ was found.

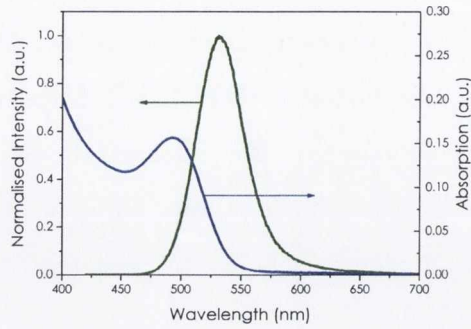


Figure 3.9: The absorption (right axis) and emission (left axis) spectra of donor QD, in solution.

Now, after deposition of the QDs in a layer, the extinction coefficient $\epsilon(\lambda_{peak})$ of the dots should not have changed. Therefore, the concentration of the QDs in a layer can be determined by comparison with the spectra of the QDs in solution. The concentration of the dots in a layer, c_{layer} , can be calculated using the following [77]

$$\begin{aligned} c_{layer} &= \frac{A_{layer}(\lambda_{peak})}{A_{sol}(\lambda_{peak})} \cdot c_{sol} \cdot \frac{l}{d_{QD}} \cdot \frac{1}{2} \cdot N_A \cdot \frac{10^3 L}{m^3} \cdot d_{QD} \\ &= \frac{A_{layer}(\lambda_{peak})}{A_{sol}(\lambda_{peak})} \cdot c_{sol} \cdot 3.011 \times 10^{24} \end{aligned}$$

where l is the path length, which is the width of the standard cuvette as mentioned above, $l = 1\text{cm} = 0.01\text{ m}$. The additional factor of $1/2$ must be introduced to account for the fact that deposition occurs on both sides of the substrate. To convert the result to a surface density i.e. to obtain c_{layer} in m^{-2} the final factor of $N_A \cdot \frac{10^3 L}{m^3} \cdot d_{QD}$ is introduced. N_A is Avogadro's number, d_{QD} is the QD diameter, as above.

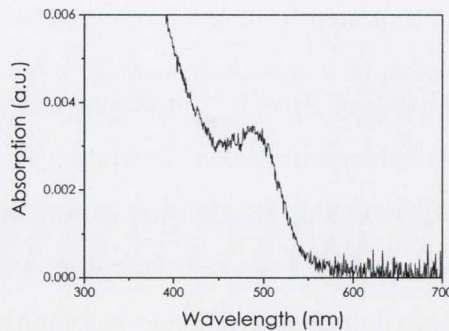


Figure 3.10: Absorption spectrum of a donor QD monolayer.

For the QD monolayer shown in Figure 3.10, the ratio of the absorption values was found to be 0.018 and using $c_{sol} = 5.02 \times 10^{-6}$ M, as quoted above, the concentration of the QDs in the layer was found to be $(2.7 \pm 0.1) \times 10^{17} \text{ m}^{-2}$.

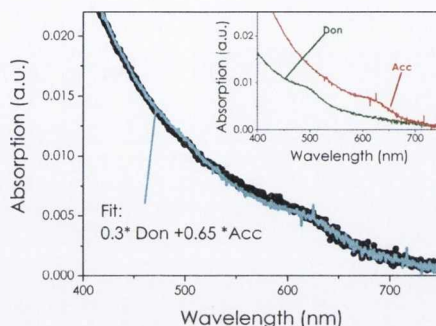


Figure 3.11: Absorption spectrum of a donor acceptor QD bilayer. Inset shows the reference spectra for the donor and acceptor.

The concentration of samples including both the donor and acceptor QDs, for example a QD bilayer, was determined by fitting the measured absorption spectrum with a linear combination of the reference spectra. Figure 3.11 shows one such fitting. The absorption peaks of the measured spectra can be reproduced using a weighted sum of the donor and acceptor references, shown in the inset, with factors of 0.3 and 0.65 for the donor and acceptor respectively.

Gold Nanoparticle Concentration

The Au NP absorption spectrum is dominated by the LSP resonance feature at ≈ 520 nm as can be seen from Figure 3.12.

The extinction coefficient was taken as $1.1 \times 10^7 \text{ M}^{-1} \text{ cm}^{-1}$ [59] and the average diameter is 5.5 nm. The LSP resonance displays a red-shift when the AuNPs form a monolayer. This shift is due to refractive index changes, and is evident even at low concentration [190,191], this sensitivity to refractive index can form the basis for plasmonic biosensing [192]. The LSP peak for the monolayer is centred at ≈ 542 nm. The concentration in a monolayer, c_{AuML} , can be calculated from the absorption value at the LSP resonance peak, A_{AuML} , using the extinction coefficient for the solution in a

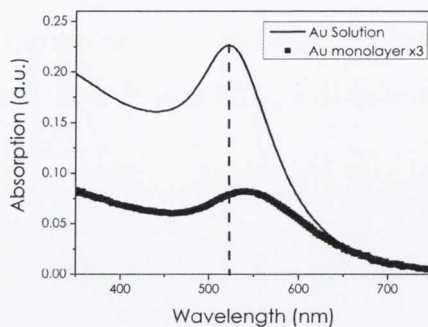


Figure 3.12: Absorption spectra of a gold nanoparticle solution and a gold nanoparticle layer deposited from the solution.

similar manner to the QD concentration

$$c_{AuML} = \frac{A_{AuML}}{1.1 \times 10^7} \cdot \frac{1}{2} \cdot 6.022 \times 10^{24} \text{ m}^{-2}$$

For the monolayer shown in Figure 3.12 $A_{AuML} = 0.027$ and the concentration is found to be $(7.39 \pm 0.08) \times 10^{15} \text{ m}^{-2}$. For 5.5 nm diameter particles the maximum coverage corresponds to a concentration of $3.1 \times 10^{16} \text{ m}^{-2}$. For samples containing QDs and AuNPs the concentration can be extracted using the same method as for samples with more than one size of QD. The total sample spectrum is fitted with a linear combination of the AuNP spectrum and the individual QD spectrum.

Silver Nanoparticles

Figure 3.13 shows the absorption spectrum of the AgNPs in solution. The dashed line shows the characteristic LSP resonance at 350 nm. Centred at 450 nm is a second broader peak, due to higher order modes and the coupling between multiple NPs with slightly different sizes and shapes [193]. This peak is slightly shifted from the 445 nm that is quoted by PlasmaChem which again could be due to slight variations in the size and shape of the NPs in the particular batch recieved [193].

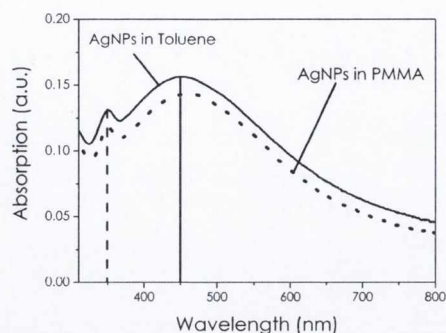


Figure 3.13: Absorption spectra of approximately 6 nm diameter AgNPs in toluene. Clearly visible is the characteristic LSP peak at 350 nm (vertical dashed line) and a second broader peak centred ≈ 450 nm (vertical solid line). When the AgNPs are dispersed in PMMA there is a further red shift of the secondary peak.

3.2.2 Photoluminescence & Quantum Yield

The PL spectra of the QD solutions and layers were recorded with a Perkin-Elmer LS 55 fluorescence spectrometer for 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 usually 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. For the 450 nm emitting QDs an excitation wavelength of 350 nm was also used and the recorded range was 380-680 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. This was not necessary when measuring QDs in a layer due to the reduced QY and lower QD concentration.

In order to determine the QY of the samples a comparison is done with a reference standard; rhodamine 6G dye for QDs emitting in the range of 500-600nm, see Figure 3.14b, which has a well known QY of 95%. For the blue emitting QDs, Quinine Sulphate is used as the reference standard, this has a QY of 58%, see Figure 3.14d. The difference 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 reference absorption at the excitation wavelength, $A_{sample}(\lambda_{ex})$ and $A_{ref}(\lambda_{ex})$, respectively. To determine the number of emitted photons the PL spectra of the sample, $I_{sample}(\lambda)$, and the reference, $I_{ref}(\lambda)$, are integrated in

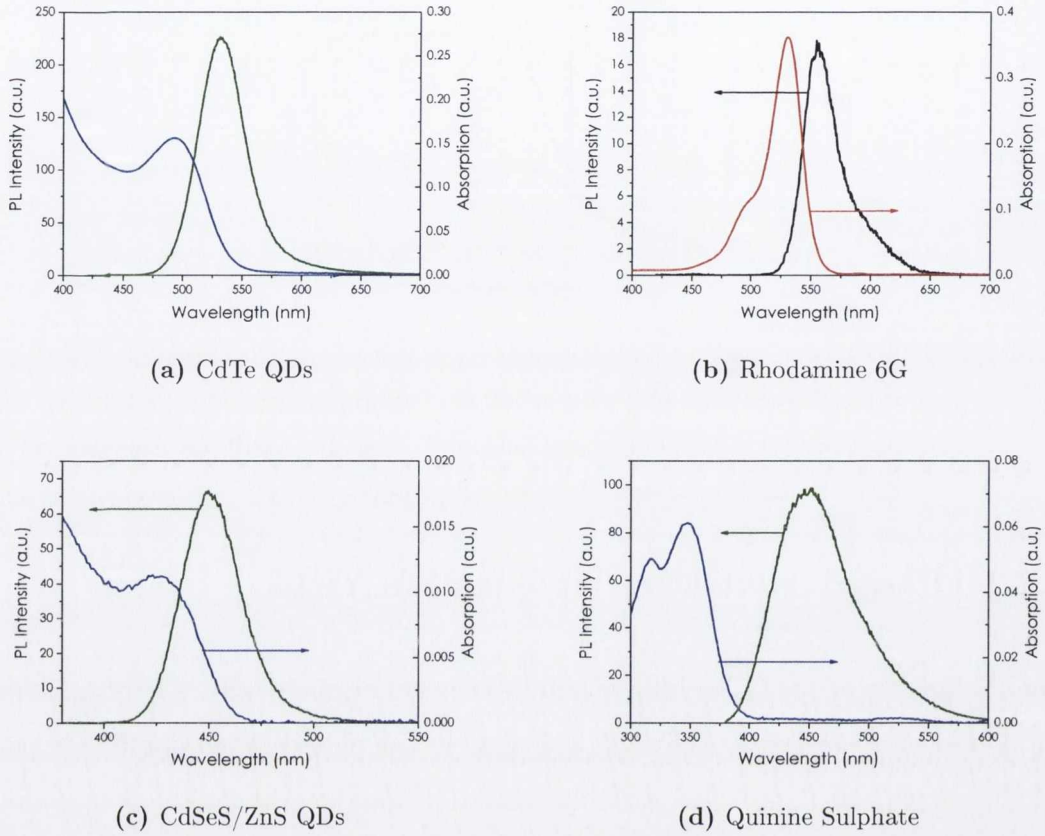


Figure 3.14: Absorption (right axis) and Photoluminescence (left axis) spectra of (a) Donor QDs and (b) Rhodamine 6G excited at 400nm (c) Absorption (right axis) and Photoluminescence excited at 350 nm (left axis) of the CdSeS/ZnS QDs (d) Absorption (right axis) and Photoluminescence excited at 350 nm (left axis) of Quinine Sulphate.

the range 500 nm to 700 nm for Rhodamine 6G, and in the range of 380 nm to 650 nm for Quinine Sulphate. 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 references 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 a sample in solution, Q_{sol} , is given by [75]

$$Q_{sol} = \frac{A_{ref}(\lambda_{ex})}{A_{sample}(\lambda_{ex})} \cdot \frac{\int I_{sample}(\lambda) d\lambda}{\int I_{ref}(\lambda) d\lambda} \cdot \left(\frac{n_{sample}}{n_{ref}} \right)^2 \cdot Q_{ref} \quad (3.4)$$

In order to determine the ratio $A_{ref}(\lambda_{ex}) / \int I_{ref}(\lambda) d\lambda$ the integrated PL is calculated

for increasing concentrations of the reference and it is plotted against the absorption at the excitation wavelength in order to extract the slope, m_{ref} . The concentration is kept relatively low for this, below an optical density of ≈ 0.01 , in order to prevent too much attenuation of the incident or emitted light (inner filtering effects) [75]. Similarly to prevent reabsorption in the QD samples the concentration/optical density is low for the measurement of the QY [194].

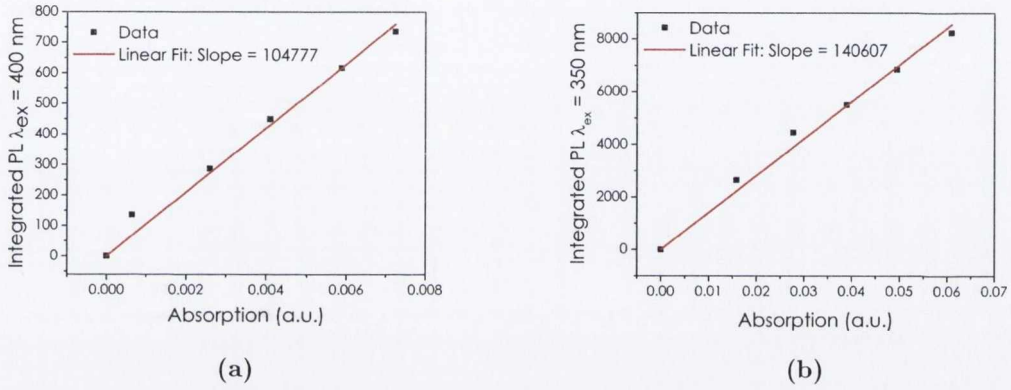


Figure 3.15: Integrated PL versus absorption for (a) Rhodamine 6G and (b) Quinine Sulphate. The line is a linear fit.

Inputting this slope into Equation (3.4) gives

$$Q_{sol} = \frac{\int I_{sample}(\lambda) d\lambda}{A_{sample}(\lambda_{ex})} \cdot \frac{1}{m_{ref}} \cdot \left(\frac{n_{sample}}{n_{ref}} \right)^2 \cdot Q_{ref} \quad (3.5)$$

For rhodamine 6G $m_{ref} = 104777$ and it was dissolved in methanol so $n_{ref} = n_{Rho} = 1.329$ and since the CdTe QDs were dissolved in water $n_{sample} = 1.333$. Substituting all these values into Equation (3.5) and using the values from the donor solution spectrum shown in Figure 3.14a one obtains

$$Q_{sol} = \frac{9697}{0.33} \cdot \frac{1}{104777} \cdot \left(\frac{1.333}{1.329} \right)^2 \cdot 0.95 \approx 0.27 \text{ or } 27\%$$

To determine the quantum yield in a monolayer an additional factor of $\frac{0.7}{0.5}$ must be included to account for the different contributions from the layers at the front and back of the sample to the spectra [77]. A refractive index of $n = 1.5$ for the ligand

surrounding the QDs as well as the PE is also used in place of n_{sample} [77]. The integrated PL values must be multiplied by a factor of 0.01 since the monolayer samples were measured without a filter, and a 1% transmission filter was used for all solution measurements. Otherwise the calculation is identical to the one for solutions.

The QY for a monolayer of the donor CdTe QDs, QY_{ML} , using the added factors quoted above can be calculated as follows

$$Q_{ML} = \frac{2026}{0.003457} \cdot \frac{1}{104777} \cdot 0.01 \cdot \left(\frac{1.5}{1.329} \right)^2 \cdot \frac{0.7}{0.5} \cdot 0.95 \approx 0.09 \text{ or } 9\%$$

In the case of the Quinine Sulphate reference $m_{ref} = 140607$ and it is dissolved in 0.1 M H_2SO_4 therefore $n_{ref} = n_{QS} = 1.42$. The QDs in this case are dispersed in PMMA, giving $n_{sample} = 1.489$. Substituting these values into Equation (3.5) and using the values from the QD solution spectrum shown in Figure 3.14c one obtains

$$Q_{sol} = \frac{2402}{0.02228} \cdot \frac{1}{140607} \cdot \left(\frac{1.489}{1.42} \right)^2 \cdot 0.58 \approx 0.49 \text{ or } 49\%$$

This is very close to the value quoted by the manufacturer which is 50%.

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 put of the fluorescence lifetime imaging microscope (FLIM) used to measure time resolved PL 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 were excited through a 40x objective using picosecond laser pulses at 405 nm with a repetition rate of 10 MHz, emission was collected back through the same objective.

3.2.3 Förster Radius

As mentioned in section 2.2.1 the Förster Radius, R_0 , is an important parameter to know and analyse in the study of FRET, especially for modelling the distance and

dependence of the energy transfer. From Equation (2.8) on page 13 the Förster distance can be computed by calculating the QY of the donor and the spectral overlap function $J(\lambda)$ and by knowing the refractive index. As mentioned before the value of κ^2 is usually taken as $2/3$ for a random orientation of dipoles. The calculation of the QY is discussed in the previous sections and the refractive index is taken as 1.9, this a volume weighted refractive index of the PE and the QDs. The overlap integral is calculated using a MATLAB program.

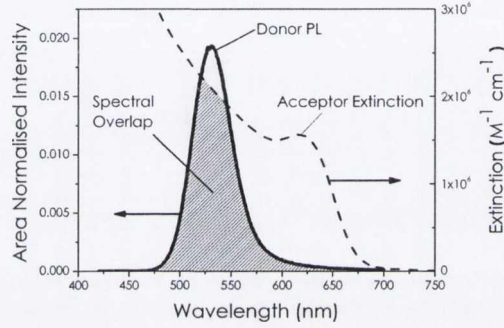


Figure 3.16: Area normalised PL spectrum of the donor QDs (left axis) and the extinction spectrum of the acceptor QDs (right axis). The shaded area indicates the spectral overlap.

Figure 3.16 shows the donor QD emission spectrum (normalised so that its area is 1) and the acceptor QD extinction spectrum. This is obtained from the absorption spectrum by adjusting the value of the first absorption peak to the value of the extinction coefficient obtained from the fitting curve given by Equation (3.3). The value of $J(\lambda)$ for this system is $J = 1.87 \times 10^{16} \text{ nm}^4 \text{ M}^{-1} \text{ cm}^{-1}$.

Substituting into Equation (2.8) gives

$$R_0 = 0.0211 \left(\frac{2/3 \cdot Q_D}{1.9^4} \cdot 1.87 \times 10^{16} \right)^{1/6} \quad (3.6)$$

The QY for donor QDs in a monolayer was calculated in Section 3.2.2 as 0.09 ± 0.03 which gives a value of $R_0 = 4.4 \pm 0.2 \text{ nm}$.

It can be seen from Figure 3.9 that there is significant overlap of the donor emission spectrum with its own absorption spectrum, which will be referred to as self-overlap. This is important as it can lead to FRET within the QD ensemble if the QDs are

sufficiently close to one another (such as in a monolayer). This can result in discrepancies between theory and measured results of donor-acceptor FRET efficiency. J and R_0 for this self-overlap can be calculated in the exact same way as above and for the donor monolayers values of $J = 3.05 \times 10^{15} \text{ nm}^4 \text{ M}^{-1} \text{ cm}^{-1}$ and $R_0 = 3.2 \pm 0.2 \text{ nm}$ are obtained.

3.2.4 Time-Resolved Photoluminescence

Time resolved PL decays were measured on a PicoQuant Microtime 200 FLIM system with 90 ps pulses. This system uses time correlated single photon counting. 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 40x objective. Decays were measured over $80 \times 80 \mu\text{m}^2$ (150×150 pixels) areas with a usual integration time of 4 ms.

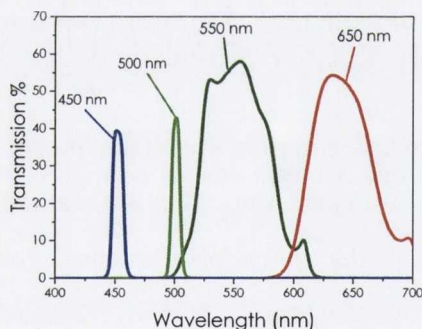


Figure 3.17: Transmission spectra of narrow band filters (FWHM $\approx 8 \text{ nm}$) with centre wavelengths of 450 nm and 500 nm, and of broad band filters (FWHM $\approx 70 \text{ nm}$) with centre wavelengths of 550 nm and 650 nm.

Broadband filters with a FWHM of approximately $75 \pm 5 \text{ nm}$ were used to spectrally resolve the LbL samples for the temperature dependent study. The spectral features of the QDs and QWs for the light harvesting were much closer so much narrower filters with a FWHM of approximately 8 nm were used in that case. The transmission spectra of these filters is shown in Figure 3.17.

The intensity decays were fitted with a two-exponential decay function:

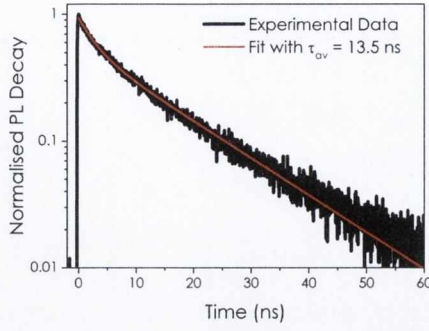


Figure 3.18: Time resolved photoluminescence decay of QDs (black). The red line is a two-exponential fit with $\tau_{av} = 13.5$ ns

$$I(t) = A_1 \cdot e^{-t/\tau_1} + A_2 \cdot e^{-t/\tau_2} \quad (3.7)$$

Where A_1 and A_2 are the intensity amplitudes of the decays with the two different lifetimes τ_1 and τ_2 . Average lifetimes were calculated using an intensity weighted means:

$$\tau_{av} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2} \quad (3.8)$$

Figure 3.18 shows an example of the decay curve and the two-exponential fitting, the average decay rate is then easily determined from this lifetime, $k_{av} = 1/\tau_{av}$.

3.2.5 Low Temperature Measurements

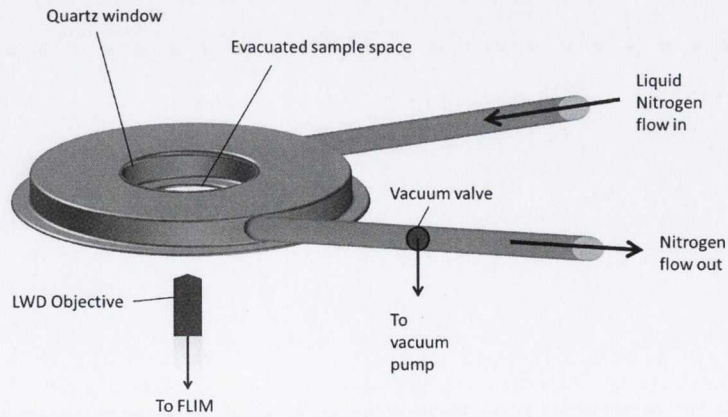


Figure 3.19: Schematic of the Janis ST 500 microscopy cryostat

A Janis ST-500 liquid nitrogen continuous flow cryostat was integrated into the FLIM system enabling measurement of TRPL and PL from ≈ 77 K up to room temperature (≈ 296 K). The objective used for room temperature measurements was replaced with a 40x long working distance (LWD) objective. Samples were placed in a small chamber which was evacuated to 10^{-5} mbar. A constant, controlled flow of liquid nitrogen slowly cooled the sample to ≈ 77 K. Once a stable minimum temperature was achieved the flow of nitrogen was slowly reduced until the temperature began to rise, then the nitrogen flow was increased slightly to reach the minimum temperature again. This ensures the minimum amount of liquid nitrogen is used to keep the sample cooled and prevents pooling of the liquid nitrogen in the sample chamber. A schematic of the cryostat is shown in Figure 3.19, not shown is the liquid nitrogen dewar. Nitrogen is transferred from dewar to cryostat via a flexible transfer line which is equipped with multiple radiation shields and vacuum insulation to ensure efficient transfer of the liquid nitrogen. The out flowing nitrogen gas is directly connected to the air vent system. A Lakeshore Model 331 Temperature Controller is used to stabilise the temperature using a resistive heater at intermediate points between 77 K and room temperature and also gives the temperature readout at each point.

3.3 Conclusions

In conclusion, this chapter has presented how the samples are prepared with controllable QD and AuNP concentration and layer separation, using LbL. This enables the preparation of the QD monolayers with varying concentration investigated in Chapter 4, and the separated bilayer and trilayer structures studied in Chapter 5. Details of spin-casting QDs and AgNPs dissolved in toluene and dispersed in PMMA is discussed which allows for the creation of the samples used in Chapter 6 (Section 6.2), to measure the distance dependence of plasmon mediated non-radiative ET with QWs of different barrier thicknesses. Development of the arrays of Ag nanoboxes and nanodiscs using EBL is also discussed, which will be the focus of the later half of Chapter 6 (Section 6.3). Furthermore the characterisation and data analysis techniques required to extract the relevant physical quantities are presented.

Chapter 4

Temperature Dependence of Quantum Dot Monolayers with Varying Concentration

A good understanding of the temperature dependent properties of monolayers of QDs is essential before investigating more complex processes such as quenching to MNPs or ET between QDs. In this chapter the temperature dependence of the average decay rate of CdTe quantum dot monolayers, prepared using QDs of two different sizes, as a function of concentration is investigated. Monolayers of three concentrations have been studied for each size of QD. The monolayer concentration is varied from sparsely packed to densely packed to investigate the effect of concentration on the temperature dependent emission properties, spectral and dynamic. The PL decays of the QD ensemble in each monolayer is characterized by an average decay rate. It will be shown that in order to accurately reproduce the temperature dependent data above 150 K it is essential to use a model which accounts for thermally activated carrier trapping in addition to the bright-dark splitting, and moreover that this trapping can become more efficient and more dominant at higher concentrations.

4.1 Initial Characterisation

All structures were prepared using the layer-by-layer (LbL) assembly method, as described in Chapter 3. LbL is based on sequential assembly of oppositely charged species onto a surface due to electrostatic forces. Colloidal CdTe QDs stabilized with carboxylic acid (COOH) ligands were acquired commercially from PlasmaChem. The COOH ligand imparts a negative surface charge to the QDs. QDs of two different sizes were used in this study, hereafter referred to as QD1 and QD2. They have average diameters of (2.2 ± 0.1) nm and (3.8 ± 0.2) nm respectively with peak emission wavelengths at room temperature of 557 nm and 690 nm respectively, as seen in Figure 4.1a. QD diameter is calculated from the position of the first absorption peak, see Equation (3.2) on page 41 [70]. The spectra shown in Figure 4.1a were measured for the highest concentration QD monolayer studied in each case, $(3.4 \pm 0.3) \times 10^{17} \text{ m}^{-2}$ and $(1.1 \pm 0.3) \times 10^{17} \text{ m}^{-2}$ respectively. A schematic of the structure is shown in Figure 3.3a on page 35 and is reproduced here in Figure 4.1b for convenience. Initially a quartz substrate is immersed in PE so that the PE can adsorb onto the surface of the quartz, subsequently four bilayers of PE are built up in order to provide a uniform surface for QD adhesion. The substrate is immersed in the QD solutions for varying times, thereby building up different concentrations of QDs in a monolayer. For QD1 the three concentrations studied were $(1.2 \pm 0.3) \times 10^{17} \text{ m}^{-2}$, $(2.7 \pm 0.3) \times 10^{17} \text{ m}^{-2}$, and $(3.4 \pm 0.3) \times 10^{17} \text{ m}^{-2}$. For QD2 they were $(1.9 \pm 0.3) \times 10^{16} \text{ m}^{-2}$, $(3.8 \pm 0.3) \times 10^{16} \text{ m}^{-2}$, and $(1.1 \pm 0.3) \times 10^{17} \text{ m}^{-2}$. These concentrations are denoted in order of increasing concentration c_1 , c_2 , and c_3 for future reference. These concentrations are calculated from the absorption spectra as described in Section 3.2.1.

4.2 Steady State Photoluminescence

The excitation density in this case was $< 1 \mu\text{J}/\text{cm}^2$, to ensure single-exciton generation [195]. The PL spectra display strong temperature dependent properties. Figure 4.2 shows the integrated PL as a function of temperature for QD1 (Figure 4.2a) and QD2 (Figure 4.2b). As the temperature increases the PL intensity decreases, this is due

4. Temperature Dependence of Quantum Dot Monolayers with Varying Concentration

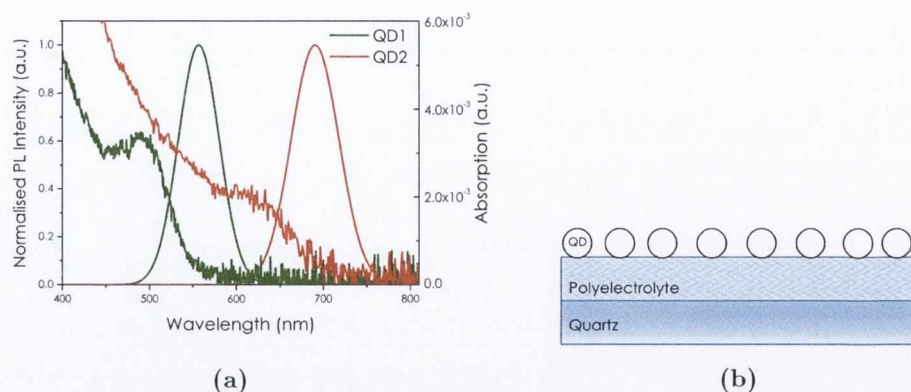


Figure 4.1: (a) Intensity normalised PL spectra (left axis) of QD1 (green lines) and QD2 (red lines) monolayers at room temperature (concentration c_3). The absorption spectra (right axis) of the two QDs monolayers are also shown. (b) Schematic of the sample. QDs (white circles) are deposited onto PE layers that were firstly deposited on the quartz substrate to form a base layer for the QD monolayer deposition.

to an onset of thermally activated carrier trapping. This trend is observed over the entire measurement range, no strong luminescence temperature anti-quenching [196] was observed.

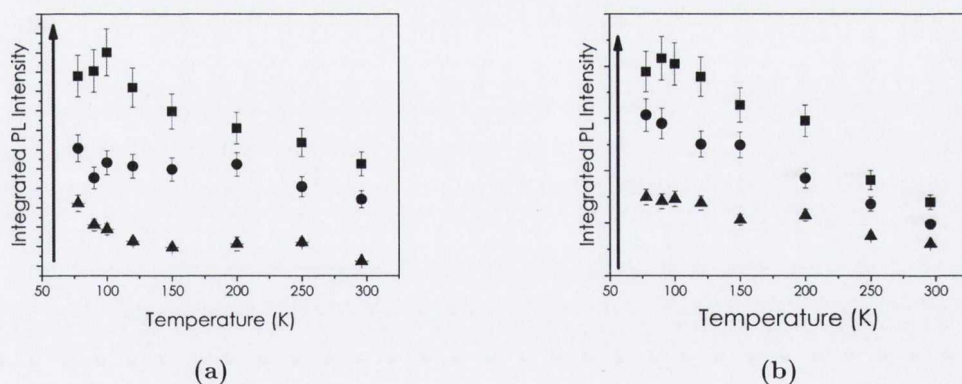


Figure 4.2: (a)[(b)] Integrated PL for QD1[QD2] as a function of temperature with increasing concentration. The arrow indicates direction of increasing concentration triangles for c_1 , circles for c_2 , and squares for c_3 .

In addition to the PL intensity decrease, the emission energy red shifts, and the FWHM of the spectra increases with increasing temperature. This is shown in Figure 4.3 for QD1 and in Figure 4.4 for QD2. The common approach for fitting the peak shift and FWHM is to use expressions originally used to describe the temperature dependence of

4. Temperature Dependence of Quantum Dot Monolayers with Varying Concentration

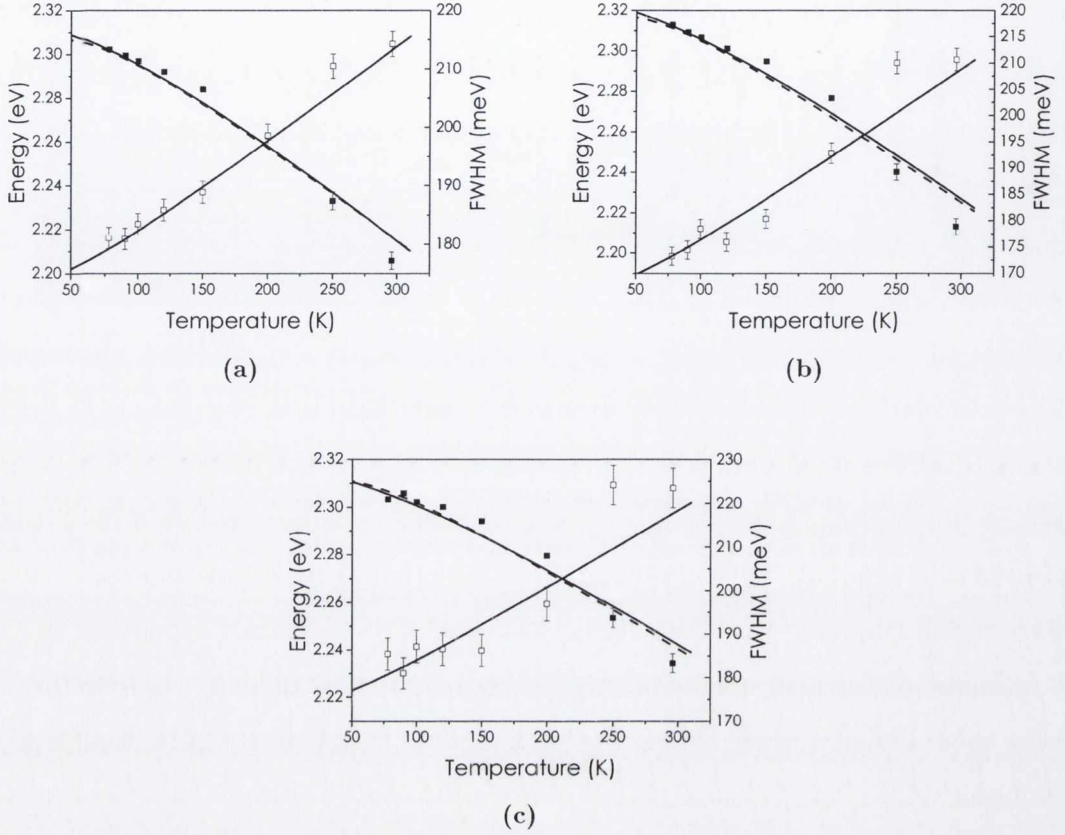


Figure 4.3: (a) - (c) PL peak energy (full squares, left axis) and FWHM (empty squares, right axis) as a function of temperature for QD1 with increasing concentration from (a) to (c). For the peak PL energy the solid lines and dashes are best-fit curves for Equations (2.33) and (2.34) respectively. For the FWHM the solid lines are best fit curves for Equation (2.32).

the band-gap and excitonic peak broadening in bulk semiconductors [161,162,173]. The temperature dependence of the FWHM, is described by Equation (2.32), reproduced here.

$$\text{FWHM}(T) = \Gamma_{inh} + \sigma T + \Gamma_{LO} [\exp(E_{LO}/k_B T) - 1]^{-1} \quad (2.32)$$

where Γ_{inh} is the temperature independent inhomogeneous broadening (due to QD size, shape, etc), σ is an exciton-acoustic phonon coupling constant, and Γ_{LO} represents the exciton-LO phonons coupling coefficient.

It is found that the FWHM can be fitted by Equation (2.32) using a single value of

4. Temperature Dependence of Quantum Dot Monolayers with Varying Concentration

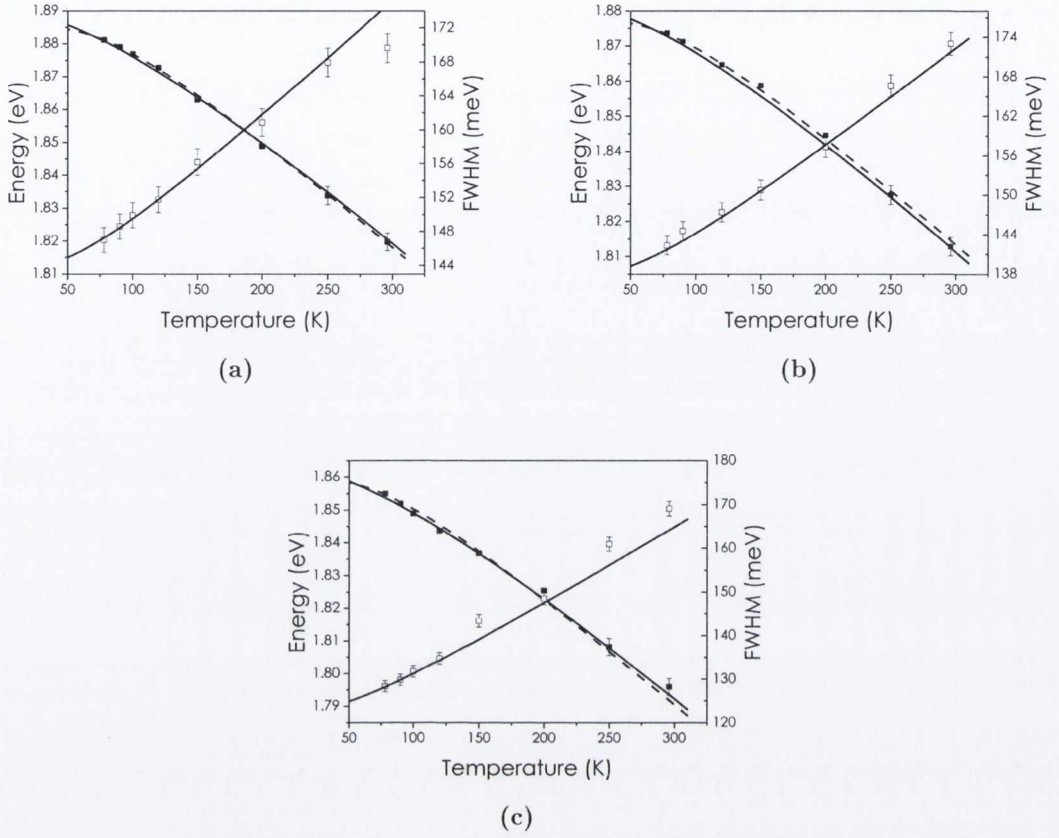


Figure 4.4: (a) - (c) PL peak energy (full squares, left axis) and FWHM (empty squares, right axis) as a function of temperature for QD2 with increasing concentration from (a) to (c). For the peak PL energy the solid lines and dashes are best-fit curves for Equations (2.33) and (2.34) respectively. For the FWHM the solid lines are best fit curves for Equation (2.32).

E_{LO} for each QD, suggesting that the temperature dependence of is dominated by the influence of carrier trapping. $E_{LO} = (18 \pm 5)$ meV for QD1 and $E_{LO} = (20 \pm 3)$ meV for QD2. The other fitting parameters in this case give $\sigma = (90 \pm 10)$ $\mu\text{eV/K}$ for QD1 and $\sigma = (60 \pm 10)$ $\mu\text{eV/K}$ for QD2. This value of σ is much larger than the estimated value for bulk CdTe due to quantum confinement [161, 173]. The increase of σ with decreasing QD size is in qualitative agreement with the increase of acoustic phonon coupling with increasing confinement in CdTe quantum wells [197]. Similarly, the value for Γ_{LO} found for QD2 ($\Gamma_{LO} = (20 \pm 3)$ meV) is in agreement with that reported by Morello *et al.* [173], and for the smaller QD1 we find $\Gamma_{LO} = (18 \pm 5)$ meV, which agrees within error. These values are smaller than the theoretical bulk value (24.5 meV) due to quantum confinement [173, 198].

4. Temperature Dependence of Quantum Dot Monolayers with Varying Concentration

The experimental data for the peak position of the PL emission can be fitted with the Varshni relation [175] which is shown in Equation (2.34) and reproduced here.

$$E_g(T) = E_g(0) - \alpha \frac{T^2}{T + \beta} \quad (2.34)$$

where $E_g(0)$ is the energy gap at 0 K, α is the temperature coefficient, the value of β is close to the Debye temperature of the material. To fit β is fixed at the bulk value of 158 K [173] and find a best fit value for α , yielding $\alpha = (4.6 \pm 0.8) \times 10^{-4}$ eV/K and $\alpha = (3.5 \pm 0.2) \times 10^{-4}$ eV/K, for QD1 and QD2, respectively. For QD2 this is close to the bulk value (3×10^{-4} eV/K) and also consistent with previously reported values for CdTe QDs [173]. QD1 is slightly larger with greater variation, however, this is still relatively close to the bulk value.

To further confirm the average value of E_{LO} the PL emission peak as a function of temperature can be fitted with a Equation (2.33) which was first proposed by O'Donnell and Chen [174]. This is shown here again for convenience

$$E_g(T) = E_g(0) - S \langle E_{LO} \rangle [\coth(\langle E_{LO} \rangle / 2k_B T) - 1] \quad (2.33)$$

in which S is a dimensionless coupling constant known as the Huang-Rhys parameter and $\langle E_{LO} \rangle$ is the average phonon energy. In this case fits can be obtained for for QD1 $\langle E_{LO} \rangle = (18 \pm 5)$ meV, $S = 2.6 \pm 0.3$ and for QD2 $\langle E_{LO} \rangle = (20 \pm 3)$ meV, $S = 1.9 \pm 0.1$, which is in agreement with what is obtained from fitting the FWHM. The decreasing value of S with increasing size is in qualitative agreement with results presented previously on CdTe [199]. Since the values of E_{LO} are the same within error for the two QDs all fitting using this parameter will be done with a single value of 20 meV.

It is interesting to note that the temperature dependent properties of the PL spectra could be fit without any consideration of a temperature dependent intra-energy transfer or exciton migration between the QDs within a monolayer. This suggests that it is not a dominant factor in the temperature dependent spectral properties of an individual QD monolayer and that it is not manifesting as a strong effect on the temperature

dependence as the QD concentration is increased. Intra-energy transfer within QD ensembles, including QD monolayers has been well studied [83, 195, 200]. A spectral feature of intra-energy transfer is red-shifting of the PL spectrum with increasing QD concentration. Only a relatively small red-shift is observed as the QD concentration is increased, Figures 4.3 and 4.4, for both QDs. Intra-energy transfer manifests in spectrally resolved TRPL measurements showing a shortening of the PL decay rate on the high energy side of the spectrum, with corresponding increase on the low energy side. However, in this study the temperature time-resolved measurements are not spectrally resolved and therefore, the measured decay rate represents an average for the entire ensemble.

The temperature dependence of the PL intensity can be described by [173]

$$I_{PL}(T) = \frac{I_0}{1 + a [\exp(-E_a/k_B T)] + b [\exp(E_{LO}/k_B T) - 1]^{-q}} \quad (4.1)$$

where I_0 is the 0 K integrated PL intensity, q is the number of LO phonons involved in thermal escape of carriers, E_{LO} is their energy. E_a is the activation energy. The trends of the PL intensity at temperatures lower than 77 K can give insight into the nature of the activation energy. It has been attributed to thermally activated transfer from the dark exciton state to the bright state [159] when coupled with a blue shift and an increase in the intensity. Many other reports have found a value of E_a much larger than the bright-dark splitting energy and have thus attributed it to trapping at surface/interface defect states [161, 173, 199]. Such attributions are beyond the scope of this work, as the focus is on the effect of carrier trapping at temperatures above 150 K. It should be noted, that using the value of E_{LO} extracted from the FWHM and peak energy fitting, in conjunction with a value of $E_a = \Delta E$ corresponding to the bright-dark splitting energy (utilised in the fitting of the decay rates) it is possible to fit the measured data for the PL intensity. However, as these measurements are taken down to approximately 77 K and not towards 0 K it is impossible to clearly determine a value of I_0 , therefore the FWHM and peak energy fitting will be the focus for extracting the appropriate parameters.

4.3 Fluorescence Lifetimes and Decay Rates

This section will consider the temperature dependence of the QD lifetimes and decay rates. Using the analytical model described in Section 2.6.1 it will be shown that is important to consider both bright and dark states and at high temperatures (> 150 K) it is vital to consider carrier trapping. Schematics of the models are shown in Figures 2.6 and 2.7 and are reproduced here for convenience.

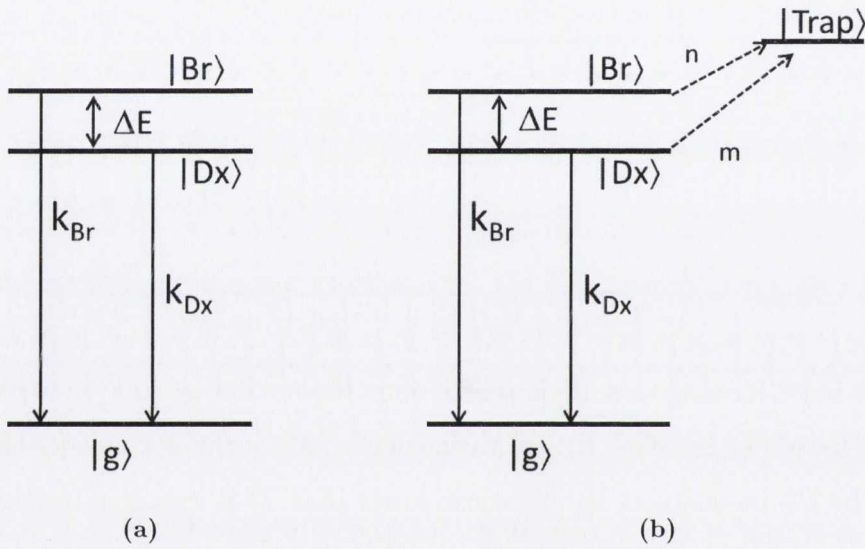


Figure 4.5: (a) Schematic of the analytic model with ground state, $|g\rangle$, dark state, $|Dx\rangle$ with decay rate k_{Dx} , and the bright state, $|Br\rangle$, with decay rate k_{Br} . (b) Schematic of the extended analytic model with ground state, $|g\rangle$, dark state, $|Dx\rangle$ with decay rate k_{Dx} , and the bright state, $|Br\rangle$, with decay rate k_{Br} . Additionally, there is an external trap state, $|Trap\rangle$. n and m are the number of phonons that will be required to interact with the trap state for the bright and dark state, respectively.

Figure 4.6 shows PL decays for the highest QD concentration monolayers for each QD, QD1c3 (shown in green) and QD2c3 (shown in red), at 296 K (lines) and 77 K (dots). The PL lifetime increases at the lower temperature, as is well documented [159, 160, 163, 164, 168, 201]. The decay is fitted with a bi-exponential decay and the average lifetime is determined from Equation (3.8) on page 51, shown again here.

$$\tau_{av} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2} \quad (3.8)$$

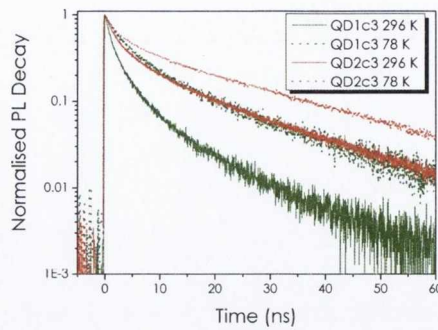


Figure 4.6: Normalised PL decays at room (≈ 296 K) and low (≈ 77 K) temperature for QD1 (green lines and dots, respectively) and QD2 (red lines and dots, respectively). The PL shown are from the highest QD concentration monolayers for both QDs, denoted c3. The average lifetime obtained from fitting the decays are $\tau(296 \text{ K})\text{QD1c3} = (6.0 \pm 0.2)$ ns and $\tau(77 \text{ K})\text{QD1c3} = (13.5 \pm 0.2)$ ns. $\tau(296 \text{ K})\text{QD2c3} = (14.4 \pm 0.5)$ ns and $\tau(77 \text{ K})\text{QD2c3} = (20.9 \pm 0.5)$ ns. See also Table 4.1.

A summary of the average lifetimes extracted from the decays shown in Figure 4.6 is given in Table 4.1. The average decay rate, $k_{QD} = \tau_{QD}^{-1}$ can be determined from the PL decays at each temperature.

	QD1	QD2
$\tau(296 \text{ K})$	$(6.0 \pm 0.2) \text{ ns}$	$(14.4 \pm 0.5) \text{ ns}$
$\tau(77 \text{ K})$	$(13.5 \pm 0.2) \text{ ns}$	$(20.9 \pm 0.5) \text{ ns}$

Table 4.1: Summary of the average lifetimes at 296 K and 77 K for QD1c3 and QD2c3.

Figure 4.7 shows the temperature dependence of the decay rate for monolayers of both QDs with the three QD concentrations, the arrow indicating direction of increasing concentration. As expected the decay rate increases as the temperature increases over the entire measured range, for both QDs, the rate also seems to increase more sharply at higher temperatures for higher concentrations.

To fit this data the analytic model presented in Section 2.6.1 is utilised in the low temperature regime (< 150 K). First considering the situation of no thermally activated carrier trapping, the schematic of the model is given in Figure 4.5a, and the ultimate equation to use is Equation (2.26) which is

4. Temperature Dependence of Quantum Dot Monolayers with Varying Concentration

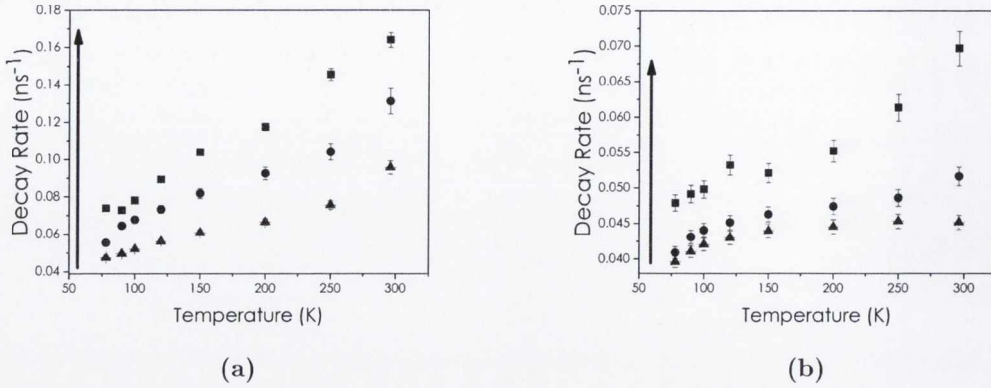


Figure 4.7: Temperature dependence of decay rate for monolayers of varying QD concentration c1-c3 (a) QD1 and (b) QD2. The arrow indicates the direction of increasing concentration, triangles for c1, circles for c2, squares for c3.

$$k_{QD}(T) = \frac{k_{Dx} + k_{Br} \exp(-\Delta E/k_B T)}{1 + \exp(-\Delta E/k_B T)} \quad (2.26)$$

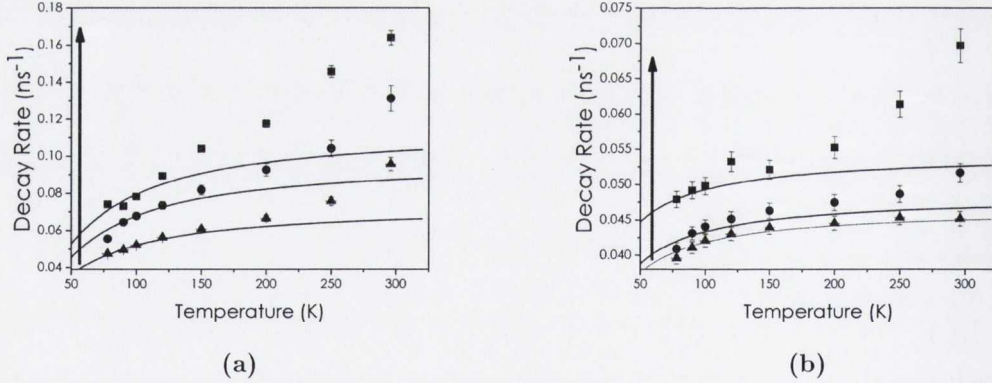


Figure 4.8: Temperature dependence of decay rate for monolayers of varying QD concentration c1-c3 (a) QD1 and (b) QD2. The arrow indicate the direction of increasing concentration. The solid lines are fits to Equation (2.26).

The fitting parameters for the initial fitting without considering traps are shown in Table 4.2, this corresponds to the solid lines shown in Figure 4.8. The value of ΔE extracted from these fits is of the order of those previously reported [166,167]. It also decreases with increasing QD size which again is in agreement with previous reports [160,166–168]. The value of k_{Br} is seen to increase with increasing concentration for both QDs and is larger for QD1 compared to QD2, agreeing with what is seen

in the experimental data. The value of k_{Dx} is relatively static for both QDs. It is obvious, however, particularly for QD1, that this model is incomplete as it does not fit the data well at higher temperatures, especially for the higher QD concentrations where the discrepancy is largest. The above model does not consider external traps which are known to strongly influence the PL emission of QDs at higher temperatures [159–162, 173, 202]. If the discrepancy between the model and data is accounted for by this additional non-radiative recombination path, then the data indicates that at higher temperatures non-radiative recombination and carrier trapping is much more dominant for samples with higher concentrations.

	k_{Br}	k_{Dx}	ΔE
QD1	$\pm 4\%$	$\pm 10\%$	$\pm 7\%$
c1	0.128 ns^{-1}	0.019 ns^{-1}	7 meV
c2	0.175 ns^{-1}	0.020 ns^{-1}	7 meV
c3	0.208 ns^{-1}	0.022 ns^{-1}	7 meV
QD2	$\pm 3\%$	$\pm 6\%$	$\pm 13\%$
c1	0.068 ns^{-1}	0.025 ns^{-1}	4 meV
c2	0.070 ns^{-1}	0.026 ns^{-1}	4 meV
c3	0.076 ns^{-1}	0.032 ns^{-1}	4 meV

Table 4.2: Fit parameters for the decay rate versus temperature based on Equation (2.26) and shown in Figure 4.8.

Qualitatively this can be attributed to an increase in the density of available traps, where either a single QD can effectively “see” defects or traps associated with other QDs nearby or the close proximity of QDs may lead to the formation of additional defects. With this in mind comparing the two QDs is interesting as the lowest concentration of QD2 fits very well with equation (2.26) over the whole temperature range while there is still significant discrepancy for QD1. The defect concentration has a strong influence on the optical properties of nanocrystals and smaller QDs typically exhibit lower QYs [194]. The smaller QD1 has a relatively higher surface to volume ratio, and there is a higher concentration of defects at the surface, giving rise to a higher density of mid-gap states acting as carrier traps. In addition the lowest concentration studied for QD1 is approximately six times greater than the lowest concentration for

4. Temperature Dependence of Quantum Dot Monolayers with Varying Concentration

QD2. In fact the highest concentration measured for QD2 is actually comparable to the lowest concentration measured for QD1. Therefore, despite the fact that the diameter of QD2 is significantly larger than QD1 the average separation of QDs for the lowest concentration, QD2c1, monolayer is greater. As discussed above this could contribute to a lower density of defects being available for non-radiative recombination for this sample.

To consider the role of such trapping in more detail the three level model is extended. This is discussed in Section 2.6.1 and the schematic detailing this extension is shown in Figure 4.5b. This model gives

$$k_{QD}(T) = \frac{ak_{Br} + k_{Dx} + k_0 [a(b-1)^{-n} + (b-1)^{-m}]}{1+a} \quad (2.31)$$

where $a = \exp(-\Delta E/k_B T)$ and $b = \exp(E_{ph}/k_B T)$, additionally $\Delta E = (m-n)E_{ph}$.

E_{ph} can be attributed to the average LO phonon energy of 20 meV calculated from the steady-state PL in Section 4.2. The other initial parameters are taken from the earlier fitting using equation (2.26), which was able to fit the low temperature data for both QDs at all concentrations. As can be seen from Figure 4.9, incorporating thermally activated carrier trapping allows for the reproduction of the data to an excellent degree.

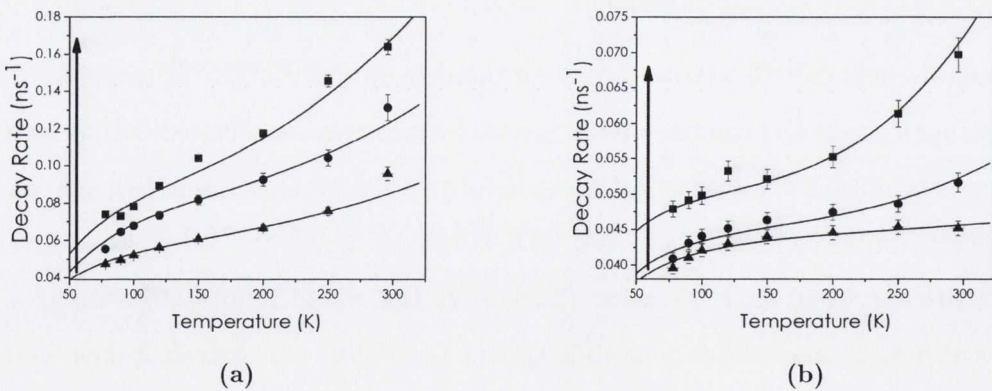


Figure 4.9: Temperature dependence of the decay rate for monolayers of varying QD concentration c1-c3 (a) QD1 and (b) QD2. The arrow indicate the direction of increasing concentration. The solid lines are fits to Equation (2.31).

All fitting parameters are shown in Table 4.3, the parameters k_{Br} , k_{Dx} , and ΔE taken

	k_{Br}	k_{Dx}	ΔE	E_{LO}	k_0	m	n
QD1					$\pm 9\%$	± 0.05	± 0.05
c1	0.128 ns^{-1}	0.019 ns^{-1}	7 meV	20 meV	0.03 ns^{-1}	2.2	1.85
c2	0.175 ns^{-1}	0.020 ns^{-1}	7 meV	20 meV	0.06 ns^{-1}	2.2	1.85
c3	0.208 ns^{-1}	0.022 ns^{-1}	7 meV	20 meV	0.09 ns^{-1}	2.2	1.85
QD2					$\pm 10\%$	± 0.05	± 0.05
c1	0.068 ns^{-1}	0.025 ns^{-1}	4 meV	20 meV	0.001 ns^{-1}	2.8	2.6
c2	0.070 ns^{-1}	0.026 ns^{-1}	4 meV	20 meV	0.009 ns^{-1}	2.8	2.6
c3	0.076 ns^{-1}	0.032 ns^{-1}	4 meV	20 meV	0.03 ns^{-1}	2.8	2.6

Table 4.3: Fit parameters for decay rate based on Equation (2.31) and shown in Figure 4.9.

from Table 4.2 are held fixed in this fitting, and therefore k_0 , m , and n are used as fitting parameters. This shows that the decay rates which prove accurate for fitting at the low end of the temperature range remain unchanged when introducing thermally activated carrier trapping, and that including this trapping accounts for all the discrepancy between the data and the model presented in Equation (2.26) at the higher temperatures. This further indicates that thermally activated carrier trapping is the dominant feature at higher temperatures. Focusing on the efficiency of the thermally induced non-radiative relaxation to trap states, k_0 , it can be seen that it is larger for QD1 and for both QDs increases as concentration increases. The larger k_0 for QD1, is in agreement with the higher defect density expected from smaller QDs, as discussed above, and the observation that the disparity between the data and the simple three level model (equation (2.26)), is greatest for QD1. This trend of k_0 demonstrates the increased efficiency of thermally activated carrier trapping QD monolayers as concentration is increased. One possible mechanism for this increased efficiency would be intra-energy transfer; at the higher monolayer concentrations the QDs are sufficiently close to transfer energy to nearby QDs. A single QD can decay radiatively, have interactions with a trap, or transfer energy to excite a nearby QD. This second QD can then also decay radiatively, interact with a trap, or transfer energy. Thus, effectively, the first QD has more opportunity to interact with traps. Information about intra-energy transfer is masked in an ensemble measurement and in order to truly investigate this one would have to spectrally filter the emission. Quantifying the intra-energy transfer

is done by monitoring the decrease in lifetime on the blue side of the emission, and the corresponding increase on the red side [83].

4.4 Conclusion

The temperature dependence of the emission decay rates of CdTe QD monolayers with varying concentration have been investigated utilising both steady-state PL and TRPL measurements. The steady-state PL properties can be explained by well-known equations and are used to extract information about the average phonon energy. The QD emission decay rate was shown to increase with temperature. The temperature dependence of the decay rate was strongly influenced by the concentration of QDs in the monolayer. The data at all concentrations was found to be well explained with an analytic model involving bright and dark states, which can both interact with a trap state. Thermally activated carrier trapping had to be considered at temperatures > 150 K. Additionally, it has been shown that interactions with these trap states become more pronounced as the concentration of QDs is increased.

Chapter 5

Temperature Dependence of Energy Transfer in Quantum Dot Systems

In this chapter the temperature dependence of the energy transfer process will be discussed. Firstly ET from QDs to AuNPs will be investigated, the two QDs have different degrees of spectral overlap (on and off resonance) with the LSP peak of the AuNP absorption. This is followed by direct QD to QD ET. Both the above situations are in separated bilayer structures. Lastly the temperature dependence of surface plasmon-mediated ET will be briefly discussed. This is achieved in a trilayer, sandwich type structure, where the AuNPs layer is between two layers of QDs.

The analytic model presented in section 2.6.1 can be extended to include ET and is shown to fit the ET from QDs to AuNPs (quenching) reasonably well. However this model proves insufficient to describe the behaviour of QD to QD ET and a completely different behaviour is observed for surface plasmon-enhanced ET. Allowing the bright and dark state decay rates to be free fit parameters produces excellent agreement with the experimental data, but raises the question as to the nature of the ET, and to whether the bright/dark ET rates have an underlying temperature dependence.

5.1 Energy Transfer from Quantum Dots to Au Nanoparticles

This section will focus on the ET from QDs to AuNPs. All structures were prepared using the layer-by-layer (LbL) assembly method as described in Section 3.1.2. QD1 and QD2, described in Section 4.1, are once again used for this study, the PL and absorption spectra are shown in Figure 5.1a. The AuNPs used have a diameter of (5.5 ± 0.1) nm and are stabilized with 4-dimethylaminopyridine (DMAP), which imparts a positive surface charge. Both QDs and AuNPs are water soluble. The LSP resonance of the AuNPs, at 540 nm, is clearly evident in the absorption spectra also shown in Figure 5.1a. Layers of charged polyelectrolyte (PE) are used as spacers to separate the QDs and AuNPs monolayers, to a distance of approximately 3 nm. A schematic of the structure is shown in Figure 5.1b. In this case the concentrations of QD1 and QD2 are $(3.4 \pm 0.3) \times 10^{17} \text{ m}^{-2}$ and $(6.3 \pm 0.3) \times 10^{17} \text{ m}^{-2}$, respectively. For the AuNP samples the immersion time is varied until the AuNP concentration of $(7.5 \pm 0.1) \times 10^{15} \text{ m}^{-2}$ is the same for both samples.

Analytic Model

As shown in Section 2.6.1 the rate equation for the number of excitons in a QD, N , is

$$\frac{dN}{dT} = -(k_{Br} + \kappa_{Br,n})N_{Br} - (k_{Dx} + \kappa_{Dx,m})N_{Dx} = -Nk(T) \quad (2.27)$$

To include ET in this model the ET rate from the bright state ($|Br\rangle$) is denoted by k_{ET}^{Br} and the ET rate from the dark state ($|Dx\rangle$) is denoted by k_{ET}^{Dx} . The rate equation for the total number of excitons should be modified as

$$\frac{dN}{dT} = -(k_{Br} + \kappa_{Br,n} + k_{ET}^{Br})N_{Br} - (k_{Dx} + \kappa_{Dx,m} + k_{ET}^{Dx})N_{Dx} = -Nk_{QD,Acc}(T) \quad (5.1)$$

Solving this equation leads to

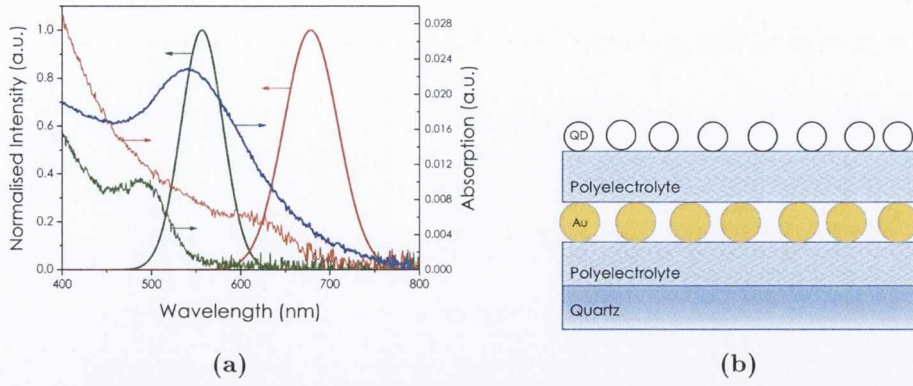


Figure 5.1: (a) Intensity normalized PL spectra (left axis) of QD1 (green lines) and QD2 (red lines) monolayers at room temperature. The absorption spectra of QD1 (right axis, green line), QD2 (right axis, red line), and of the AuNPs (right axis, blue line) is also shown. (b) Schematic of the sample. QDs (white circles) are deposited onto a PE spacer layer of ≈ 3 nm which is on top of the layer of the 5.5 nm diameter AuNPs. A number of PE layers were firstly deposited on the quartz substrate to form a base layer for the QD monolayer deposition. In this case the PE spacer layer thickness is ≈ 3 nm, the concentrations of QD1 and QD2 are $(3.4 \pm 0.3) \times 10^{17} \text{ m}^{-2}$ and $(6.3 \pm 0.3) \times 10^{17} \text{ m}^{-2}$, respectively, and the AuNP concentration is $(7.5 \pm 0.1) \times 10^{15} \text{ m}^{-2}$.

$$k_{QD,Acc}(T) = \frac{k_{Dx} + \kappa_{Dx,m} + k_{ET}^{Dx} + (k_{Br} + \kappa_{Br,m} + k_{ET}^{Br}) \exp(-\Delta E/k_B T)}{1 + \exp(-\Delta E/k_B T)} \quad (5.2)$$

This rate includes both the rate of a QD alone, $k_{QD}(T)$ and the ET rate, $k_{ET}(T)$. Therefore to extract the ET rate, the rate of a QD alone is subtracted from the final rate, $k_{ET}(T) = k_{QD,Acc}(T) - k_{QD}(T)$. Equation (2.30) gives the decay rate for a QD alone, and it is reproduced here for convenience.

$$k_{QD}(T) = \frac{k_{Dx} + \kappa_{Dx,m} + (k_{Br} + \kappa_{Br,m}) \exp(-\Delta E/k_B T)}{1 + \exp(-\Delta E/k_B T)} \quad (2.30)$$

Hence, $k_{ET}(T)$ is given by Equation (5.2) - Equation (2.30), leading to

$$k_{ET}(T) = \frac{k_{ET}^{Dx} + a k_{ET}^{Br}}{1 + a} \quad (5.3)$$

where $a = \exp(-\Delta E/k_B T)$ and $\Delta E = (m - n)E_{ph}$ as before. Interestingly the effect of thermally activated carrier trapping is not presented in this equation, it is accounted

for in the rate of the QD alone, $k_{QD}(T)$, and in the rate for the QD with an acceptor, $k_{QD,Acc}(T)$, and therefore cancels out in the subtraction.

Kim *et al.* [164] set the ratio of the bright and dark ET rates to be equal to the ratio of k_{Br} and k_{Dx} from the fitting of the QD only decay rates, this procedure will be followed initially.

Spectral Overlap

From Figure 5.1a it can be seen that the emission of QD1 overlaps well with the LSP resonance of the AuNPs at 540 nm. QD2 on the other hand sits much further off resonance. In order to quantify this we calculate the spectral overlap, $J(\lambda)$, and the Förster Radius, R_0 , as described in Sections 2.2.1 and 3.2.3. The relevant equations are reproduced here for convenience.

$$J(\lambda) = \int_0^\infty I_D(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda \quad (2.6)$$

$I_D(\lambda)$ is the area normalised donor emission, $\epsilon_A(\lambda)$ is the acceptor extinction. To calculate the extinction spectra from the absorption spectra the extinction coefficient is needed. For the QDs this can be calculated from the diameter [70], see Equations (3.2) and (3.3). This is $(5.18 \pm 0.03) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and $(1.7 \pm 0.03) \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ for QD1 and QD2, respectively. For the AuNPs, the extinction coefficient is calculated from Mie Theory [203] and was taken as $1.1 \times 10^7 \text{ M}^{-1} \text{ cm}^{-1}$ [59].

$$R_0 = 0.0211 \left(\frac{\kappa^2 Q_D}{n^4} \cdot J(\lambda) \right)^{1/6} \quad (2.8)$$

κ is an orientation factor, usually taken to be $2/3$, n is the refractive index, this is calculated using a volume weighted refractive index of the AuNPs ($n = 1.38$), PE ($n = 1.5$), and QDs ($n = 3.4$). QD1-AuNP n is 1.87, QD2-AuNP n is 1.93. This can be used to quantify the degree of interaction between the QDs and the AuNPs and between the two QDs. For QD1-AuNPs $R_0 = (9.3 \pm 0.2) \text{ nm}$, QD2-AuNPs $R_0 = (8.5 \pm 0.2) \text{ nm}$.

The Förster radius is smaller for QD2 interacting with the AuNPs, indicating that the efficiency of ET would also be smaller.

Steady State Photoluminescence

Samples are excited as in Section 4.2. The same temperature dependent trends are also observed, namely; as the temperature is increased the PL intensity decreases, the emission energy red shifts, and the FWHM of the spectra increases. These are shown in Figure 5.2 for QD1 and Figure 5.3 for QD2. The trends are fitted using Equations (2.33) and (2.34) for the peak energy shift, and Equation (2.32) for the FWHM, as they were previously. These are reproduced here for convenience.

$$\text{FWHM}(T) = \Gamma_{inh} + \sigma T + \Gamma_{LO} [\exp(E_{LO}/k_B T) - 1]^{-1} \quad (2.32)$$

$$E_g(T) = E_g(0) - S \langle E_{LO} \rangle [\coth(\langle E_{LO} \rangle / 2k_B T) - 1] \quad (2.33)$$

$$E_g(T) = E_g(0) - \alpha \frac{T^2}{T + \beta} \quad (2.34)$$

The values extracted from the fits for these samples agree well with what was found in Chapter 4 and this is summarised in Table 5.1.

Sample	E_{LO} (meV)	Γ_{LO} (meV)	σ ($\mu\text{eV/K}$)	S	α (eV/K)	β (K)
QD1	18 ± 5	18 ± 5	90 ± 10	2.6 ± 0.3	$(3.5 \pm 0.2) \times 10^4$	158
QD2	20 ± 3	20 ± 4	60 ± 10	1.9 ± 0.2	$(3.5 \pm 0.2) \times 10^4$	158

Table 5.1: Fit parameters extracted from the steady state PL using Equations (2.32) to (2.34).

PL and Lifetime Quenching

The energy decay of an excited donor species occurs with an average lifetime $\tau_D = (k_r + k_{nr})^{-1}$. Introducing an acceptor species with available states in resonance in

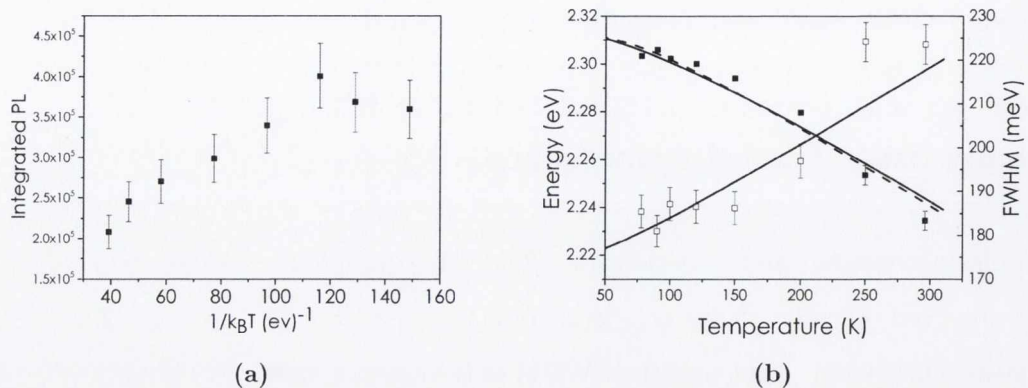


Figure 5.2: (a) Integrated PL for QD1 as a function of temperature. (b) PL peak energy (full squares, left axis) and FWHM (empty squares, right axis) as a function of temperature for QD1. For the peak PL energy the solid lines and dashes are best-fit curves for Equations (2.33) and (2.34) respectively. For the FWHM the solid lines are best fit curves for Equation (2.32).

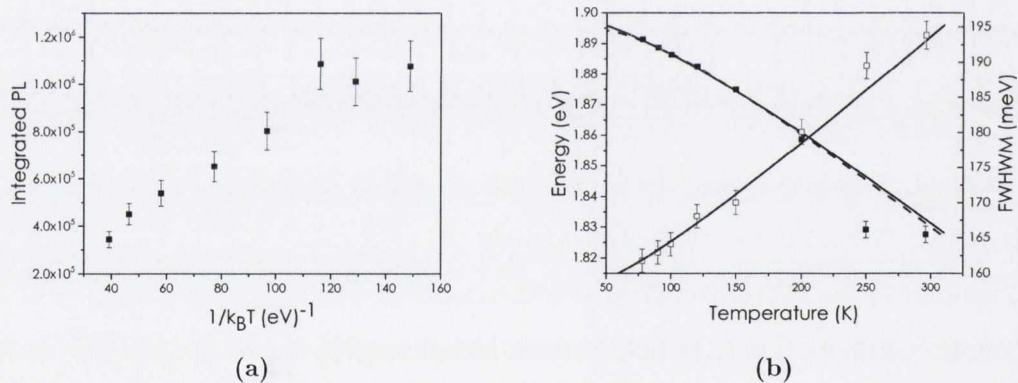


Figure 5.3: (a) Integrated PL for QD2 as a function of temperature. (b) PL peak energy (full squares, left axis) and FWHM (empty squares, right axis) as a function of temperature for QD2. For the peak PL energy the solid lines and dashes are best-fit curves for Equations (2.33) and (2.34) respectively. For the FWHM the solid lines are best fit curves for Equation (2.32).

close proximity means the energy has an additional decay channel, with rate, k_{ET} . Now the average lifetime of the donor in the presence of an acceptor is decreased $\tau_{DA} = (k_r + k_{nr} + k_{ET})^{-1}$. Therefore the signature of ET is a decrease of the donor lifetime and a reduction in it's fluorescence.

All lifetimes quoted are average lifetimes calculated from Equation (3.8), this is because

Sample	296 K (ns)	78 K (ns)
QD1	6.0 ± 0.2	13.5 ± 0.2
QD1-AuNPs	2.9 ± 0.3	6.9 ± 0.3
QD2	11.7 ± 0.2	17.0 ± 0.2
QD2-AuNPs	6.4 ± 0.3	9.8 ± 0.3

Table 5.2: Summary of the average lifetimes extracted from the decays shown in Figures 5.4a and 5.5a calculated using Equation (3.8).

the short and long lifetime components both follow the same trends with temperature and previous work within this group has focused on the average lifetimes, generally seeing good agreement with theory [54–57, 83]. The PL decays for QD1 with and without AuNPs are shown in Figure 5.4a. QD1 monolayer has average decay lifetime at room temperature of (6.0 ± 0.2) ns. In the presence of AuNPs the lifetime is reduced to (2.9 ± 0.3) ns. When the temperature is decreased to 78 K the average decay lifetime of QD1 alone increases to (13.5 ± 0.2) ns, as is well documented [159,160,163,164,168,201], this is due to the increasing fraction of the decay coming from the long lived dark exciton state. There is still quenching at 78 K and the lifetime is reduced to (6.9 ± 0.3) ns in the presence of AuNPs. Further evidence of the ET to the AuNPs is the quenching of the QD emission; this is presented in Figure 5.4b. Emission quenching is clearly visible for both temperatures, giving credence to the assertion that there is ET from the QDs to the AuNPs. Similar evidence of lifetime and PL quenching is found in samples using QD2 and AuNPs, shown in Figure 5.5. A summary of the average lifetimes is also given in Table 5.2.

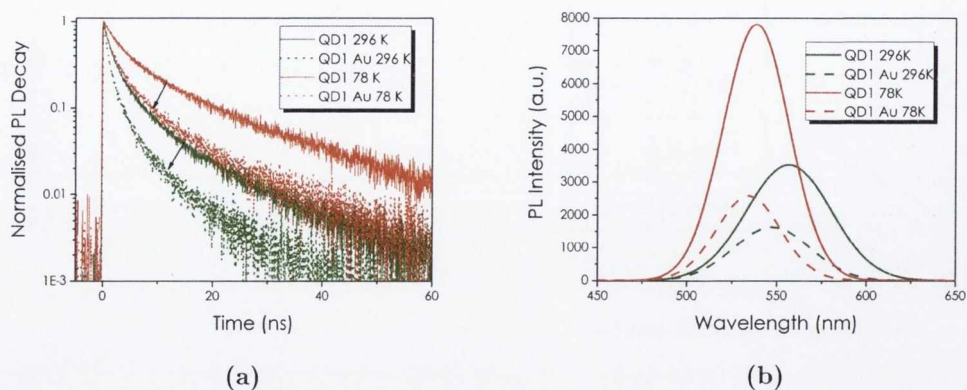


Figure 5.4: (a) Normalized PL decays for QD1 at 296 K (green line), QD1-AuNPs at 296 K (green dots), QD1 at 78 K (red line), and QD1-AuNPs (red dots). The black arrows are a guide indicating the reduction of the lifetime on addition of the AuNPs at 296 K and 78 K (b) PL spectra for the QD1 monolayer at 296 K (green line) and in the bilayer with AuNPs (green dash), and spectra for QD1 monolayer at 78 K (red line) and in the bilayer with AuNPs (red dash).

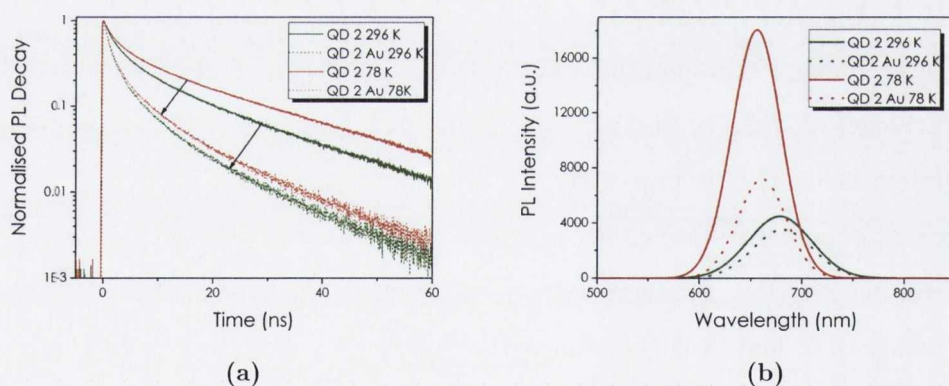


Figure 5.5: (a) Normalized PL decays for QD2 at 296 K (green line), QD2-AuNPs at 296 K (green dots), QD2 at 78 K (red line), and QD2-AuNPs (red dots). The black arrows are a guide indicating the reduction of the lifetime on addition of the AuNPs at 296 K and 78 K (b) PL spectra for the QD2 monolayer at 296 K (green line) and in the bilayer with AuNPs (green dash), and spectra for QD2 monolayer at 78 K (red line) and in the bilayer with AuNPs (red dash).

Decay Rates and Energy Transfer Rates

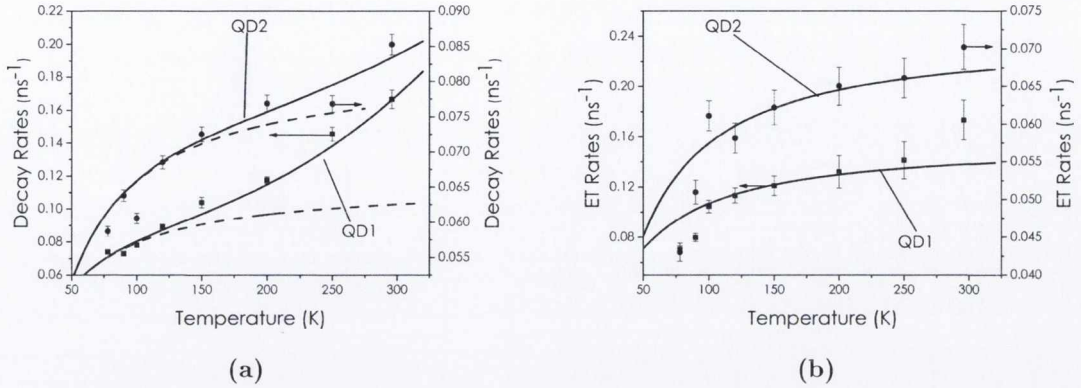


Figure 5.6: (a) Temperature dependence of the decay rates from 78 K to 296 K for QD1 (squares, left axis) and QD2 (circles, right axis). The solid curves are the calculated result using Equation (2.31). The dashed curves represent the analytic model without including interaction with a trap state, Section 2.6.1. (b) Temperature dependence of the ET rates from 78 K to 296 K for QD1-AuNPs (squares, left axis) and QD2-AuNPs (circles, right axis). Solid curves are the calculated result using Equation (5.3).

Figure 5.6a shows the temperature dependence of the average decay rate for the two QD monolayers. The decay rate increases as the temperature increases over the entire measured range for both QDs. The decay rates of QD1 are much faster than QD2. This is fitted using Equation (2.31) in the exact same manner as for Chapter 4. The low temperature (< 150 K) range is first fitted with the model excluding carrier trapping (Equation 2.26). The extracted parameters are then used in Equation (2.31) with the value of E_{LO} determined from the steady state PL.

Figure 5.6b gives the measured temperature dependence of the ET rates for samples QD1-AuNPs and QD2-AuNPs. Both increase with increasing temperature, but for QD1-AuNPs, the on resonance case, the ET rate is faster. In the FRET model the ET rate is proportional to the decay rate of the donor and the spectral overlap. For QD1 the decay rate and the spectral overlap is much larger than in QD2, leading to a larger ET rate, this also agrees with the fact that R_0 is larger for QD1-AuNPs.

Equation (5.3) is used to fit the experimental ET rates. As mentioned above the ratio of k_{ET}^{Br} and k_{ET}^{Dx} is set equal to the ratio of k_{Br} and k_{Dx} determined from the fitting of the decay rate of the QD alone. k_{ET}^{Br} is then used as a fitting parameter and k_{ET}^{Dx} is

determined from this ratio. The other parameters from the fit of the QD alone, such as ΔE , E_{LO} and m-n, are left unchanged. This model produces a reasonable fit to the measured data over the full temperature range. However, there appears to be some deviation from the model at the extremes of the measured range particularly for QD1. A summary of the fitting parameters is given in Table 5.3, the extracted value of k_{ET}^{Br} for QD1-AuNP is much larger than for QD2-AuNPs, which is to be expected from the raw data and from spectral overlap arguments, while the values of k_{ET}^{Dx} are comparable.

Sample	k_{Br} / k_{Dx}	ΔE	E_{LO}	m-n	k_{ET}^{Br}	k_{ET}^{Dx}
QD1	9.65	7 meV	20 meV	0.35	0.28 ns ⁻¹	0.029 ns ⁻¹
QD2	5.45	5 meV	20 meV	0.25	0.123 ns ⁻¹	0.022 ns ⁻¹

Table 5.3: Fit parameters for ET rate based on Equation (5.3) and shown in Figure 5.6b.

5.2 Energy Transfer between Quantum Dot Bilayers

In this section ET between the two QDs, QD1 and QD2, will be discussed. For clarity in this section to distinguish the monolayer reference samples they shall be referred to as QD-D (QD donor) and QD-A (QD acceptor). To refer to the donor QD in the bilayer it shall be denoted QD-DA, and to refer to the acceptor in the bilayer it shall be denoted QD-AD. A schematic of the structure is shown in Figure 5.7, and the PL and absorption spectra of the samples have already been shown in Figure 5.1a.

The Förster radius for the two QDs can be calculated using Equations (2.6) and (2.8). In this case $R_0 = (4.4 \pm 0.3)$ nm.

Steady State Photoluminescence

Yet again the steady state PL is used to extract the value of E_{LO} . Figure 5.8 shows the integrated PL, peak energy, and FWHM variation with temperature for the donor reference, QD-D. A value of (20 ± 4) meV is determined for E_{LO} , in agreement with previous samples. The additional fitting parameters; $\Gamma_{LO} = (18 \pm 4)$ meV, $\sigma = (75 \pm$

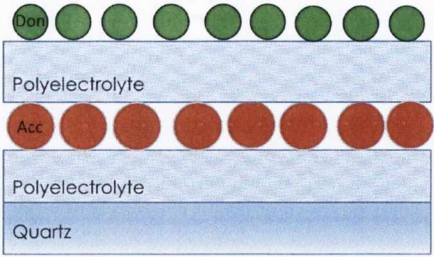


Figure 5.7: Schematic of the QD-QD bilayer sample. A number of PE layers were firstly deposited on the quartz substrate to form a base layer for the QD monolayer deposition. Donor QDs (green circles) are deposited on PE spacer ≈ 3 nm away from acceptor QDs (red circles). The concentrations of QD1 and QD2 are $(2.0 \pm 0.3) \times 10^{17} \text{ m}^{-2}$ and $(6.3 \pm 0.3) \times 10^{17} \text{ m}^{-2}$, respectively.

10) $\mu\text{eV/K}$, $S = 2.3 \pm 0.3$, $\alpha = 3.8 \times 10^4 \text{ eV/K}$; all agree quite well with previous measurements of this QD.

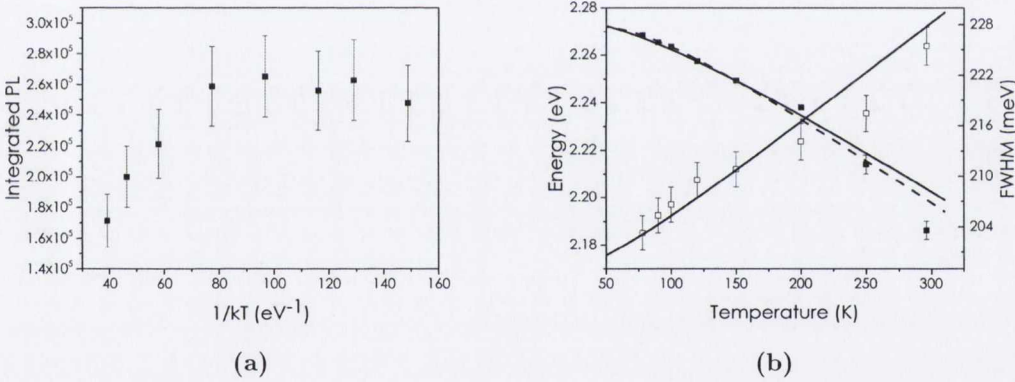


Figure 5.8: (a) Integrated PL for QD-D as a function of temperature with increasing concentration. (b) PL peak energy (full squares, left axis) and FWHM (empty squares, right axis) as a function of temperature for QD-D. For the peak PL energy the solid lines and dashes are best-fit curves for Equations (2.33) and (2.34) respectively. For the FWHM the solid lines are best fit curves for Equation (2.32).

PL and Lifetime Quenching

Figure 5.9 shows the lifetime and PL quenching of the donor in the QD-QD bilayer. The average lifetimes extracted from these decays are shown in Table 5.4, clearly evident is the dramatic lifetime quenching at both 296 K and 78 K. This quenching is also evident in the PL spectra. These factors, coupled with the acceptor enhancement visible from the PL signal, give a clear signature of ET between the QDs in a QD-QD bilayer.

Sample	296 K (ns)	78 K (ns)
QD-D	7.7 ± 0.3	16.5 ± 0.5
QD-DA	3.0 ± 0.3	5.0 ± 0.3

Table 5.4: Summary of the average lifetimes extracted from the decays shown in Figure 5.9a calculated using Equation (3.8).

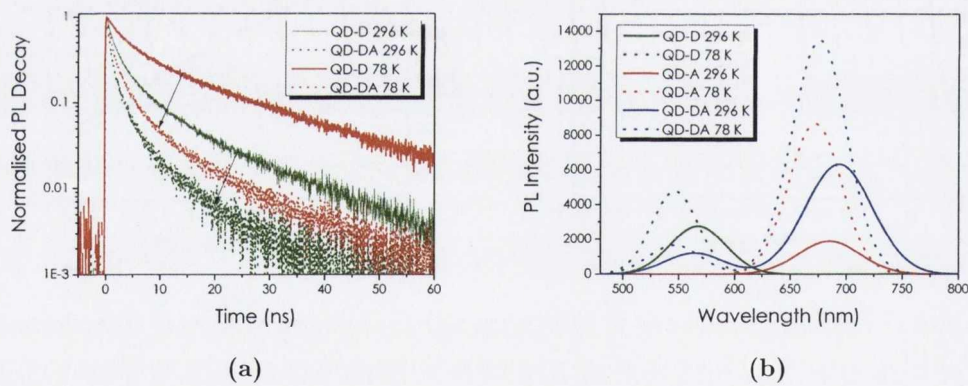


Figure 5.9: (a) Normalized PL decays for QD-D at 296 K (green line), QD-DA at 296 K (green dots), QD-D at 78 K (red line), and QD-DA (red dots). The black arrows are a guide indicating the reduction of the lifetime on addition of the acceptor QDs at 296 K and 78 K (b) PL spectra for the QD-D monolayer at 296 K (green line) and at 78 K (green dash), and spectra for QD-A monolayer at 296 K (red line) and at 78 K (red dash). Also shown is the QD-DA bilayer at 296 K (blue line) and at 78 K (blue dash). Clearly evident is donor PL quenching with acceptor PL enhancement.

Decay Rates and Energy Transfer Rates

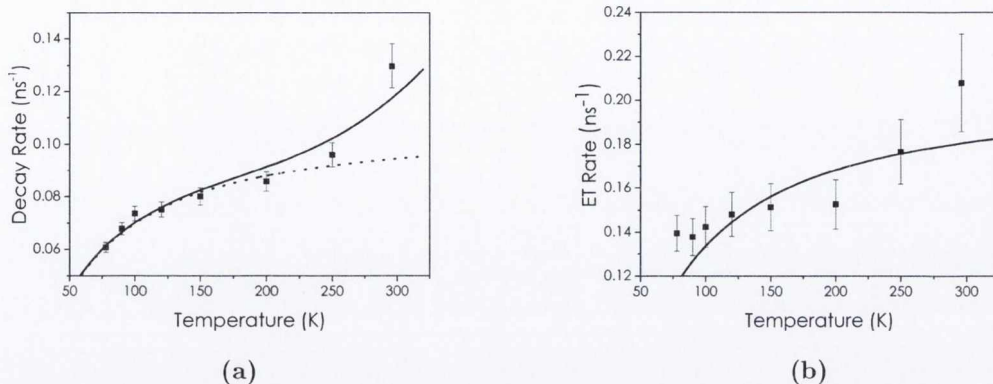


Figure 5.10: (a) Decay rate versus temperature for the QD donor reference, QD-D. Solid line is the best fit curve to Equation (2.31), the dashed line is again represents the model without accounting for trap states. (b) ET rates versus temperature for QD-QD bilayer. In this case the dashed curve is a fit from Equation (5.3).

In this section the analytic model will be applied to ET in the QD-QD bilayer. Figure 5.10a shows the decay rate of the donor reference QD-D. Using the same parameters as before for ΔE and E_{LO} this can be fitted with Equation (2.31), giving $k_{Br} = 0.196 \text{ ns}^{-1}$, $k_{Dx} = 0.02 \text{ ns}^{-1}$, $k_0 = 0.33 \text{ ns}^{-1}$, $\Delta E = 8 \text{ meV}$, $m - n = 0.4$, and $E_{LO} = 20 \text{ meV}$. This is close to the values found for QD1 previously, some fluctuation from sample to sample is expected. The fitting is shown in Figure 5.10a as the solid line, again the dashed line is the fit without considering the traps; as expected the discrepancy is largest at room temperature. The ET rate is calculated from the QD-D rate and the QD-DA rate as before, $k_{ET} = k_{QD-DA} - k_{QD-D}$. This is shown in Figure 5.10b, an attempt at a fit can be made using Equation (5.3) again setting the ratio of the bright and dark ET rates to be equal to the ratio of k_{Br} and k_{Dx} from the decay rate fitting, finding $k_{ET}^{Br} = 0.38 \text{ ns}^{-1}$ and $k_{ET}^{Dx} = 0.04 \text{ ns}^{-1}$.

The solid curve in Figure 5.10b represents this fitting. The fit is reasonable from approximately 90 K up to 150 K, the point at 200 K is completely missed and the fit shows a saturation behaviour at the higher temperatures, similar to the QD-AuNP samples. However it seems that the ET rate is actually increasing further at room temperature and not saturating. Some evidence of this is seen with the QD1-AuNP sample, but is more obvious here.

In order to find a better match with the experimental data, the ratio of the bright and dark rate is allowed to vary. Additionally, the total QD decay rate is fit and the modelled ET rate is extracted in the same manner as the experimental data by subtracting the fit of the QD-D alone from the total decay rate of the QD-DA i.e. $k_{ET} = k_{QD-DA} - k_{QD-D}$.

Figure 5.11a shows the decay rate of the QD donor in the presence of the acceptor, QD-DA. The dashed line is a fit to Equation (5.2) with $k_{Br} = 0.196 \text{ ns}^{-1}$, $k_{Dx} = 0.02 \text{ ns}^{-1}$, $k_0 = 0.03 \text{ ns}^{-1}$, $\Delta E = 8 \text{ meV}$, $m - n = 0.4$, and $E_{LO} = 20 \text{ meV}$, the same as for the QD-D case. $k_{ET}^{Br} = 0.29 \text{ ns}^{-1}$ and $k_{ET}^{Dx} = 0.08 \text{ ns}^{-1}$ are the values extracted for the best fit, however the model clearly underestimates the decay rate at room temperature. The solid line is a fit with the same parameters except k_0 is increased to 0.1 ns^{-1} , providing much better agreement at room temperature. Figure 5.11b shows the corresponding ET rate extracted from the fit of the total decay rate in Figure 5.11a, again the solid line, with the increased value of k_0 is best able to reproduce the data over the full measured range. This increase in k_0 is curious, as it indicates increased trap interaction efficiency. The model has already accounted for the traps present in the donor species via the monolayer reference, however the close proximity of the acceptor QDs could increase the density of traps and/or introduce further traps, or there may be some other mechanism which isn't accounted for in this model. For example the effect of thermally activated carrier trapping falls out of this model when considering ET, however it has been shown that exciton recycling from defect states is possible via ET [9, 31, 204, 205].

Kim *et al.* [164] fixed the ratio of k_{ET}^{Br} and k_{ET}^{Dx} by the ratio of k_{Br} and k_{Dx} . This is because in the FRET model the ET rate is proportional to the initial donor decay rate, $k_{ET} \propto k_{QD}$, $k_{ET}^{Br} \propto k_{Br}$, and $k_{ET}^{Dx} \propto k_{Dx}$. By fixing the ratio the assumption is that the proportionality constants is the same for both bright and dark states. This may not be the case, as the orientation factor, spectral overlap, and QY could be different for the two states. Requiring that the bright and dark state ET rates be free fit parameters could also be indicative of some deeper underlying temperature dependence of these two terms that requires further investigation.

Utilising this new method of allowing the bright and dark ET rates to vary the ET

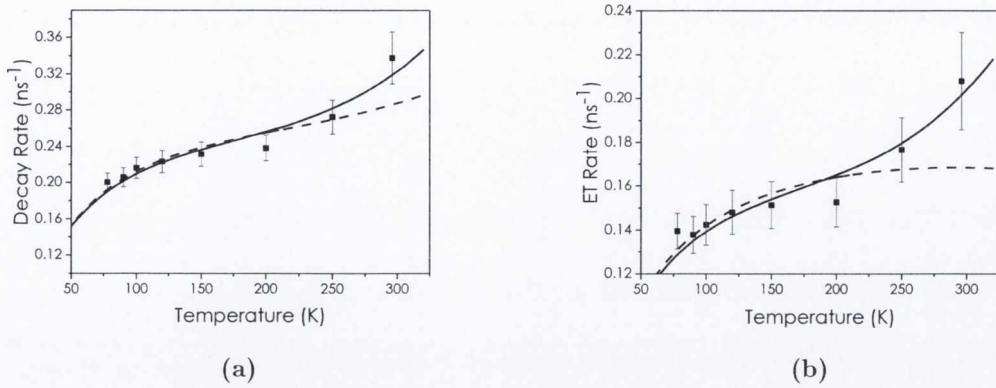


Figure 5.11: (a) Decay rate versus temperature for the QD donor in the presence of the acceptor, QD-DA. Dashed line is the best fit curve to Equation (5.2), the solid line is a fit to the same equation with the value of k_0 increased from the QD-D case. (b) ET rates versus temperature for QD-QD bilayer. In this case the dashed curve is obtained by subtracting the fit of the QD-D from the QD-DA fit. The solid line is the ET rate with the larger value of k_0 .

Sample	k_{Br}	k_{Dx}	ΔE	E_{LO}	m-n	k_0
QD1	0.21 ns ⁻¹	0.02 ns ⁻¹	7meV	20 meV	0.35	0.10 ns ⁻¹
QD2	0.14 ns ⁻¹	0.02 ns ⁻¹	5 meV	20 meV	0.25	0.01 ns ⁻¹

Table 5.5: Fit parameters for total decay rate based on Equation (5.2) and shown in Figure 5.12a.

from QDs to AuNPs can be revisited. Figure 5.12a shows the total decay rates for QD1-AuNPs and QD2-AuNPs, all the parameters are the same as for the QD alone case (Figure 5.6a), these are given in Table 5.5. The best fit gives $k_{ET}^{Br} = 0.34$ ns⁻¹ and $k_{ET}^{Br} = 0.15$ ns⁻¹ for QD1-AuNPs and QD2-AuNPs respectively. k_{ET}^{Dx} approaches zero in both cases. Figure 5.12b shows the extracted ET rate fit for this, as can be seen the match with experimental data is much better at the temperature extremes than the fit presented in Figure 5.6b, this is particularly obvious for QD1 at room temperature.

The fact that k_{ET}^{Dx} approaches zero for the ET between QDs and AuNPs is interesting, and raises several questions. As the dark state is optically passive, it could be expected to play no role in the ET process. Therefore the assumed dark state ET in the QD-QD case could have some other origin, perhaps exciton recycling as previously mentioned. However, recent work involving enhancing the ET rate in magnetic fields has shown

that the dark exciton state does contribute to the ET [206]. If the dark state does normally play a role in the ET process, then the QD-AuNPs could be a special case, in that it somehow inhibits ET from the dark state.

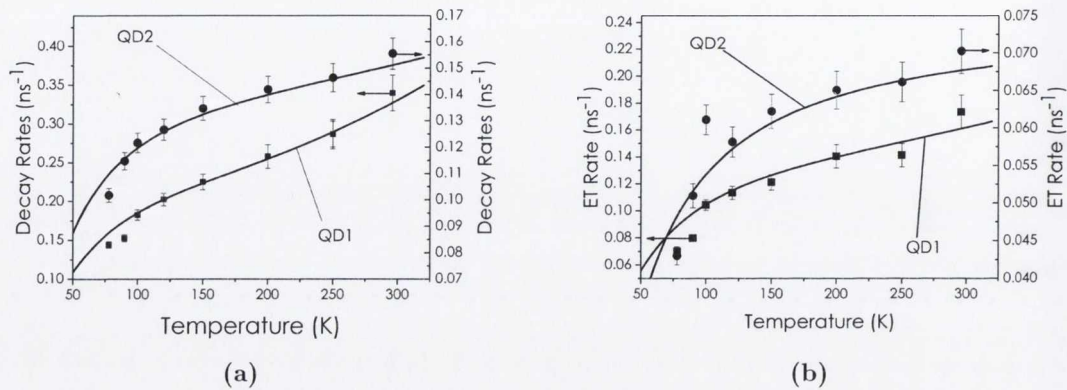


Figure 5.12: (a) Temperature dependence of the decay rates from 78 K to 296 K for QD1-AuNPs (squares, left axis) and QD2-AuNPs (circles, right axis). The solid curves are the calculated result using Equation (5.2). (b) Temperature dependence of the ET rates from 78 K to 296 K for QD1-AuNPs (squares, left axis) and QD2-AuNPs (circles, right axis). Solid curves are the extracted ET rate fits.

5.3 Surface Plasmon-Mediated Energy Transfer

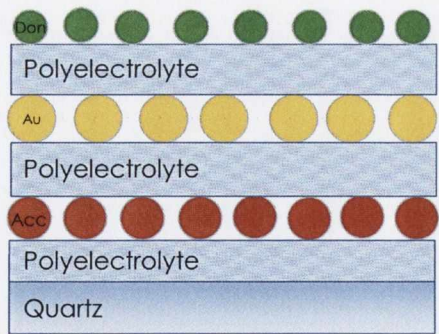


Figure 5.13: Schematic of the full trilayer sample.

This section combines the two previous situations in order to investigate the temperature dependence of surface plasmon-mediated ET in QD systems. A schematic of the sample is shown in Figure 5.13. Acceptor QDs are deposited onto a quartz substrate that has four PE bilayers as a base layer. A 3 nm spacer layer of PE is used to separate

the acceptor QDs and the AuNPs. Above the AuNPs a further 3 nm of PE spacer is used before depositing donor QDs. This puts the total centre to centre distance between the donor and acceptor QDs at 14.5 nm, which is a relatively large distance for FRET. The Förster radius for the pair of QDs was previously calculated as (4.4 ± 0.3) nm which means that the ET between them is non existent at this distance. This is confirmed by observing no change in the donor lifetime in a donor-acceptor bilayer structure with a PE spacer layer thickness of approximately 14 nm.

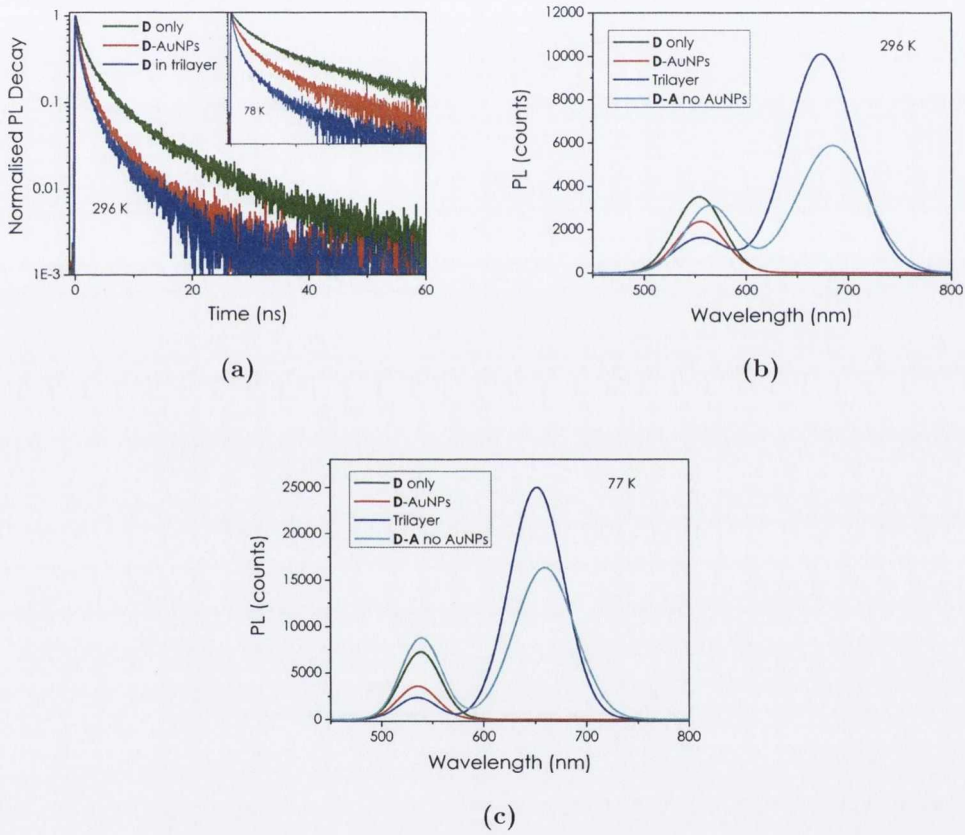


Figure 5.14: (a) Normalised PL decays of the donor only (green), donor in the presence of AuNPs (red), and donor in the trilayer structure with both AuNPs and the acceptor QD (blue), all at 296 K. The inset shows the decays at 77 K. (b) PL spectra at 296 K of the donor alone (green), donor with AuNPs (red), the trilayer structure (blue), and donor and acceptor bilayer with 14 nm spacer (cyan). (c) PL spectra at 77 K with the same colour scheme as for the spectra at 296 K.

Despite this large distance, ET is observed in the trilayer system. Figure 5.14a shows normalised PL decays for the donor reference (green), donor in the presence of AuNPs (red), and the donor in the trilayer (blue). The main graph shows these decays at room

temperature (296 K), the inset shows them at 77 K. Clearly visible is lifetime quenching on the AuNPs, and importantly further quenching in the trilayer structure, indicating surface plasmon-mediated ET. Further evidence of surface plasmon-mediated ET is found in the steady state PL spectra, shown for 296 K in Figure 5.14b, and for 77 K in Figure 5.14c. Clearly visible is successive donor quenching in the presence of the AuNPs and in the trilayer structure, this is coupled with acceptor enhancement in the trilayer structure compared to the bilayer that exhibits no ET.

There is significant evidence, therefore, of surface plasmon-mediated ET in this system at the two temperature extremes, the temperature dependence of this is shown in Figure 5.15a, along with the temperature dependence of the decay rate of the donor alone, and the quenching rate of the donor to AuNPs. Figure 5.15b shows how the surface plasmon-mediated ET rate compares with the direct QD-QD ET rate.

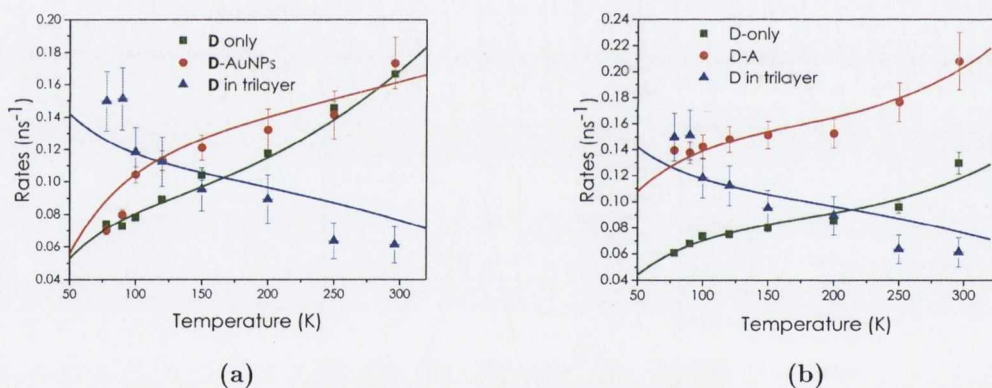


Figure 5.15: (a) Decay rates versus temperature of the donor alone (green squares), quenching rates of the donor to AuNPs versus temperature (red circles), and the surface plasmon-mediated ET rates versus temperature (blue triangles). (b) Decay rates versus temperature of the donor alone (green squares), ET rate versus temperature of the donor to the acceptor (red circles), and the surface plasmon-mediated ET rates versus temperature (blue triangles). The solid lines in both fits represent extracted ET rate fits.

Interestingly the observed trend is completely opposite to what has been seen before for QDs alone, QD-AuNP ET, and QD-QD ET. That is, the surface plasmon-mediated ET rate decreases with increasing temperature. Following the same method as above the total decay rate of the trilayer is fit with Equation (5.2), the values of k_{Br} , k_{Dx} , k_0 , ΔE , $m - n$, and E_{LO} are initialised to the values obtained for the QD1-AuNPs

fitting, see Table 5.5. The best fit gives values of $k_{ET}^{Br} = 0.34 \text{ ns}^{-1}$ and $k_{ET}^{Dx} = 0.17 \text{ ns}^{-1}$, this bright ET rate is comparable with the ET rate between the QDs and AuNPs, while the dark ET is larger than for the QD-QD case. The extracted fit for the surface plasmon-mediated ET rate is shown as the blue lines in Figure 5.15.

One explanation for this trend is that the surface plasmon-mediated ET rate has to compete with the two other rates, quenching by the AuNPs, and the spontaneous emission rate. Therefore when these rates are relatively small, at low temperature the surface plasmon-mediated ET rate can dominate. However as the temperature increases the surface plasmon-mediated ET rate has more competition from the increasing rates and therefore decreases with increasing temperature. It is clear that the temperature dependence of the surface plasmon-mediated ET is a complex process that requires more investigation, particularly at the theoretical level. Kos *et al.* [207] presented an in depth theoretical study into the different regimes of ET between QWs and QDs with a semi-classical approach utilising Fermi's Golden Rule to calculate the radiative transition rates and ET rates. More recently radiative lifetimes of excitons in MoS_2 were investigated [208], again using Fermi's Golden rule (and verified with a many body Green's function approach). Other theoretical work based on a microscopic analysis of the ET mechanism [209], or considering the role of higher multipoles [210] could also be an avenue for further work. Perhaps extending the theoretical formalism presented in those publications could lead to insight into the temperature dependence of ET between QDs.

5.4 Conclusion

The temperature dependence of ET in various QD systems has been investigated. Firstly, the temperature dependence of the ET between on and off resonance QDs and AuNPs. The ET rate was shown to increase with temperature and that the ET rate is highest for the on resonance case. Specific ranges of the experimental data can be explained to a reasonably degree with an analytic model involving bright and dark states which can both interact with a trap state, showing the importance of accounting for thermally activated carrier trapping at temperatures greater than 150 K. This also

extends the validity of this model to QD-AuNPs systems as it has only previously been used to describe QD-QD systems.

The ET rate for a QD-QD bilayer was also shown to increase with temperature, however in this instance it appears to be still increasing at room temperature, rather than reaching a plateau as the model would indicate. This appears to be more pronounced than the QD-AuNPs system. Allowing the bright and dark ET rates to be freely fitted gives a much better match to the experimental data. However there is still some open questions; allowing k_{ET}^{Br} and k_{ET}^{Dx} as free fit parameters leads to the situation where the best fit for the QD-AuNPs case is one where there is little or no ET from the dark state. This is in contrast to the QD-QD case, where ET from the dark state is required to reproduce the data at low temperatures. Further investigation is required to determine if this assumed dark state ET in the QD-QD is actually a manifestation of some other mechanism. For example, exciton recycling which has been observed in several publications where the emission from an acceptor in an ET system is larger than expected, in this case this has been attributed to ET from defect states [9, 31, 204, 205]. Additionally it could be that in AuNPs the QD-AuNP case are somehow inhibiting ET from the dark state. Additionally, in order to reproduce the room temperature ET rate data in the QD-QD case, the value of k_0 , which characterises the efficiency of interactions with thermally activated traps, must be larger than in the QD-D alone case. This seems to suggest that at room temperature the interactions with traps is more efficient in the presence of the acceptor QDs, or that there is a creation of further traps, due to the close proximity of the acceptor QDs.

Finally, it was found that the surface plasmon-mediated ET has the opposite trend and decreases with increasing temperature. One possible explanation is via competing rates, where the surface plasmon-mediated ET dominates when all other rates are relatively low. Further study is required in order to completely characterise this complex system, and to perhaps include the possibility of exciton recycling into this ET model.

Chapter 6

Surface Plasmon-Mediated Energy Transfer from Quantum Dot to Quantum Well

Systems with applications mainly for light harvesting will be the area of study in this chapter. As has been mentioned previously, QDs look promising for developing photovoltaics as they provide the capability to collect sunlight over the full visible spectrum, and into the infrared [2, 3, 36]. Plasmonic MNPs can be used as sub-wavelength scattering elements to trap propagating waves into a thin semiconductor layer. MNPs are also used to increase the effective absorption cross section of semiconductors as sub-wavelength antennas where the plasmonic near-field can be coupled to the semiconductor [152]. This is particularly useful as thin semiconductor layers are desirable, both for reduced cost and electrical transport benefits. Plasmonics could allow for the use of physically thin, but optically thick semiconductor layers.

NRET methods for transfer of solar energy have been demonstrated [6, 8], benefiting from the excellent optical properties, such as the high extinction coefficient, of the QDs and enabling a pathway for coupling this with materials with excellent electrical properties. One route is coupling QDs with QWs, which can be easily contacted for the extraction of generated photocurrent.

QDs will be utilised as an energy donor to non-radiatively transfer energy into epitaxial QWs. QDs have been shown to be efficient energy donors to fluorescent dyes [35], and recently to 2D nanoplatelets [65], transition metal dichalcogenides [66]. MNPs will also be incorporated into the sample as not only can they enhance non-radiative interactions in order to help overcome limitations on the distance of this transfer but, as mentioned above, they have been shown to be useful in light harvesting systems [60,61].

In the first system studied, QDs and AgNPs were dispersed into a PMMA layer together and the distance dependence of the direct and plasmon-mediated ET was investigated by monitoring the QD average lifetime on the three QWs with different barrier thicknesses. The direct QD to QW ET has the characteristic Förster-like distance dependence to a 2D acceptor falling off as d^{-4} , showing that it is the dimensionality of the acceptor that drives the distance dependence, which has previously been theoretically predicted [211]. Following on from this, the first demonstration of surface plasmon-mediated ET from QDs to QWs is presented for the AgNPs dispersed together in a PMMA matrix with QDs. The distance dependence of the surface plasmon-mediated ET to QWs with different barrier thicknesses is also found to follow a d^{-4} distance dependence. In the second system studied, arrays of Ag nanoboxes and nanodiscs were fabricated onto a 3 nm barrier QW sample and again surface plasmon-mediated ET was observed. The AgNP arrays are highly tunable; it is demonstrated that by changing the geometry of the array component from nanodisc to nanobox, it is possible to go from a situation of overall quenching of the acceptor QW emission to one of emission enhancement relative to the QW alone.

6.1 Initial Characterisation

Absorption and PL

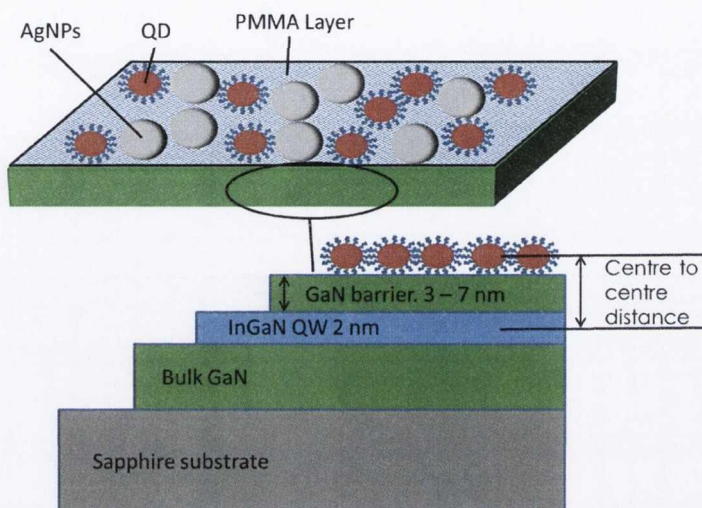


Figure 6.1: Schematic of the QD AgNP sample showing the mixed layer of QDs and AgNPs and the centre-to-centre distance.

Commercial CdSeS/ZnS with a diameter of (6.0 ± 0.5) nm QDs and Ag nanoparticles also with a diameter of (6.0 ± 0.5) nm both dispersed in toluene were obtained from Sigma, and PlasmaChem, respectively. They were then dispersed together with 0.1% w/w solution of PMMA in toluene and spin cast onto MOVPE prepared QWs with differing GaN barrier thickness, a schematic was shown in Figure 3.5 and is reproduced in Figure 6.1 for convenience. The dispersions were made up to 100 μL with 20 μL of QDs, 40 μL AgNPs, and 40 μL of PMMA. This produced a mixed layer of QDs with a thickness of approximately 6 nm; this thickness is confirmed by AFM (Figure 6.2). To produce the reference layers either the QDs or AgNPs were removed and replaced with the same volume of toluene to preserve the same PMMA:sample ratio. For example to produce the QD reference layer 20 μL of QDs, 40 μL of toluene, and 40 μL of PMMA were dispersed together.

Figure 6.3 shows the extinction spectrum of the AgNPs in a PMMA solution and in a layer spun onto a quartz substrate. Clearly in a layer the overall extinction is reduced, the LSP resonance also appears to be broadened, this is indicative of aggregation of

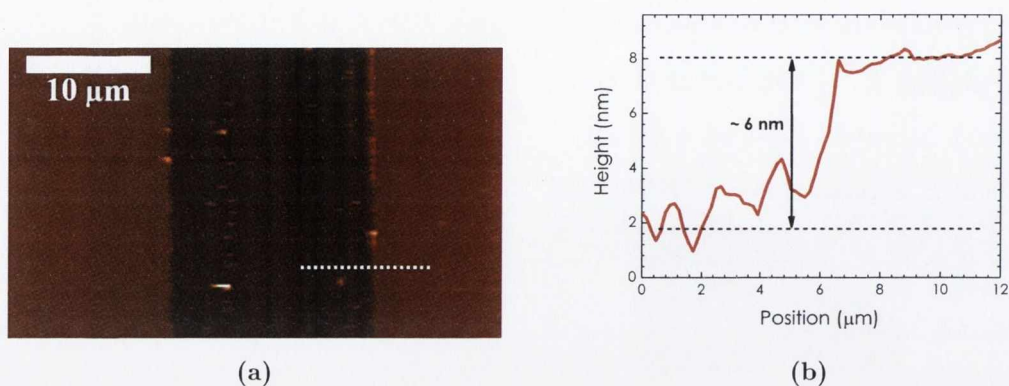


Figure 6.2: AFM of a cut in the QD PMMA layer (b) Measurement of the step height of the layer. AFM measurements were carried out by Robbie O'Connell.

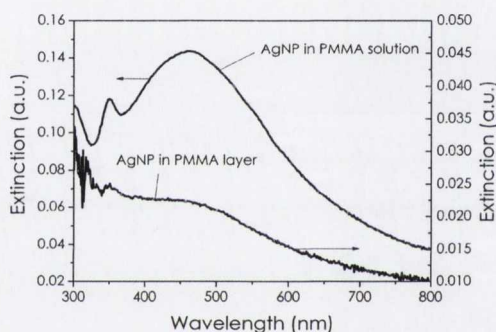


Figure 6.3: Extinction spectrum of AgNPs dispersed in a PMMA solution and in a PMMA layer. In this case the reference layer of AgNPs in PMMA was spun onto quartz.

the AgNPs. To confirm this SEM images of a layer produced from the same solution were taken, only this time spun onto a silicon wafer (to prevent charging during SEM imaging). Clearly visible in Figure 6.4 are large aggregations of AgNPs, up to tens of microns in size, agreeing with what is observed in the absorption spectrum.

A calculation of the concentration of the QDs can be done based on the number of QDs per mg quoted by the manufacturers, this is 1.2×10^{15} . The stock solution is 5 mL at 1 mg/mL, therefore the total number of dots in the stock solution is 6×10^{15} . Aliquots of 20 μL are used for mixing with the PMMA and AgNPs, in each 20 μL of the stock solution there must be 2.4×10^{13} QDs. This aliquot is made up to 100 μL when mixing with the PMMA and AgNPs giving a concentration of 2.4×10^{13} per 100 μL or $2.4 \times 10^{17} \text{ L}^{-1}$. Converting to cubic metres gives a concentration of 2.4×10^{20}

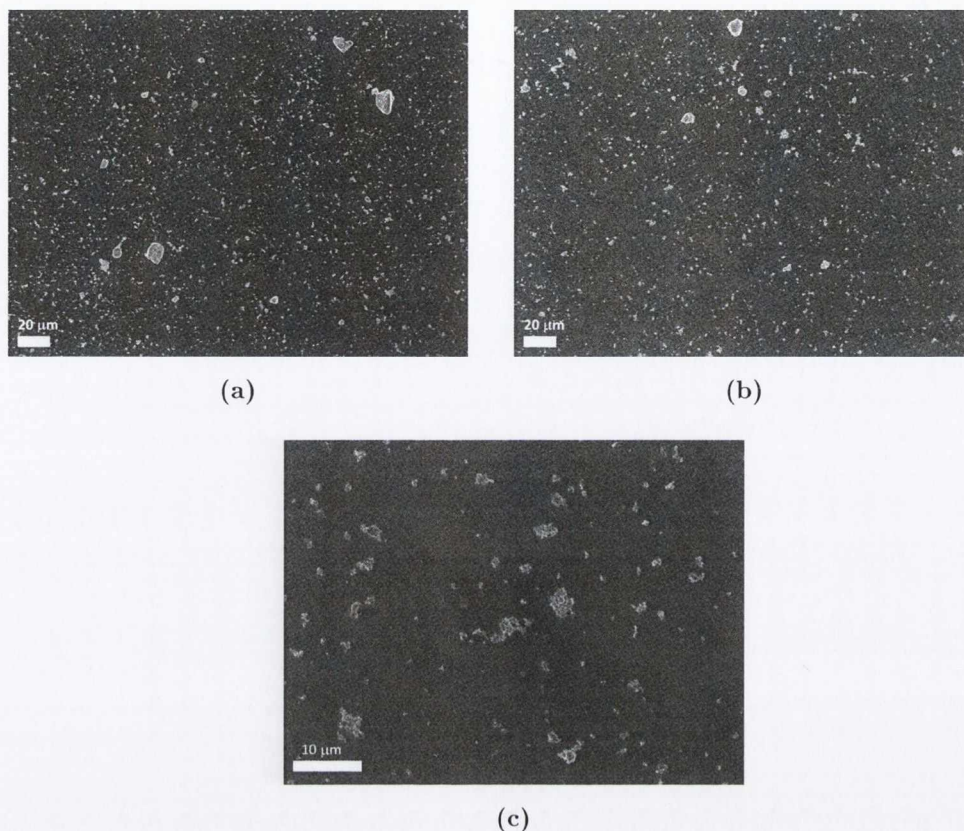


Figure 6.4: SEM images of AgNPs in PMMA layer spun onto a silicon substrate. (a) - (c) are different areas on the same sample. Images taken by Jorge Garcia.

m^{-3} .

The PL spectra of the QDs, and the different QWs are shown in Figure 6.5, also shown is the AgNP extinction to indicate the overlap of the spectra with the LSP peak. The QD PL is centred on 450 nm. The QWs have different centre peaks for the different barrier thicknesses, 530 nm for the 3 nm barrier, 500 nm for the 5 nm barrier, and 510 nm for the 7 nm barrier.

Power Dependences

The dependence of the QD lifetime and PL intensity on excitation power is shown in Figure 6.6. The QD lifetime increases with increasing power (Figure 6.6a), the PL intensity increases linearly with excitation power (Figure 6.6b) ensuring single exciton generation in each QD. The fall off in both the lifetime and PL intensity at high power

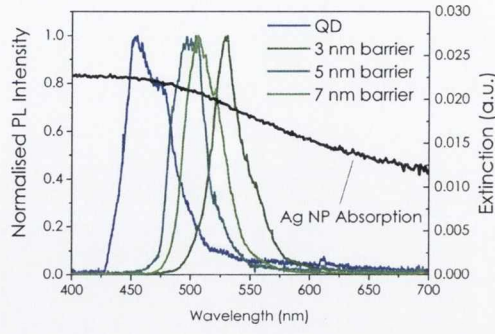


Figure 6.5: PL spectra of the QDs and the 3, 5, and 7 nm barrier QW (left axis). The AgNP extinction is also shown (right axis).

is attributed to the onset of photobleaching.

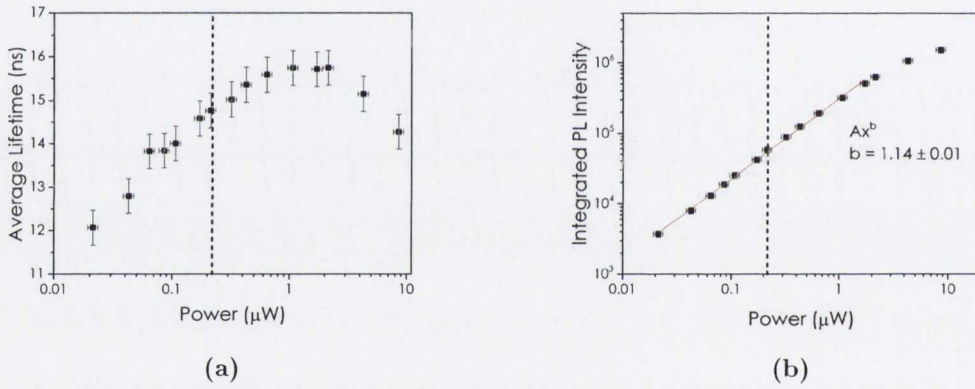


Figure 6.6: (a) Dependence of the QD lifetime on excitation power. Dashed line represents the power at which subsequent measurements were taken. (b) Dependence of the QD integrated PL intensity on excitation power. Solid red line is a fit to a power law with $b = 1.14 \pm 0.01$, i.e. a linear increase with power, ensuring that only single exciton generation in each QD. The dashed line is the power at which subsequent measurements are taken.

The different QWs are also characterised with respect to power, in this case it is possible to calculate the carrier density generated in the QW, n , for a given excitation power, P . This is given by [212]

$$n = \frac{P}{\hbar\omega \cdot S \cdot d_{\text{InGaN}} \cdot \gamma} \cdot e^{-\alpha_{\text{GaN}}d_{\text{GaN}}} \cdot [1 - e^{-\alpha_{\text{InGaN}}d_{\text{InGaN}}}] \cdot (1 - R) \quad (6.1)$$

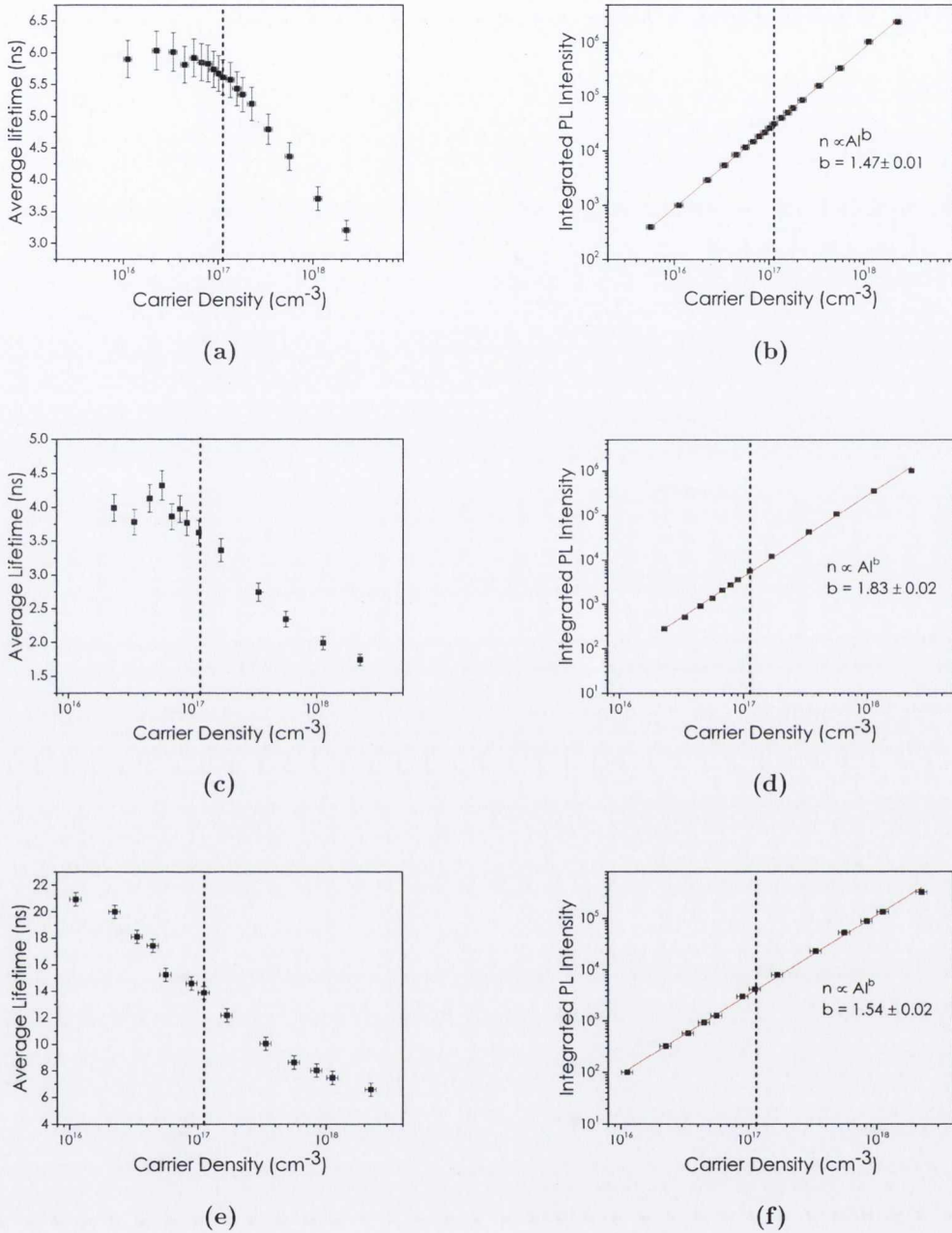


Figure 6.7: Dependence of the QW lifetime on carrier density for the (a) 3 nm, (c) 5 nm , and (e) 7 nm barrier .Dependence of the QW integrated PL intensity on carrier density for the (b) 3 nm, (d) 5 nm, and (f) 7 nm barrier. Solid red line is a fit to a power law. The dashed lines in all the graphs is again the power at which subsequent measurements are taken.

where $\hbar\omega$ is the excitation photon energy, S is the spot size of the pump laser, R is the reflectance of the pump laser at 405 nm, α is the absorption efficiency, d is the thickness of the active QW layer, γ is the repetition rate of the pulsed laser. The

excitation wavelength is 405 nm, therefore $\hbar\omega = 3.1$ eV. This allows for pumping of the InGaN QW only without pumping the GaN (3.4 eV), hence $\alpha_{\text{GaN}} = 0$. $\alpha_{\text{InGaN}} = 10^4$ cm^{-1} [63, 213], $d_{\text{InGaN}} = 2$ nm and $\gamma = 10$ MHz. $S = 0.43$ μm , and $R = 0.15$ [63].

The QW decay lifetime versus the excitation power is determined by complex carrier formation as well as different decay dynamics, such as, the population of free carriers, heavy and light free excitons, and bound excitons [214, 215]. An increase in decay lifetime with power can be attributed to the capture of carriers by defect states [212]. Decreasing decay lifetime with increasing carrier density indicates that the defect states have been saturated and that radiative recombination dominates [207].

The carrier density dependences of the decay lifetime and PL intensity for the 3 different QW barrier thickness are shown in Figure 6.7. Initially the decay lifetime seems static with increasing carrier density for the 3 nm and 5 nm barriers (Figures 6.7a and 6.7c), before decreasing. For the 7 nm barrier QW (Figure 6.7e) the lifetime is always decreasing. The dashed line indicates the power at which subsequent measurements were carried out, this is on the down slope of the decay lifetime trend, where radiative recombination is dominant. To further investigate integrated PL intensity is monitored for increasing carrier density and is fitted with a power law, $n \propto I^b$, with $b = 1.47 \pm 0.01$ for the 3 nm barrier case indicating radiative recombination that is somewhat between exciton and free carrier processes [216, 217].

The 5 nm and 7 nm barrier QW display similar PL intensity trends to that observed for the 3 nm case with $b = 1.83 \pm 0.02$, and $b = 1.54 \pm 0.02$ for the 5 nm and 7 nm barrier QW respectively.

6.2 Energy Transfer with Ag Nanoparticles

The main signature of NRET in a system is a decrease in the lifetime of the donor species. The lifetime of the donor is therefore measured alone as a reference in a QD layer on a GaN substrate (QD only), in the presence of the QW (QD-QW), in the presence of AgNPs (QD-Ag), and finally in the presence of both the AgNPs and the QW (QD-Ag-QW). Representative PL decay plots of these four samples are shown in

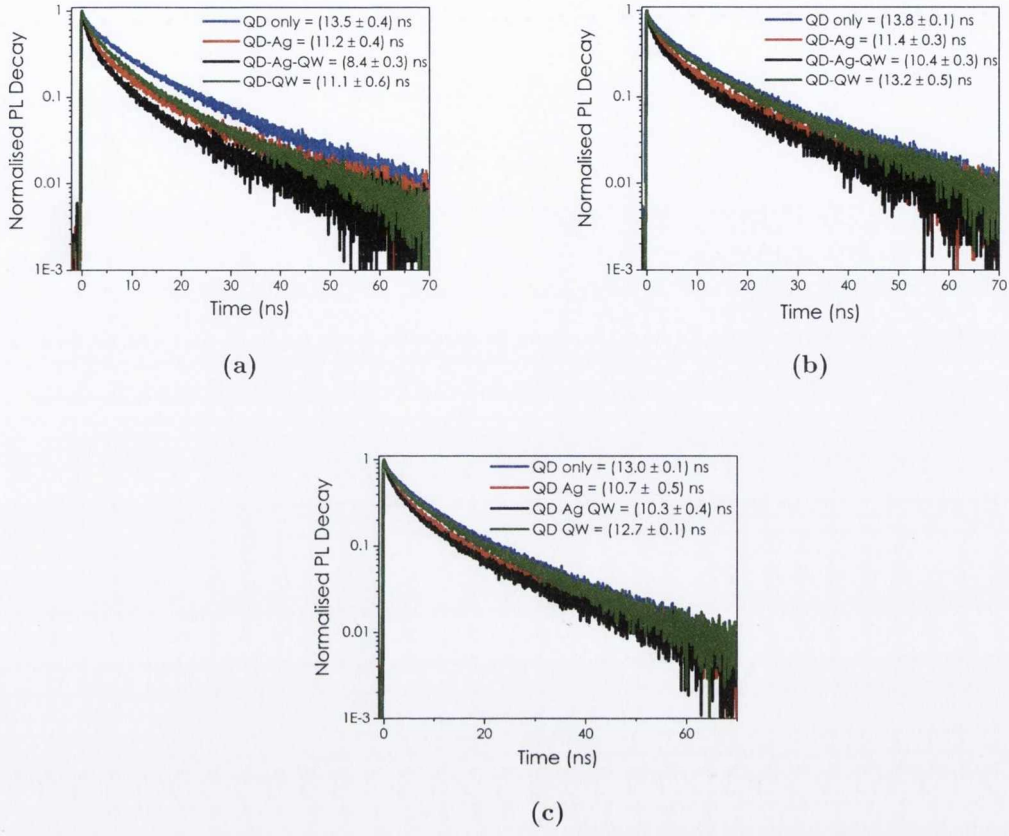


Figure 6.8: Representative PL decay plots for the four samples, QD only (blue), QD-Ag (red), QD-QW (green), QD-Ag-QW (black); using QWs with three different barrier thicknesses; 3 nm in (a), 5 nm in (b), 7 nm in (c)

Figure 6.8a for the 3 nm barrier QW, in Figure 6.8b for the 5 nm barrier QW, and in Figure 6.8c for the 7 nm barrier QW. For each QW barrier thickness there is a decrease in the lifetime in the presence of the AgNPs, which would be expected from the overlap of the QD PL and the AgNP extinction in Figure 6.5. There is also a further decrease of the QD lifetime in the presence of the QW, indicating plasmon-mediated ET. This is most obvious for the 3 nm barrier QW in Figure 6.8a. To make this clearer plots showing this average lifetime of the QDs on each QW for the four samples are shown in Figure 6.9, the average lifetime is calculated using Equation (3.8).

The quenching efficiency of the QDs is calculated by

$$E_Q = 1 - \frac{\tau_{QD-Ag}}{\tau_{QD}}$$

where τ_{QD} is the average lifetime of the QD-only sample and τ_{QD-Ag} is the average

lifetime of the QD-Ag sample. The quenching efficiency is approximately 17 % for each QD-Ag sample.

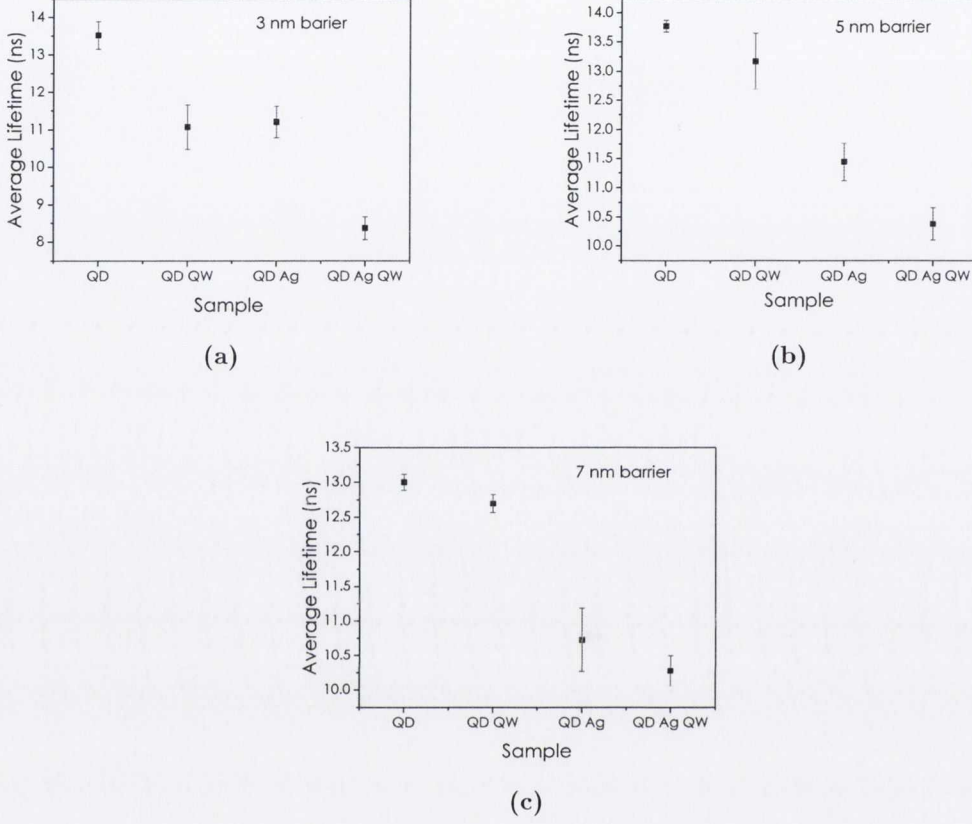


Figure 6.9: Average decay lifetimes for the four samples, QD only, QD-Ag, QD-QW, QD-Ag-QW; on the QWs with three different barrier thicknesses; 3 nm in (a), 5 nm in (b), 7 nm in (c)

Focusing on the decrease of the lifetime from QD only to QD-QW, i.e. the blue to the green lines in Figure 6.8. It is evident from Figure 6.8 and Figure 6.9 that this interaction is strongest for the 3 nm barrier QW, which is to be expected as NRET is very strongly distance dependent. It has been shown that the dimensionality of the acceptor determines the distance dependence [211], therefore, since the QW is a 2D material a d^{-4} dependence is expected. The ET efficiency can be calculated from the measured decay lifetimes. For the direct QD to QW interaction this is

$$E_D = 1 - \frac{\tau_{QD-QW}}{\tau_{QD}} \quad (6.2)$$

where τ_{QD} is defined as in the previous case, and τ_{QD-QW} is the lifetime of the QD-QW sample. Equation (2.18) on page 16 gives the NRET efficiency when dealing with a planar system, this has the form

$$E_{NRET} = \frac{1}{1 + kr^4} \quad (6.3)$$

where k is a constant, and r is the centre to centre distance. From Equation (2.18) it can be seen that $k = 2/c_{Acc}\pi R_0^6$. c_{Acc} is the acceptor concentration and R_0 is the Förster radius.

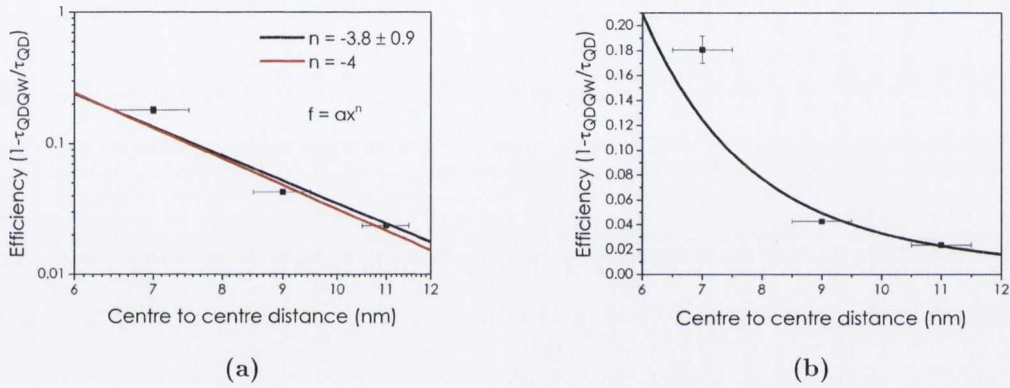


Figure 6.10: (a) Logarithmic plot of the ET efficiency and fit to a power law confirming the d^{-4} dependence. The black line is a free fit with a power law, producing $n = -3.8 \pm 0.9$. The red line is a power law fit with $n = -4$ to demonstrate how close this fitting is to the ideal. (b) ET efficiency for QD to QW versus centre to centre distance between the QDs and QW. The solid line is a fit to Equation (6.3) with $k = 2.9 \times 10^{-3} \text{ nm}^{-4}$.

To check that the dependence is truly represented by d^{-4} , a logarithmic plot of the efficiency versus distance is produced and fitted to a power law (ax^n). This is shown in Figure 6.10a, where the black line is a free fit indicating a power of $n = -3.8 \pm 0.9$. This is close to ideal $n = -4$, which is shown in the red line indicating that the ET is Förster-like and governed by a d^{-4} dependence. Figure 6.10b shows the ET efficiency of the QD to QW interaction calculated from Equation (6.2) with the solid line representing the fit to Equation (6.3) with $k = 2.9 \times 10^{-3} \text{ nm}^{-4}$.

In the presence of both AgNPs and the QWs, sample QD-Ag-QW, it is clear from Figures 6.8 and 6.9 that there is further reduction in the lifetime of the QD. The

surface plasmon-mediated ET efficiency can be determined from

$$E_P = 1 - \frac{\tau_{QD-Ag-QW}}{\tau_{QD-Ag}} \quad (6.4)$$

where τ_{QD-Ag} is the lifetime of the QDs in a mixed layer with the AgNPs on a GaN reference, and $\tau_{QD-Ag-QW}$ is the lifetime of the QDs in a mixed layer with the AgNPs on the QW.

Figure 6.11a is the plasmon-mediated ET efficiency data represented on a logarithmic plot, the black line is a free fit to a power law with the exponent, $n = -3.9 \pm 0.2$. This shows clearly that the surface plasmon-mediated ET follows the same d^{-4} distance dependence as NRET. Figure 6.11b shows this same efficiency with the solid line representing a fit to Equation (6.3), this time $k = 1.6 \times 10^{-3} \text{ nm}^{-4}$. Since $k = 2/c_{Acc}\pi R_0^6$, a decrease in the value of k can be attributed to an increase in the acceptor concentration, or to an increase in the Förster radius [54, 80]. In this case the same QW is used for the QD-QW and QD-Ag-QW samples, and therefore a decrease in the value of k can be attributed to the increase of the Förster radius, R_0 . The d^{-4} distance dependence and the decrease in the the fitting parameter k (corresponding to an increase in the Förster radius) indicates that the combined QD-Ag can be treated as an enhanced donor dipole relative to the QD alone in a NRET model, similar to what has been reported for QD-QD plasmon-mediated NRET [57, 120]

Ideally, an enhancement of the acceptor PL would be present in an ET system with two emitting species. However no modification of the QW PL is observed in this study. This may be due to the close proximity of the mixed QD-AgNP layer to the acceptor QW resulting in significant quenching by the AgNPs. Increasing the barrier thickness would reduce quenching of the acceptor emission [57]. Additionally, the variation in the QW PL is rather large, on the order of 15 %. This would preclude seeing any enhancement for the direct QD to QW ET as the efficiencies are close to the variation of the PL. This also prevents seeing any evidence of QW PL enhancement in the 5 nm and 7 nm QW for the surface plasmon enhanced ET case as the efficiencies are well below 15 %.

An advantage of this system is that it utilises simple processing techniques like spin

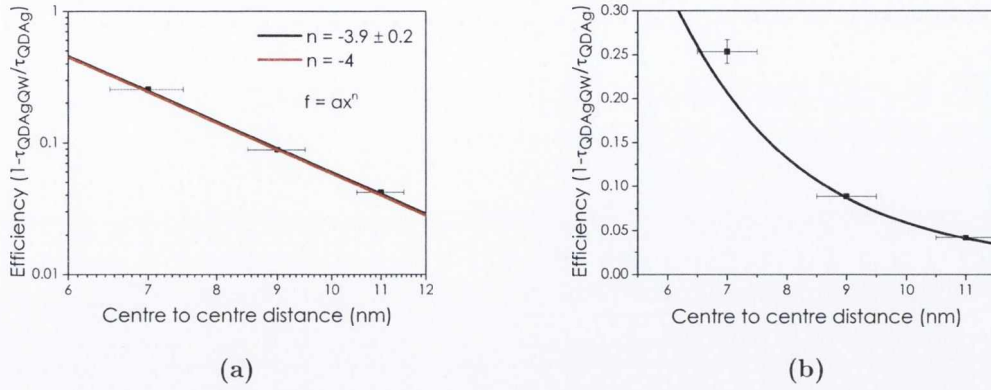


Figure 6.11: (a) Logarithmic plot of the ET efficiency and fit to a power law confirming the d^{-4} dependence. The black line is a free fit with a power law, producing $n = -3.9 \pm 0.2$. The red line is a power law fit with $n = -4$ to demonstrate how close this fitting is to the ideal. (b) Surface plasmon-mediated ET efficiency versus centre to centre distance between the QDs and QW. The solid line is a fit to Equation (6.3) with $k = 1.6 \times 10^{-3} \text{ nm}^{-4}$.

coating of colloidal samples that are easily scalable, however some obstacles do still have to be overcome. Firstly this is not the optimum geometry for surface plasmon-enhanced ET. As mentioned previously 180 degrees separation between the donor, metal nanoparticle, and acceptor is ideal [47, 120], in this case the QDs and AgNPs are both in the same plane. Therefore slightly more complex steps involving spacer layers could give a great boost to the ET efficiency. Additionally the aggregation of the AgNP needs to be overcome, having more isolated NPs could sharpen the LSP resonance giving an overall larger effect. Finally it would be interesting to study this system from an electrical standpoint, even though there is no obvious optically enhancement in the QW it is still possible that if this system was electrically contacted increases in the photocurrent could be observed with the addition of AgNPs. Overall this system requires further study.

6.3 Energy Transfer using Ag Nanoparticle Arrays

Nanobox (NBs) and nanodisc (NDs) arrays were fabricated by EBL. A focused beam of electrons is used to draw a pattern of boxes or discs in an electron sensitive resist

layer. The resist layer in this case is a 100 nm thick layer of PMMA, this is modified by the electron beam by causing the long chained PMMA to break up into shorter chains. These shorter chained regions are then soluble in methyl-isobutylketone(MIBK), thereby removing these regions within the resist. After this development process metal is then deposited everywhere by metal evaporation. First 5 nm of Ti is deposited as an adhesion layer, followed by 35 nm of Ag. The remaining resist is removed by a lift off process in acetone, taking the metal from unexposed regions off with it. Therefore only metal from areas that were exposed by the electron beam remain. SEM images of the arrays are shown in Figure 6.12. These arrays are fabricated both on a GaN reference substrate on a QW with a 3 nm barrier thickness.

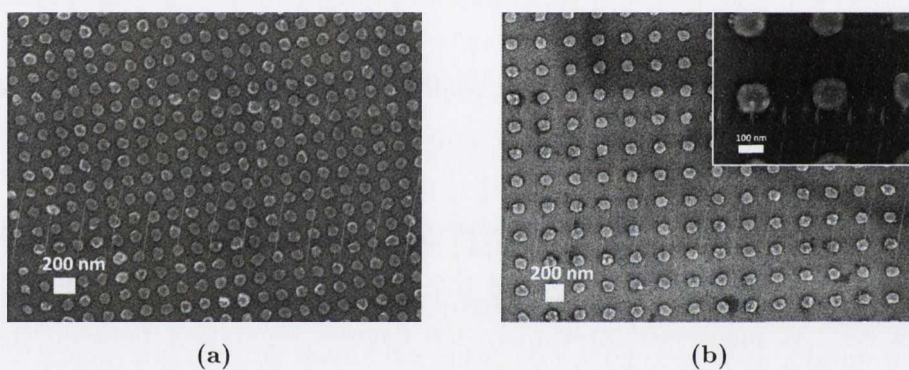


Figure 6.12: (a) SEM of the nanodiscs (b) SEM of the nanoboxes, inset is a zoomed image. Images taken by Luke Higgins.

The arrays consist of 200×200 units, the NDs have a diameter of 90 nm with an 80 nm gap, giving a total area of $34 \mu\text{m} \times 34 \mu\text{m}$. The NBs consist of $100 \text{ nm} \times 100 \text{ nm}$ boxes with a 200 nm gap giving a total area of $60 \mu\text{m} \times 60 \mu\text{m}$. While the individual structures are not perfectly defined due to the limitations of EBL, the plasmonic response depends also on the overall array geometry.

These dimensions were chosen as simulations of their extinction spectra indicate good overlap with the QD and emission. All simulations were performed on the commercial Lumerical finite-difference time-domain (FDTD) simulation software with the aid of Dr. Vasilios Karanikolas. The absorption and scattering profiles of the arrays can be extracted and can be used to give insight into the interaction. The extinction (absorption + scattering) of the arrays are simulated using a plane-wave excitation. The PMMA

and GaN layers are modelled with a constant dielectric permittivity of $\epsilon_{PMMA} = 2.2$ and $\epsilon_{GaN} = 5.35$ respectively. The dielectric permittivity of the Ag and Ti materials are included using experimentally measured data [218].

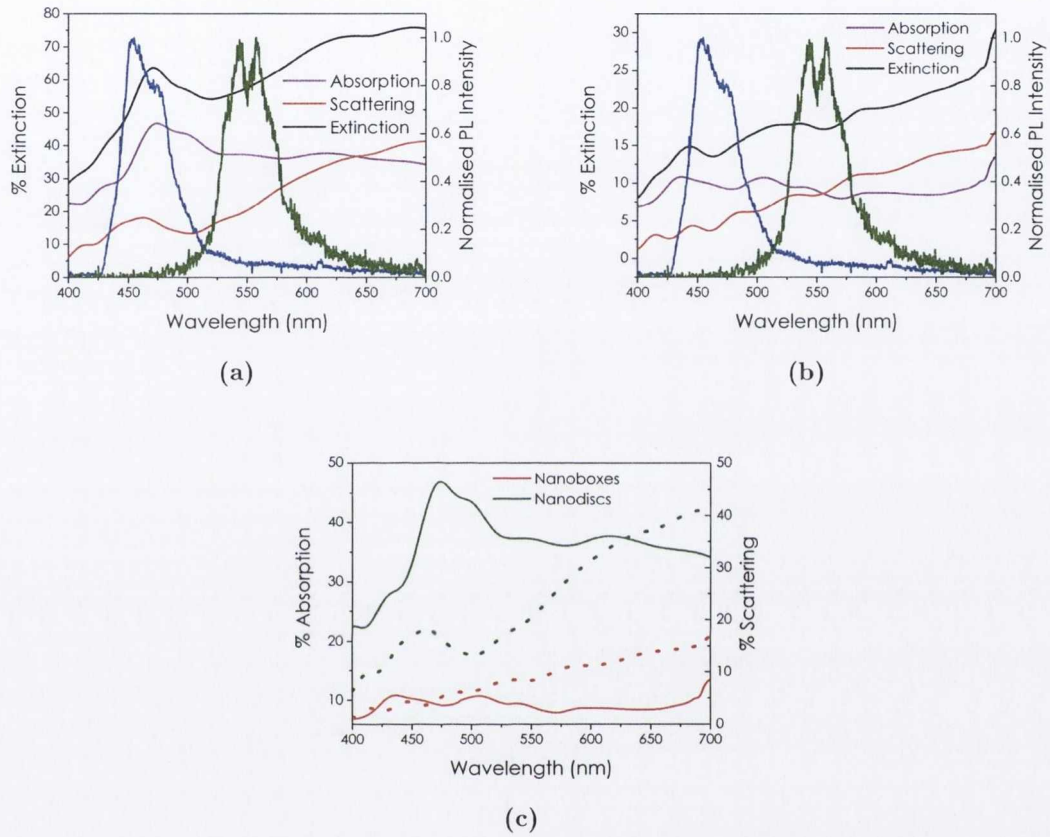


Figure 6.13: (a) Left axis, absorption (pink line), scattering (red line), and extinction (black line) spectra for the ND array. Right axis, QD (blue line) and QW (green line) normalised PL emission. (b) Left axis, absorption (pink line), scattering (red line), and extinction (black line) spectra for the NB array. Right axis, QD (blue line) and QW (green line) normalised PL emission. (c) Comparison between the ND (green) absorption (solid, left axis) and scattering (dashed, right axis) and the NB (red) absorption (solid, left axis) and scattering (dashed, right axis).

As can be seen from Figures 6.13a and 6.13b there is significant spectral overlap between the extinction of the ND and NB array extinction and the PL of the QD and QW. From Figure 6.13c it is clear that the ND has the stronger absorption and scattering, which could indicate that it will have the strongest interaction. The concentration of QDs for this study is reduced slightly compared to the study involving the AgNPs, in this case the concentration is $6 \times 10^{19} \text{ m}^{-3}$.

Measuring the lifetime of QDs deposited on top of these arrays using the FLIM with the standard $80 \times 80 \mu\text{m}^2$ area allows for the measurement of false colour maps representing the lifetime and intensity on these arrays, see Figure 6.14.

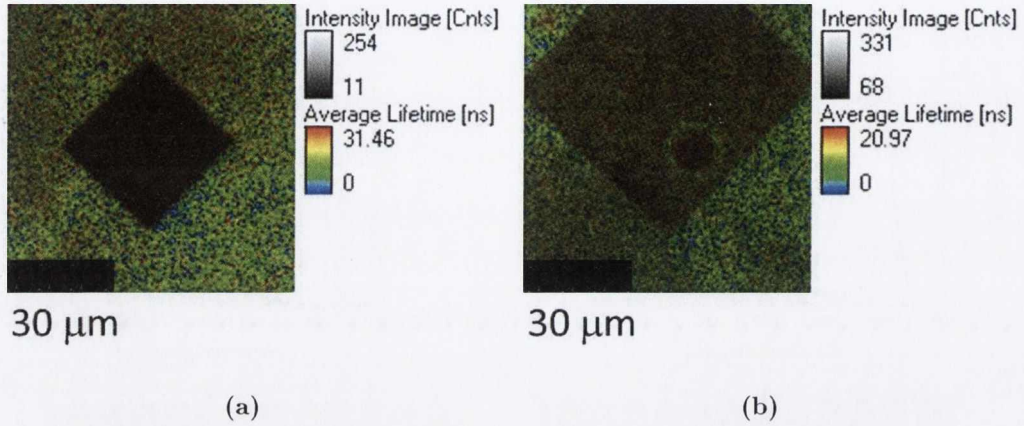


Figure 6.14: False colour images of the emission from QDs on the NDs (a) and NBs (b) collected from the FLIM system

Clearly visible on these images is the lifetime and intensity quenching of the QDs, which, being the donors in this system, is a clear indication of ET, though not specifically to the QW. Therefore in order to characterise this system the lifetime and PL intensity of the QDs will be measured on and off the arrays on a GaN reference substrate and on a 3 nm barrier QW. To complete the study the lifetime and PL intensity of the QW will be measured on and off the array firstly without the QDs present and then in the presence of the QD donors. To do this $20 \times 20 \mu\text{m}^2$ sub-areas of the FLIM scans are measured on the array and off it.

To quantify the level of ET the efficiency will once again be used. The quenching efficiency, $E_{Q,\text{array}}$, of QDs emission by the array on the GaN reference chip is given by

$$E_{Q,\text{array}} = 1 - \frac{\tau_{QD-\text{array}}}{\tau_{QD}} \quad (6.5)$$

where τ_{QD} is the lifetime of the QD away from the array and $\tau_{QD-\text{array}}$ is the lifetime of the QD on the array, replace array with ND or NB for the nanodiscs or nanoboxes respectively. The direct QD to QW ET, E_D , is given by

$$E_D = 1 - \frac{\tau_{QD-QW}}{\tau_{QD}} \quad (6.6)$$

where τ_{QD-QW} is the lifetime of the QD away from the array, on the QW. The plasmon-enhanced ET efficiency, $E_{P,array}$, is then

$$E_{P,array} = 1 - \frac{\tau_{QD-QW-array}}{\tau_{QD-array}} \quad (6.7)$$

where $\tau_{QD-QW-array}$ is the lifetime of the QD on the array, on the QW.

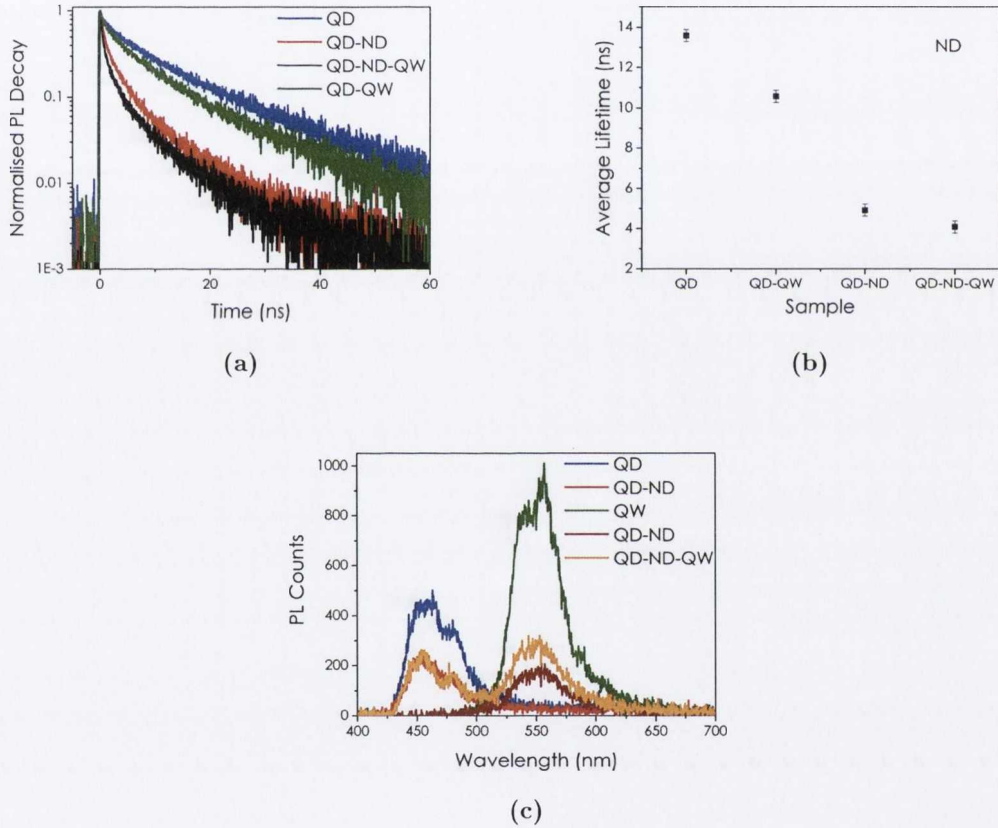


Figure 6.15: (a) PL decays for four situations with the ND array. QD (blue), QD-ND (red), QD-ND-QW (black), QD-QW (green) (b) Average lifetimes from the PL decay of the QD on all four samples. (c) PL spectra showing QD (blue), QD-ND (red), QW (green), QW-ND (wine), QD-ND-QW (orange).

Taking firstly the ND array, Figure 6.15a shows PL decays QD alone (blue) and QD on the ND (QD-ND, red). Clearly visible is quenching by the ND array. On the QW (QD-ND-QW, black) it is clear that there is still a further reduction of the decay

lifetime indicating plasmon-mediated ET. Notice also for the QD-QW (green) decay that there is a reduction compared to the QD (blue) decay, indicating some direct QD to QW non-radiative ET. These quenching and ET processes can be characterised by the efficiencies calculated from Equations (6.5) to (6.7). Figure 6.15b shows the average lifetimes for the four situations and the corresponding efficiencies are $E_{Q,ND} = (64 \pm 4)\%$ $E_D = (22 \pm 1)\%$ and $E_{P,ND} = (17 \pm 2)\%$.

For the PL in Figure 6.15c there is clear emission quenching of the QDs on the ND array, followed by very slight further quenching in the QD-ND-QW case. There is firstly quenching of the QW emission when on the ND array (QW-ND, wine), but with the addition of the QDs the QW emission recovers (QD-ND-QW, orange) above this quenched level, however it does not recover beyond the starting emission (QW, green).

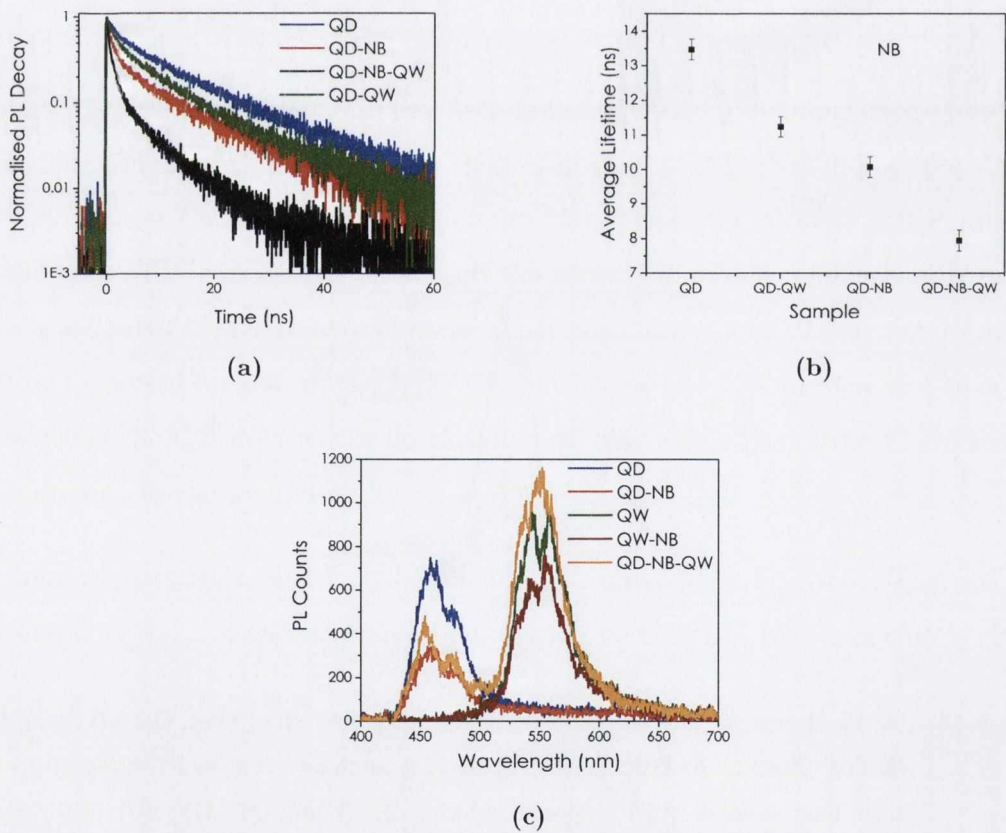


Figure 6.16: (a) PL decays for four situations with the NB array. QD (blue), QD-NB (red), QD-NB-QW (black), QD-QW (green) (b) Average lifetimes from the PL decay of the QD on all four samples. (c) PL spectra showing QD (blue), QD-NB (red), QW (green), QW-NB (wine), QD-NB-QW (orange).

Moving on to the situation of the NB array. Figure 6.16a shows the PL decays for the QD (blue) and QD on the NBs (QD-NB, red). Clearly visible is quenching to the NB array. On the QW (QD-NB-QW, black) it is clear that there is a further reduction of the decay lifetime again indicating plasmon-mediated ET. Notice also for the QD-QW (green) decay that there is a reduction compared to the QD (blue) decay, indicating some direct QD to QW non-radiative ET as seen previously in Figure 6.15a.

The efficiencies can be extracted from Figure 6.16b using Equations (6.5) to (6.7). $\tau_{QD} = (13.5 \pm 0.3)$ ns and $\tau_{QD-NB} = (10.1 \pm 0.3)$ ns, hence $E_{Q,NB} = (25 \pm 1)\%$, much smaller than in the ND case. Similarly, $\tau_{QD-QW} = (11.2 \pm 0.3)$ ns and $\tau_{QD-NB-QW} = (7.9 \pm 0.3)$ ns, therefore $E_{D,NB} = (17 \pm 1)\%$ and $E_{P,NB} = (21 \pm 1)\%$.

For the PL in Figure 6.16c there is clear emission quenching of the QDs on the NB array. Most importantly in this case is the observation of PL enhancement for the Ag NP decorated QW sample. There is firstly quenching of the QW emission when on the NB array (QW-NB, wine), but with the addition of the QDs the QW emission recovers (QD-NB-QW, orange), and in fact is higher than the starting emission (QW, green). This is in contrast with the ND which never recovers beyond the initial level of the QW emission, and would be in agreement with the simulation data presented in Figure 6.13c. Figure 6.17 shows the PL spectra of NB sample with a focus on the QW emission this time. It is clear that the enhancement of the QW emission is not as large in the plasmon-mediated case as it is for the direct QD-QW non-radiative ET case. However, the high level of tunability observed from just the two arrays studied suggests that this is an optimisation issue and that further improvement of the plasmon-mediated case could be achieved.

A summary of the efficiencies comparing the two structures is given in Figure 6.18a. Some insight into the efficiencies can be gained by looking at the underlying rates, which are also plotted in Figure 6.18b. The quenching rate to the array is much larger for the ND, giving rise to a much larger quenching efficiency for this array compared to the NB. This explains why the plasmon-mediated efficiency is smaller for the ND array, it is not able to compete very well with the exceptionally fast rate of quenching to the ND array. Contrast this with the NB array where the quenching rate and the plasmon-mediated rate are comparable, enabling the plasmon-mediated ET to compete and to have an

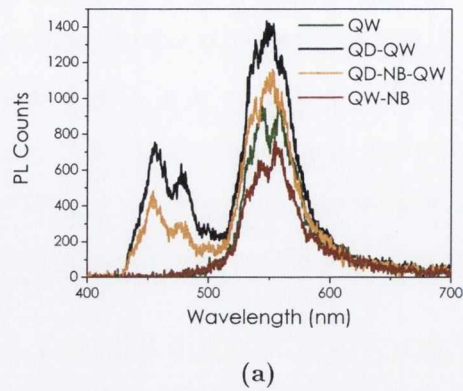


Figure 6.17: PL spectra showing QW (green), QD-QW (black), QW-NB (wine), QD-NB-QW (orange).

efficiency larger than the direct QD-QW ET. This very large quenching in the case of the ND, leads to the large quenching of the QW emission and prevents enhancement of the PL in the plasmon-mediated case. Careful adjustment of the structure and a clearer understanding of the trade off between the quenching rate and the plasmon-mediated ET rate could allow for further tuning of the acceptor enhancement in this system.

Some modification of the level of direct quenching to the plasmonic array could allow for the QW emission to be overall enhanced relative to the direct ET case. This could be done by varying the spacing between the NB in the array, changing the size of the individual units or by changing the shape entirely to triangles or rings for example [219]. This will modify the absorption and scattering profiles of the arrays [219], which can dramatically alter the emission of the QDs and QWs. Also, it is not clear that the plasmonic system would not benefit from a much greater increase in the photocurrent when a bias is applied, this may avoid the quenching seen in the PL.

Using a slightly thicker layer of QDs would mean that on average QDs would be further away from the QW and the NB, therefore the system could benefit from the plasmon enhancement at a distance where direct NRET is impossible. Additionally using a QW with a larger barrier thickness should give less quenching to the array, so it is entirely possible that changing the distance allows movement from a regime of quenching to one of enhancement [93,158]. As mentioned previously a thicker barrier is also advantageous

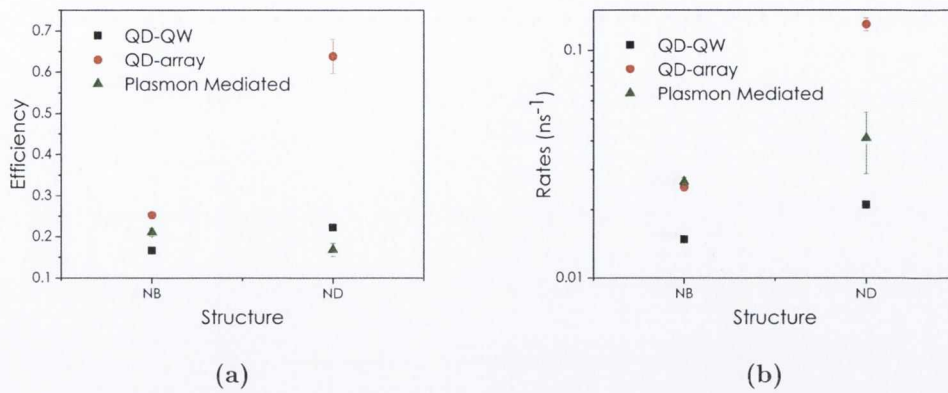


Figure 6.18: (a) Efficiency versus structure for the QD-QW ET (black square), QD-array quenching (red circle), and plasmon-mediated ET (green triangles). (b) QD-QW ET rate (black squares), QD-array quenching rate (red circles), and plasmon-mediated ET rate (green triangles) for the NB and ND arrays.

for device applications as it reduces non-radiative losses.

In order to help justify the assertions of the previous section that the optimisation of the array geometry could lead to larger QW acceptor enhancement further FDTD simulations were undertaken. Figure 6.19 shows how the absorption and scattering profiles of NB arrays change when the gap between the NB is varied. Clearly as the gap size is reduced the absorption and scattering increases. The dramatic changes in the strength of the absorption and scattering just by varying the gap size and leaving the dimensions of the NB untouched show the great scope for optimisation in these array structures.

Field profiles around the NB can also be a good indicator for the level of interaction expected. Figure 6.20a shows the field profile around a NB at 550 nm. This will indicate if a QW with a thicker barrier is a better candidate for observing acceptor enhancement. The bottom corner of the box is magnified in Figure 6.20b to investigate how the field penetrating into the barrier and the QW evolves with distance. Clearly, the field falls off as it penetrates further into the barrier, in fact it is almost at the background level 6 nm away. This indicates that the interaction of a thicker barrier QW, say 7 nm, with the NB will be quite minimal. This should hopefully lead to reduced direct quenching of the QW emission by the NB array, leading to an overall

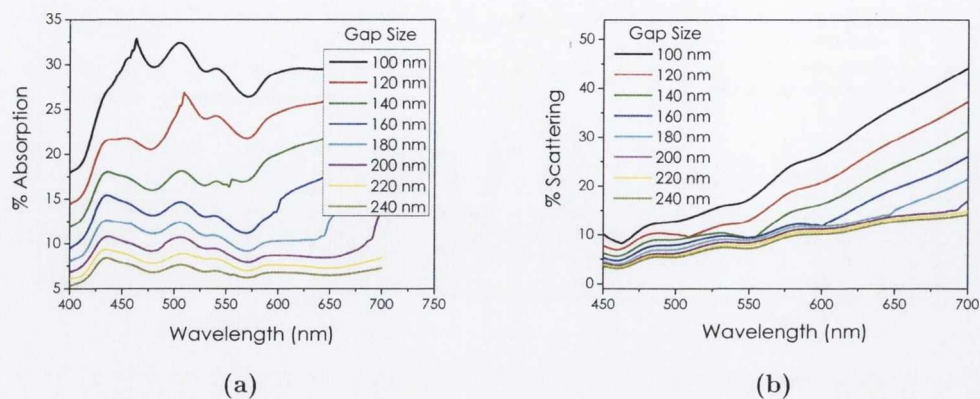


Figure 6.19: Simulated absorption (a) and scattering (b) profiles versus wavelength for the NB arrays with varying gap size from 100 nm to 250 nm

situation of acceptor enhancement.

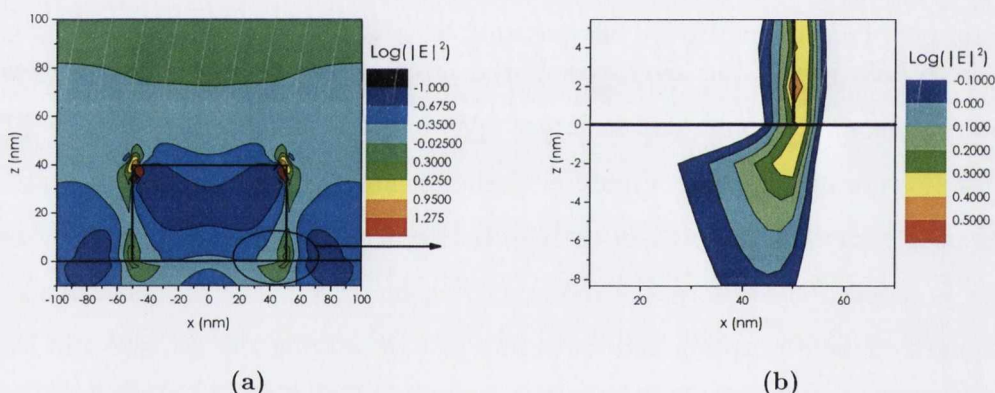


Figure 6.20: (a) Field profile around the NB calculated at 550 nm. (b) Magnification of the indicated area in (a), the colour scale is adjusted for clarity.

6.4 Conclusion

This work has demonstrated the distance dependence of QD to QW ET using Cd-SeS/ZnS QDs emitting at 450 nm and InGa_N/Ga_N QWs with Ga_N barrier thickness of 3, 5, and 7 nm, respectively. It has been shown that the NRET efficiency falls off with the characteristic d^{-4} distance dependence of Förster-like ET to a plane. This also verifies the assertion that the dimensionality of the acceptor drives the distance

dependence [211].

This work has also shown the first demonstration of plasmon-mediated ET from a QD to a QW, using both colloidal AgNPs and AgNP arrays. With the AgNPs it was possible to investigate the distance dependence of the surface plasmon-mediated ET efficiency, and a d^{-4} dependence was determined. No acceptor enhancement was observed in the colloidal system, however there is much room for optimisation, both in the geometry of the system and in the quality of the NPs and their resulting LSP resonance.

Within the AgNP array system two different structures were investigated, NBs and NDs. The varying levels of acceptor enhancement for these two structures show the possibility to tune the QW emission. The ND structure proved to have the greatest interaction with the QDs and QW, however this high level of quenching meant that the QW was only able to slightly recover in the plasmon-mediated case, leading to an overall situation of quenching compared to the QW alone. For the NBs the quenching was more moderate, leading to an overall enhancement of the QW emission in the plasmon-mediated case compared to the QW alone. This opens the door for a high level of tunability by varying the structure, which would be advantageous for both light harvesting and light emitting devices.

Chapter 7

Conclusions and Outlook

7.1 Summary

This thesis has investigated interactions in hybrid systems of QDs, MNPs, and QWs. This has varied from fundamental investigations by probing the temperature dependent properties of QDs and the ET between them, to more device driven studies enhancing ET between a QD and QW via coupling to surface plasmons for light harvesting applications.

Chapter 2 presented the basic theory of FRET and how it can be applied to systems involving QDs. Additionally, a simple analytic model of the temperature dependence of QD decay rates was presented. This model takes account of the interesting property of QDs, whereby they have a so called dark state in which optical transitions to the ground state are forbidden by spin transition rules lying below the optically active bright state. This creates a situation in which as the temperature decreases the QD lifetime increases due to an increasing fraction of excitons being “frozen” into this dark state. This simple model has proved effective for fitting low temperature decay lifetimes/rates of QDs however it breaks down as the temperature is increased towards room temperature, i.e. between 150 K and 296 K. Thermally activated carrier trapping plays a prominent role in this temperature range. Therefore to account for this the analytic model is extended to include such trapping.

Investigations into this extended model in QD monolayers of various concentrations is presented in Chapter 4. It is shown that the coupling to this trap state occurs via interactions with LO phonons which have energies that can be determined from fitting steady state PL with well known expressions, originally used to describe the temperature dependence of the PL in bulk semiconductors. The strength of the thermally activated carrier trapping increases with increasing concentration of the QD monolayers. This is attributed to an increasing efficiency of interaction with these traps due to an increase in the density of available traps, as the QDs are brought closer and closer together an individual QD could effectively interact with trap sites of neighbouring QDs, and/or the increasing density of QDs could introduce additional defect sites for trapping, for example through the interactions of the ligands surrounding the QDs.

Extending the discussion of temperature dependence to ET systems is the focus of Chapter 5. Firstly the analytic model is extended to account for ET and used to explain the quenching behaviour observed between QDs and AuNPs. The final expression obtained is notable for the absence of terms accounting for thermally activated carrier trapping. Reasonable agreement with the model is observed, the largest discrepancies are found at the extremes of the measured temperature range. Allowing the bright and dark ET rate to vary freely as fit parameters produces a much better match to the experimental data, though this raises the question of the precise nature of the dark state ET rate term. The dark ET rate term approaches zero for the QD-AuNPs samples, but is observed to play an important role in the modelling of the QD-QD samples. This could mean that this added ET rate is falsely attributed to the dark state for the QD-QD case and could be related to some other mechanism, for example exciton recycling. Additionally in the QD-QD case in order to accurately fit the data at room temperature requires that the efficiency of interactions with traps term be larger than for the QD alone case. This could suggest the creation of additional trap sites due to the close proximity of the acceptor QDs.

Finally in this chapter the temperature dependence of surface plasmon-mediated ET between the QDs is presented. The trend observed is completely disparate to the other observed ET trends, and the trends in the decay rates of QD monolayers; a decreasing ET rate with increasing temperature. A possible explanation for this is

that the surface plasmon-mediated ET rate has to compete with quenching to the AuNPs, and the spontaneous emission rate. Therefore when these rates are relatively small, at low temperature the surface plasmon-mediated ET rate can be larger. As the temperature increases the surface plasmon-mediated ET rate has more competition from the other increasing rates and therefore decreases with increasing temperature.

Overall it seems that this simple model is able to account for the trends observed for decay rates of QDs alone once thermally activated carrier trapping is accounted for. Moving on to more complex situations such as quenching to MNPs and ET between separated layers of QDs, the limitations of the model become apparent. With deviations observed at both low and high temperatures for the QD-AuNPs sample, this is particularly evident for QD1 which is on resonance with the LSP peak of the AuNPs. More pronounced deviations are observed for the QD-QD ET case. These discrepancies can be rectified in the fit by allowing the bright and dark ET rates to be free parameters, and in the QD-QD ET case accounting for an increased efficiency of interactions with traps. This leaves open questions as to the physical meaning of these parameters, but could be explained by exciton recycling and additional traps created due to the close proximity of acceptor QDs. A completely opposite trend is found for the temperature dependence of surface plasmon-mediated ET, requiring further study.

Chapter 6 presents the first demonstration of surface plasmon mediated ET from a QD to a QW. Firstly this chapter shows that the distance dependence of direct QD to QW ET can be well described by a d^{-4} dependence consistent with FRET theory. This is an important insight itself, extending the FRET formalism further from its origin in molecular systems towards systems used in the opto-electronics industry. It is also a verification of a generalised theory on Förster-type non-radiative ET [211], in that it is the dimensionality of the acceptor that decides the distance dependence of the ET. The plasmon mediated system also obeys a d^{-4} distance dependence, with an enhanced characteristic distance, which is in agreement with previous work in this group [59]. This indicates that in a strongly coupled donor-plasmon system the donor-plasmon acts as an enhanced donor dipole relative to the QD alone.

Moving on from colloidal systems, arrays of Ag nanoparticles are used to investigate surface plasmon mediated ET. ET efficiencies of up to an additional 21 % over direct

QD to QW ET are found, coupled with an enhancement of the QW emission beyond the levels of the QW alone. By varying the structure geometry it is possible to tune the level of the interaction, in this case the QW-plasmon interaction is most sensitive. Quenching efficiencies of $\approx 64\%$ are observed on the nanodisc array, which can be reduced to $\approx 25\%$ on the nanobox array. This provides a means to tune the acceptor emission through careful fabrication of the array.

In conclusion, this thesis has shown the importance of considering thermally activated carrier trapping in QD systems in the higher temperature range, particularly at high concentrations. The temperature dependence of surface-plasmon mediated ET has been shown. To the author's knowledge this is the first presentation of the temperature dependence of this complex process. The trend of decreasing ET rate with increasing temperature is opposite to the spontaneous emission rate, the quenching rate to AuNPs, and the direct QD-QD ET. This interesting, and unexpected result requires further work to gain a better understanding of the competing processes at play. Surface plasmon-mediated ET in a QD QW system has been demonstrated for the first time. The surface plasmon-mediated ET efficiency follows the typical d^{-4} donor distance dependence for planar systems. Utilising a highly ordered array of AgNPs the QW emission can be easily tuned. This hybrid system is a further step towards light harvesting applications; the plasmonic array can enhance photocurrent, QDs have a large extinction coefficient so would be good solar absorbers. Also, NRET has the potential to be a more efficient way of transferring the solar energy absorbed in the QD to the QW when compared with radiative transfer, therefore this plasmon-mediated system could lead to an overall more efficient conversion of solar energy to electrical energy.

7.2 Outlook

The temperature dependent studies presented in Chapters 4 and 5 gave good insight into the properties of QDs, however it does leave some open questions. The QDs studied have relatively low QY, QD1 having $\approx 9\%$. An in-depth study into the role the QY plays in the density of trapping could be beneficial.

Similarly it is clear that the simple analytic model has its limitations in describing ET processes.. A thorough theoretical study in the same vein as work presented on excitons in QWs [207] and in MoS₂ [208], or microscopic analysis based on the Kane model [209], or considering the role of higher multipoles [210] could compliment the experimental work presented here. As well as further experimental work into several different ET systems; this could be as simple as varying the emission wavelengths of the QDs, or tuning the plasmon resonance by utilising Ag nanoprisms [220], or introducing different acceptors such as QWs or even 2D materials such as graphene [221–223], or MoS₂ [223, 224]. Temperature dependent studies involving the above systems could give a greater insight into the dynamics of excitons in QDs at low temperatures. Additionally, introducing magnetic fields can give insight into the nature of the fine structure of excitons in nanocrystals [225–228] and the its role in ET [206, 229].

Showing that plasmon-enhanced ET obeys a d^{-4} distance dependence in a QD-QW system is of fundamental interest, however the overall enhancement of characteristic distance the is relatively small, only approximately 1.1 times that of the case without AgNPs. It would therefore be prudent to continue this work by optimising the strength of this interaction. Firstly by optimising the geometry of the hybrid system; the mixed layer of QD and AgNPs was sufficient to display an interaction however the best situation is having the MNP between the donor and acceptor. This could prove difficult from a materials standpoint at the moment, as in this case both the QDs and AgNPs are soluble in similar solvents, therefore spin coating them in separate layers without a spacer or buffer would be impossible. Moving to water soluble MNPs, such as the AuNPs used in Chapters 4 and 5 would be a possibility, however due to fact that QD emission needs to be of a higher energy than the QW the QDs are limited to organic solvents. Spin coating separated layers has been shown to work if the two building blocks are soluble in different classes of solvents [230, 231], therefore this is a possible avenue of study to produce separated bilayers of QDs and MNPs. Using this method it could also be possible to increase the distance between the QDs and MNPs, and ultimately the acceptor QW, thereby giving a larger distance range to investigate. This should also elucidate the role the QD-MNP and MNP-QW distances plays in the ET, from previous studies in this group we would expect the donor-MNP distance to be the most sensitive [59].

The array structures have already shown promise with regards to tunability. The trade off between quenching to the array and plasmon mediated ET can lead to the tuning of the acceptor emission enhancement. The possibility to vary the gap between the individual units of the nanoboxes or nanodiscs could lead to fine control of this enhancement tuning. Utilising other geometries, such as rings or split rings [188], or triangles could lead to additional avenues to explore such as enhanced radiative transfer, enhanced scattering, in addition to the plasmon mediated ET.

Collaborators at Tyndall have developed a novel contacting method for InGaN/GaN QWs, it would be interesting and useful to electrically characterise these ET systems. This could involve both the light emitting and light harvesting aspects of this work. By electrically pumping a QW and observing the emission it should be possible to see surface plasmon enhanced ET to a QD deposited above the QW, and therefore be one step closer to realising commercial devices with this technology. With this method we would not be directly pumping the QDs electrically and the only way for the QDs to emit light would be from pumping via the QW, either by radiative or non-radiative means. This can lead to colour conversion devices, and white light emitting devices by utilising QDs of different emission wavelengths to mix with the emission of the QW. Similarly the system could be modified to be a light harvesting structure using the QDs as light harvesters and monitoring the photocurrent generated in the QW both in the presence of the QDs alone and with MNPs. This would give insight into how applicable this technology is as a possible photovoltaics technology. MNPs have already been shown to be useful as light focusing elements so could enhance the photocurrent by themselves, the possibility of further enhancement with surface plasmon-enhanced ET is an exciting possibility.

Appendices

Appendix A

Sample Recipes

A.1 Hydrophillic Samples

To provide a slight negative surface charge to the quartz, the substrate is immersed in the following solutions sequentially and sonicated for the time denoted.

- Millipore water for 10 minutes,
- 1 M NaOH (4-5 g of NaOH in 75 mL of millipore water) for 15 minutes,
- Ethanol + NaOH (4-6 pellets in Ethanol) for 15 minutes,
- Fresh millipore water for 10 minutes.

This then imparts a slightly negative surface charge, enabling better adsorption of the PE for LbL. The procedure for LbL is as follows

- Immersion of (surface treated) quartz substrate in positively charged PDDA solution for 10 minutes,
- Rinsing with millipore water for 1 minute to remove loosely adsorbed polyelectrolytes,
- Immersion into negatively charged PSS solution for 10 minutes,
- Rinsing with fresh millipore water for 1 minute.

- Repeat until four bilayers of PDDA/PSS are built as a buffer layer.
- Immersion into solution containing the QDs or the AuNPs.

The concentration of the QD/AuNP solution and the immersion time will determine the final concentration of the monolayer. The fresh millipore water for the rinsing steps prevents cross-contamination. Four bilayers of polyelectrolyte buffer are chosen as the influence of the substrate vanishes after a few deposition cycles so the optical properties of the QD/AuNP monolayers are only influenced by the polyelectrolyte [176].

PSS in powder form with a molecular weight of approximately 70,000 g/M, and a 20% w/w solution of PDDA with a molecular weight of 100,000 to 200,000 g/M in water were obtained from Sigma Aldrich. 543 mg PSS powder dissolved in 10 mL of millipore water is used as PSS stock solution. PDDA is used as a stock solution as purchased and is simply decanted into a smaller glass vial.

The recipes for the 0.1M PDDA/PSS solutions for LbL are

PDDA 170 μ L PDDA stock + 0.2 mL NaCl (3M) + 5.8 mL millipore water.

PSS 560 μ L PDDA stock + 0.2 mL NaCl (3M) + 5.3 mL millipore water.

A.2 Hydrophobic Samples

PMMA with a molecular weight of 996,000 g/M was purchased from Sigma and a solution of 0.1% w/w in toluene was prepared. The density of toluene is 0.867 g/cm³ so 20 mL of toluene has a mass of 17.84 mg. Therefore a 0.1% w/w solution is prepared by dissolving 0.01784 mg of the PMMA in 20 mL of toluene.

5 mL of CdSeS/ZnS QDs with diameter (6.0 ± 0.5) nm and dispersed in toluene were obtained from Sigma Aldrich at a concentration of 1 mg/mL. This is used as a stock solution.

Hydrophobic AgNPs with average particle size of 6-7 nm were obtained in powdered form from PlasmaChem. These were dissolved in toluene at a concentration of 10 mg/4 mL. This is then used as a stock solution.

PMMA and QD/AgNP dispersions were all made up to 100 μL and all dispersions were sonicated for 20 seconds to ensure they were well mixed.

The dispersions used in Section 6.2 consist of:

20 μL of QDs, 40 μL AgNPs, and 40 μL of PMMA.

20 μL of QDs, 40 μL toluene, and 40 μL of PMMA.

20 μL of toluene, 40 μL AgNPs, and 40 μL of PMMA.

The dispersions used in Section 6.3 consist of:

5 μL of QDs and 95 μL of PMMA.

A.3 Ag Nanoparticle Arrays by EBL

Arrays of nanoboxes and nanodiscs were fabricated using electron beam lithography (EBL) using a Carl Zeiss Supra. A focused beam of electrons is used to draw a pattern of boxes or discs in an electron sensitive resist layer. The resist layer in this case is a 100 nm thick layer of PMMA, this is modified by the electron beam by causing the long chained PMMA to break up into shorter chains. These shorter chained regions are then soluble in methyl-isobutylketone (MIBK), thereby allowing for the removal of these regions within the resist. After this development process metal is then deposited everywhere by metal evaporation. Firstly 5 nm of Ti as an adhesion layer, followed by 35 nm of Ag. The remaining resist is removed by a lift off process in acetone, taking the metal from unexposed regions off with it. Therefore, only metal from areas that were exposed by the electron beam remain.

A typical recipe is given below

- Accelerating voltage = 15 kV
- Aperture = 10 μm
- Current = 35.1 pA
- Working distance = 5.1 mm

- Approximate dose for nanoboxes = $196 \mu\text{C}/\text{cm}^2$
- Approximate dose for nanodiscs = $168 \mu\text{C}/\text{cm}^2$

References

- [1] A. Luque and S. Hegedus, eds., *Handbook of Photovoltaic Science and Engineering*. Wiley, 2003.
- [2] G. I. Koleilat, L. Levina, H. Shukla, S. H. Myrskog, S. Hinds, A. G. Pattantyus-Abraham, and E. H. Sargent, "Efficient, stable infrared photovoltaics based on solution-cast colloidal quantum dots," *ACS Nano*, vol. 2, no. 5, pp. 833–840, 2008.
- [3] S. A. McDonald, G. Konstantatos, S. Zhang, P. W. Cyr, E. J. D. Klem, L. Levina, and E. H. Sargent, "Solution-processed PbS quantum dot infrared photodetectors and photovoltaics," *Nature Materials*, vol. 4, no. 2, pp. 138–142, 2005.
- [4] M. C. Beard, K. P. Knutsen, P. Yu, J. M. Luther, Q. Song, W. K. Metzger, R. J. Ellingson, and A. J. Nozik, "Multiple exciton generation in colloidal silicon nanocrystals," *Nano Letters*, vol. 7, no. 8, pp. 2506–12, 2007.
- [5] I. Robel, V. Subramanian, M. Kuno, and P. V. Kamat, "Quantum dot solar cells. harvesting light energy with CdSe nanocrystals molecularly linked to mesoscopic TiO₂ films," *Journal of the American Chemical Society*, vol. 128, no. 7, pp. 2385–93, 2006.
- [6] S. Itzhakov, S. Buhbut, E. Tauber, T. Geiger, A. Zaban, and D. Oron, "Design Principles of FRET-Based Dye-Sensitized Solar Cells with Buried Quantum Dot Donors," *Advanced Energy Materials*, vol. 1, no. 4, pp. 626–633, 2011.
- [7] T. Förster, "Zwischenmolekulare energiewanderung und fluoreszenz," *Annalen der Physik*, vol. 2, no. 6, pp. 55–75, 1948.
- [8] S. Buhbut, S. Itzhakov, D. Oron, and A. Zaban, "Quantum Dot Antennas for Photoelectrochemical Solar Cells," *Journal of Physical Chemistry Letters*, vol. 2, no. 15, pp. 1917–1924, 2011.

- [9] 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.
- [10] J. Lee, A. O. Govorov, and N. A. Kotov, "Bioconjugated superstructures of CdTe nanowires and nanoparticles: Multistep cascade Förster resonance energy transfer and energy channeling," *Nano Letters*, vol. 5, pp. 2063–2069, 2005.
- [11] 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. 642–6, 2004.
- [12] N. Cicek, S. Nizamoglu, T. Ozel, E. Mutlugun, D. U. Karatay, V. Lesnyak, T. Otto, N. Gaponik, A. Eychmüller, and H. V. Demir, "Structural tuning of color chromaticity through nonradiative energy transfer by interspacing CdTe nanocrystal monolayers," *Applied Physics Letters*, vol. 94, no. 6, p. 061105, 2009.
- [13] S. Chanyawadee, P. G. Lagoudakis, R. T. Harley, M. D. B. Charlton, D. V. Talapin, H. W. Huang, and C. H. Lin, "Increased Color-Conversion Efficiency in Hybrid Light-Emitting Diodes utilizing Non-Radiative Energy Transfer," *Advanced Materials*, vol. 22, pp. 602–606, 2010.
- [14] S. Nizamoglu, E. Sari, J.-H. Baek, I.-H. Lee, and H. V. Demir, "White light generation by resonant nonradiative energy transfer from epitaxial InGaN/GaN quantum wells to colloidal CdSe/ZnS core/shell quantum dots," *New Journal of Physics*, vol. 10, no. 12, p. 123001, 2008.
- [15] W. R. Algar, K. Susumu, J. B. Delehanty, and I. L. Medintz, "Semiconductor quantum dots in bioanalysis: Crossing the valley of death," *Analytical Chemistry*, vol. 83, no. 23, pp. 8826–8837, 2011.
- [16] I. L. Medintz, H. T. Uyeda, E. R. Goldman, and H. Mattoussi, "Quantum dot bioconjugates for imaging, labelling and sensing," *Nature Materials*, vol. 4, pp. 435–446, 2005.
- [17] J. K. Jaiswal and H. Mattoussi, "Long-term multiple color imaging of live cells using quantum dot bioconjugates," *Nature Biotechnology*, vol. 21, pp. 47–51, 2003.
- [18] 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.

-
- [19] I. L. Medintz, A. R. Clapp, H. Mattoussi, E. R. Goldman, B. Fisher, and J. M. Mauro, "Self-assembled nanoscale biosensors based on quantum dot FRET donors," *Nature Materials*, vol. 2, no. 9, pp. 630–638, 2003.
- [20] D. M. Willard, T. Mutschler, M. Yu, J. Jung, and A. Van Orden, "Directing energy flow through quantum dots: towards nanoscale sensing," *Analytical and Bioanalytical Chemistry*, vol. 384, no. 3, pp. 564–71, 2006.
- [21] T. T. Ruckh, C. G. Skipwith, W. Chang, A. W. Senko, V. Bulovic, P. O. Anikeeva, and H. A. Clark, "Ion-Switchable Quantum Dot Förster Resonance Energy Transfer Rates in Ratiometric Potassium Sensors," *ACS Nano*, vol. 10, no. 4, pp. 4020–4030, 2016.
- [22] T.-H. Kim, K.-S. Cho, E. K. Lee, S. J. Lee, J. Chae, J. W. Kim, D. H. Kim, J.-Y. Kwon, G. Amaratunga, S. Y. Lee, B. L. Choi, Y. Kuk, J. M. Kim, and K. Kim, "Full-colour quantum dot displays fabricated by transfer printing," *Nature Photonics*, vol. 5, no. 3, pp. 176–182, 2011.
- [23] M. Achermann, M. A. Petruska, D. D. Koleske, M. H. Crawford, and V. I. Klimov, "Nanocrystal-based light-emitting diodes utilizing high-efficiency nonradiative energy transfer for color conversion," *Nano Letters*, vol. 6, no. 7, pp. 1396–400, 2006.
- [24] V. Klimov, A. Mikhailovsky, S. Xu, A. Malko, J. Hollingsworth, C. A. Leatherdale, H. Eisler, and M. G. Bawendi, "Optical gain and stimulated emission in nanocrystal quantum dots," *Science*, vol. 290, no. 5490, pp. 314–317, 2000.
- [25] K. H. Lee, C. Y. Han, H. D. Kang, H. Ko, C. Lee, J. Lee, N. Myoung, S. Y. Yim, and H. Yang, "Highly Efficient, Color-Reproducible Full-Color Electroluminescent Devices Based on Red/Green/Blue Quantum Dot-Mixed Multilayer," *ACS Nano*, vol. 9, no. 11, pp. 10941–10949, 2015.
- [26] E. Schubert, *Light-Emitting Diodes - 2nd Edition*. Cambridge University Press, 2006.
- [27] 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.
- [28] V. L. Colvin, M. C. Schlamp, and A. P. Alivisatos, "Light-Emitting-Diodes Made from Cadmium Selenide Nanocrystals and a Semiconducting Polymer," *Nature*, vol. 370, pp. 354–357, 1994.

- [29] Q. Dai, C. E. Duty, and M. Z. Hu, "Semiconductor-nanocrystals-based white light-emitting diodes," *Small*, vol. 6, no. 15, pp. 1577–1588, 2010.
- [30] G. He, "Warm-white light-emitting diodes integrated with colloidal quantum dots for high luminous efficacy and color rendering," *Optics Letters*, vol. 35, no. 20, pp. 3372–3374, 2010.
- [31] S. Nizamoglu and H. V. Demir, "Förster resonance energy transfer enhanced color-conversion using colloidal semiconductor quantum dots for solid state lighting," *Applied Physics Letters*, vol. 95, no. 15, p. 151111, 2009.
- [32] 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, p. 243107, 2009.
- [33] P. V. Kamat, "Quantum Dot Solar Cells. Semiconductor Nanocrystals as Light Harvesters," *Journal of Physical Chemistry C*, pp. 18737–18753, 2008.
- [34] Z. Liang, K. L. Dzienis, J. Xu, and Q. Wang, "Covalent layer-by-layer assembly of conjugated polymers and CdSe nanoparticles: Multilayer structure and photovoltaic properties," *Advanced Functional Materials*, vol. 16, no. 4, pp. 542–548, 2006.
- [35] E. Mutlugun, S. Nizamoglu, and H. V. Demir, "Highly efficient nonradiative energy transfer using charged CdSe/ZnS nanocrystals for light-harvesting in solution," *Applied Physics Letters*, vol. 95, no. 3, p. 033106, 2009.
- [36] S. Chanyawadee, R. T. Harley, M. Henini, D. V. Talapin, and P. G. Lagoudakis, "Photocurrent enhancement in hybrid nanocrystal quantum-dot p-i-n photovoltaic devices," *Physical Review Letters*, vol. 102, no. 7, p. 077402, 2009.
- [37] S. Chanyawadee, R. T. Harley, D. Taylor, M. Henini, A. S. Susha, A. L. Rogach, and P. G. Lagoudakis, "Efficient light harvesting in hybrid CdTe nanocrystal/bulk GaAs p-i-n photovoltaic devices," *Applied Physics Letters*, vol. 94, no. 23, p. 233502, 2009.
- [38] T. A. Klar, T. Franzl, A. L. Rogach, and J. Feldmann, "Super-efficient exciton funneling in layer-by-layer semiconductor nanocrystal structures," *Advanced Materials*, vol. 17, no. 6, pp. 769–773, 2005.
- [39] W. R. Algar, H. Kim, I. L. Medintz, and N. Hildebrandt, "Emerging non-traditional Förster resonance energy transfer configurations with semiconductor quantum dots:

- Investigations and applications,” *Coordination Chemistry Reviews*, vol. 263-264, no. 1, pp. 65–85, 2014.
- [40] S. Gaponenko, *Introduction to Nanophotonics*. Cambridge University Press, 2005.
- [41] 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. 3157–64, 2007.
- [42] P. P. Pompa, L. Martiradonna, A. Della Torre, F. Della 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. 126–30, 2006.
- [43] K. Okamoto, S. Vyawahare, and A. Scherer, “Surface-plasmon enhanced bright emission from CdSe quantum-dot nanocrystals,” *Journal of the Optical Society of America B*, vol. 23, no. 8, pp. 1674–1678, 2006.
- [44] 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.
- [45] 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. 3115–9, 2005.
- [46] X. M. Hua, J. I. Gersten, and A. Nitzan, “Theory of energy transfer between molecules near solid state particles,” *Journal of Chemical Physics*, vol. 83, no. 7, pp. 3650–3659, 1985.
- [47] A. O. Govorov, J. Lee, and N. A. Kotov, “Theory of plasmon-enhanced Förster energy transfer in optically excited semiconductor and metal nanoparticles,” *Physical Review B*, vol. 76, no. 12, p. 125308, 2007.
- [48] J. Zhang, Y. Fu, and J. R. Lakowicz, “Enhanced Förster Resonance Energy Transfer (FRET) on a Single Metal Particle,” *Journal of Physical Chemistry C*, pp. 50–56, 2007.
- [49] 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.

- [50] X. Zhao, P. Wang, and B. Li, "Surface plasmon enhanced energy transfer in metal-semiconductor hybrid nanostructures," *Nanoscale*, vol. 3, no. 8, pp. 3056–3059, 2011.
- [51] L. Zhao, T. Ming, L. Shao, H. Chen, and J. Wang, "Plasmon-Controlled Förster Resonance Energy Transfer," *Journal of Physical Chemistry C*, vol. 116, no. 14, pp. 8287–8296, 2012.
- [52] M. L.-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.
- [53] V. K. Komarala, A. L. Bradley, Y. P. Rakovich, S. J. Byrne, Y. K. Gun'ko, and A. L. Rogach, "Surface plasmon enhanced Förster resonance energy transfer between the CdTe quantum dots," *Applied Physics Letters*, vol. 93, no. 12, p. 123102, 2008.
- [54] 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. 3341–5, 2011.
- [55] M. Lunz, X. Zhang, V. A. Gerard, Y. K. Gun'ko, V. Lesnyak, N. Gaponik, A. S. Sussha, A. L. Rogach, and A. L. Bradley, "Effect of metal nanoparticle concentration on localized surface plasmon mediated Förster resonant energy transfer," *Journal of Physical Chemistry C*, vol. 116, no. 50, pp. 26529–26534, 2012.
- [56] X. Zhang, C. A. Marocico, M. Lunz, V. A. Gerard, Y. K. Gun, V. Lesnyak, N. Gaponik, A. S. Sussha, A. L. Rogach, and A. L. Bradley, "Distance Dependence of Nonradiative Energy Transfer to a Plane of Gold Nanoparticles," *ACS Nano*, vol. 6, no. 10, pp. 9283–9290, 2012.
- [57] 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 förster resonance energy transfer," *ACS Nano*, vol. 8, no. 2, pp. 1273–1283, 2014.
- [58] P. Ghenuche, J. D. Torres, S. B. Moparthi, and V. Grigoriev, "Nanophotonic Enhancement of the Förster Resonance Energy- Transfer Rate with Single Nanoapertures," *Nano Letters*, vol. 14, pp. 4707–4714, 2014.

-
- [59] X. Zhang, *Localised Surface Plasmon Mediated Energy Transfer in Quantum Dot Systems*. PhD thesis, Trinity College Dublin, 2014.
- [60] A. Aubry, D. Y. Lei, A. I. Fernandez-Dominguez, Y. Sonnefraud, S. A. Maier, and J. B. Pendry, "Plasmonic Light-Harvesting Devices over the Whole Visible Spectrum," *Nano Letters*, vol. 10, pp. 2574–2579, 2010.
- [61] S. Chandra, J. Doran, S. McCormack, M. Kennedy, and A. Chatten, "Enhanced quantum dot emission for luminescent solar concentrators using plasmonic interaction," *Solar Energy Materials and Solar Cells*, vol. 98, pp. 385–390, 2012.
- [62] S. Jin, H.-J. Son, O. K. Farha, G. P. Wiederrecht, and J. T. Hupp, "Energy Transfer from Quantum Dots to Metal - Organic Frameworks for Enhanced Light Harvesting," *Journal of American Chemical Society*, vol. 135, pp. 955–958, 2013.
- [63] L. Higgins, V. Karanikolas, C. Marocico, A. Bell, T. C. Sadler, P. Parbrook, and A. Bradley, "Carrier density dependence of plasmon-enhanced nonradiative energy transfer in a hybrid quantum well-quantum dot structure," *Optic Express*, vol. 23, no. 2, p. 1377, 2015.
- [64] S. Nizamoglu, E. Sari, J.-H. Baek, I.-H. Lee, and H. V. Demir, "Nonradiative resonance energy transfer directed from colloidal CdSe/ZnS quantum dots to epitaxial In-GaN/GaN quantum wells for solar cells," *Physica Status Solidi (RRL) - Rapid Research Letters*, vol. 4, no. 7, pp. 178–180, 2010.
- [65] M. Olutas, B. Guzelturk, Y. Kelestemur, K. Gungor, and H. V. Demir, "Highly Efficient Nonradiative Energy Transfer from Colloidal Semiconductor Quantum Dots to Wells for Sensitive Noncontact Temperature Probing," *Advanced Functional Materials*, vol. 26, no. 17, pp. 2891–2899, 2016.
- [66] K. M. Goodfellow, C. Chakraborty, K. Sowers, P. Waduge, M. Wanunu, T. Krauss, K. Driscoll, and A. N. Vamivakas, "Distance-dependent energy transfer between CdSe/CdS quantum dots and a two-dimensional semiconductor," *Applied Physics Letters*, vol. 108, no. 2, p. 021101, 2016.
- [67] 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.

- [68] 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.
- [69] N. Gaponik, D. V. Talapin, A. L. Rogach, K. Hoppe, V. Shevchenko, A. Kornowski, and A. Eychmüller, "Thiol-Capping of CdTe Nanocrystals: An Alternative to Organometallic Synthetic Routes," *Journal of Physical Chemistry B*, pp. 7177–7185, 2002.
- [70] 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," *Journal of Physical Chemistry C*, pp. 14628–14637, 2007.
- [71] P. Reiss, J. Bleuse, and A. Pron, "Highly Luminescent CdSe/ZnSe Core/Shell Nanocrystals of Low Size Dispersion," *Nano*, pp. 21–24, 2010.
- [72] 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.
- [73] 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, pp. 44–47, 2008.
- [74] A. L. Rogach, ed., *Semiconductor Nanocrystal Quantum Dots: Synthesis, Assembly, Spectroscopy and Applications*. Springer Wien New York, 2008.
- [75] J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*. Springer, 3 ed., 2006.
- [76] I. L. Medintz and N. Hildebrandt, *FRET - Forster Resonance Energy Transfer: From Theory to Applications*. Wiley-VCH, 2014.
- [77] M. Lunz, *Förster Resonant Energy Transfer in Nanocrystal Quantum Dot Structures*. PhD thesis, Trinity College Dublin, 2010.
- [78] 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.
- [79] P. K. Wolber and B. S. Hudson, "An analytic solution to the Förster energy transfer problem in two dimensions.," *Biophysical Journal*, vol. 28, no. 2, pp. 197–210, 1979.

-
- [80] M. Lunz, A. Bradley, V. Gerard, S. Byrne, Y. Gun'ko, V. Lesnyak, and N. Gaponik, "Concentration dependence of Förster resonant energy transfer between donor and acceptor nanocrystal quantum dot layers: Effect of donor-donor interactions," *Physical Review B*, vol. 83, no. 11, p. 115423, 2011.
- [81] G. Scholes and D. Andrews, "Resonance energy transfer and quantum dots," *Physical Review B*, vol. 72, no. 12, p. 125331, 2005.
- [82] M. Lunz, A. L. Bradley, W.-Y. Chen, and Y. K. Gun'ko, "Förster resonant energy transfer in quantum dot layers," *Superlattices and Microstructures*, vol. 47, no. 1, pp. 98–102, 2010.
- [83] M. Lunz, A. L. Bradley, V. Lesnyak, and N. Gaponik, "Influence of quantum dot concentration on Förster resonant energy transfer in monodispersed nanocrystal quantum dot monolayers," *Physical Review B*, vol. 81, no. 20, p. 205316, 2010.
- [84] D. L. Dexter, "A Theory of Sensitized Luminescence in Solids," *Journal of Chemical Physics*, vol. 21, no. 5, p. 836, 1953.
- [85] R. A. Marcus, "On the Theory of Oxidation-Reduction Reactions Involving Electron Transfer. I," *Journal of Chemical Physics*, vol. 24, no. 5, p. 966, 1956.
- [86] R. A. Marcus, "Electrostatic Free Energy and Other Properties of States Having Nonequilibrium Polarization. I," *Journal of Chemical Physics*, vol. 24, no. 5, p. 979, 1956.
- [87] D. L. Andrews, "A unified theory of radiative and radiationless molecular energy transfer," *Chemical Physics*, vol. 135, no. 2, pp. 195–201, 1989.
- [88] R. M. Clegg, "Förster Resonance Energy transfer-FRET what is it, why do it, and how it's done," in *FRET and FLIM Techniques* (T. Gadella, ed.), ch. 1, pp. 1–48, Elsevier Science, 1 ed., 2009.
- [89] P. Andrew and W. L. Barnes, "Energy Transfer Across a Metal Film Mediated by Surface Plasmon Polaritons," *Science*, vol. 306, no. 5698, pp. 1002–1005, 2004.
- [90] P. F. Barbara, T. J. Meyer, and M. A. Ratner, "Contemporary Issues in Electron Transfer Research," *Journal of Physical Chemistry*, vol. 100, no. 31, pp. 13148–13168, 1996.

- [91] D. D. Adams, L. Brus, C. Chidsey, S. Creager, C. Creutz, C. Kagan, P. Kamat, O. Marya Lieberman, S. Lindsay, R. Marcus, and Others, "Charge transfer on the nanoscale: current status," *Journal of Physical Chemistry B*, vol. 107, no. 28, pp. 6668–6697, 2003.
- [92] K. A. Willets and R. P. Van Duyne, "Localized surface plasmon resonance spectroscopy and sensing," *Annual Review of Physical Chemistry*, vol. 58, pp. 267–297, 2007.
- [93] P. Anger, P. Bharadwaj, and L. Novotny, "Enhancement and Quenching of Single-Molecule Fluorescence," *Physical Review Letters*, vol. 96, p. 113002, mar 2006.
- [94] 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 Letters*, vol. 4, no. 3, pp. 451–457, 2004.
- [95] Y.-P. Hsieh, C.-T. Liang, Y.-F. Chen, C.-W. Lai, and P.-T. Chou, "Mechanism of giant enhancement of light emission from Au/CdSe nanocomposites," *Nanotechnology*, vol. 18, no. 41, p. 415707, 2007.
- [96] J. Lee, A. O. Govorov, J. Dulka, and N. A. Kotov, "Bioconjugates of CdTe Nanowires and Au Nanoparticles: Plasmon-Exciton Interactions, Luminescence Enhancement, and Collective Effects," *Nano Letters*, vol. 4, no. 12, pp. 2323–2330, 2004.
- [97] J. Lee, T. Javed, T. Skeini, A. O. Govorov, G. W. Bryant, and N. A. Kotov, "Bioconjugated Ag nanoparticles and CdTe nanowires: metamaterials with field-enhanced light absorption," *Angewandte Chemie (International ed. in English)*, vol. 45, no. 29, pp. 4819–23, 2006.
- [98] 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.
- [99] 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.
- [100] K. Okamoto, I. Niki, A. Shvartsner, 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.

- [101] K. Okamoto, I. Niki, A. Scherer, Y. Narukawa, T. Mukai, and Y. Kawakami, "Surface plasmon enhanced spontaneous emission rate of InGaN/GaN quantum wells probed by time-resolved photoluminescence spectroscopy," *Applied Physics Letters*, vol. 87, no. 7, p. 071102, 2005.
- [102] 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.
- [103] 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.
- [104] 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.
- [105] 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*, 2006.
- [106] 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. 5462–7, 2006.
- [107] Y. Chen, M. B. O'Donoghue, Y. F. Huang, H. Kang, J. A. Phillips, X. Chen, M. C. Estevez, C. J. Yang, and W. Tan, "A surface energy transfer nanoruler for measuring binding site distances on live cell surfaces," *Journal of the American Chemical Society*, vol. 132, no. 46, pp. 16559–16570, 2010.
- [108] G. P. Acuna, M. Bucher, I. H. Stein, C. Steinhauer, A. Kuzyk, P. Holzmeister, R. Schreiber, A. Moroz, F. D. Stefani, T. Liedl, F. C. Simmel, and P. Tinnefeld, "Distance dependence of single-fluorophore quenching by gold nanoparticles studied on DNA origami," *ACS Nano*, vol. 6, no. 4, pp. 3189–3195, 2012.
- [109] E. Dulkeith, A. C. Morteani, T. Niedereichholz, T. A. Klar, J. Feldmann, S. A. Levi, F. C. J. M. van Veggel, D. N. Reinhoudt, M. Möller, and D. I. Gittins, "Fluorescence

- quenching of dye molecules near gold nanoparticles: radiative and nonradiative effects,” *Physical Review Letters*, vol. 89, no. 20, p. 203002, 2002.
- [110] P. Reineck, D. Gomez, S. H. Ng, M. Karg, T. Bell, P. Mulvaney, and U. Bach, “Distance and wavelength dependent quenching of molecular fluorescence by Au@SiO₂ core-shell nanoparticles,” *ACS Nano*, vol. 7, no. 8, pp. 6636–6648, 2013.
- [111] S. Chowdhury, Z. Wu, A. Jaquins-Gerstl, S. Liu, A. Dembska, B. A. Armitage, R. Jin, and L. A. Peteanu, “Wavelength dependence of the fluorescence quenching efficiency of nearby dyes by gold nanoclusters and nanoparticles: The roles of spectral overlap and particle size,” *Journal of Physical Chemistry C*, vol. 115, no. 41, pp. 20105–20112, 2011.
- [112] Z. Gueroui and A. Libchaber, “Single-molecule measurements of gold-quenched quantum dots,” *Physical Review Letters*, vol. 93, no. 16, p. 166108, 2004.
- [113] M. Li, S. K. Cushing, Q. Wang, X. Shi, L. A. Hornak, Z. Hong, and N. Wu, “Size-Dependent Energy Transfer between CdSe/ZnS Quantum Dots and Gold Nanoparticles,” *Journal of Physical Chemistry C*, vol. 2, pp. 2125–2129, 2011.
- [114] J. Zhang, R. Badugu, and J. R. Lakowicz, “Fluorescence quenching of CdTe nanocrystals by bound gold nanoparticles in aqueous solution,” *Plasmonics*, vol. 3, no. 1, pp. 3–11, 2008.
- [115] K. K. Haldar, T. Sen, and A. Patra, “Metal Conjugated Semiconductor Hybrid Nanoparticle-Based Fluorescence Resonance Energy Transfer,” *Journal of Physical Chemistry C*, vol. 114, no. 11, pp. 4869–4864, 2010.
- [116] S. Saraswat, A. Desireddy, D. Zheng, L. Guo, H. P. Lu, T. P. Bigioni, and D. Isailovic, “Energy Transfer from Fluorescent Proteins to Metal Nanoparticles,” *Journal of Physical Chemistry C*, vol. 115, no. 35, pp. 17587–17593, 2011.
- [117] 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. 9383–91, 2010.
- [118] X. Li, J. Qian, L. Jiang, and S. He, “Fluorescence quenching of quantum dots by gold nanorods and its application to DNA detection,” *Applied Physics Letters*, vol. 94, no. 6, pp. 2007–2010, 2009.
- [119] 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.

- [120] 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," *Journal of Chemical Physics*, vol. 144, no. 2, p. 024108, 2016.
- [121] 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," *Journal of Fluorescence*, vol. 13, no. 1, 2003.
- [122] 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 förster energy transfer between semiconductor quantum dots via dual-resonance nanoantenna effects," *Applied Physics Letters*, vol. 96, no. 4, pp. 2008–2011, 2010.
- [123] 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. 10–13, 2010.
- [124] R. G. West and S. M. Sadeghi, "Enhancement of energy transfer between quantum dots: The impact of metallic nanoparticle sizes," *Journal of Physical Chemistry C*, vol. 116, no. 38, pp. 20496–20503, 2012.
- [125] 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.
- [126] 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.
- [127] T. Ozel, S. Nizamoglu, M. A. Sefunc, O. Samarskaya, I. O. Ozel, E. Mutlugun, V. Lesnyak, N. Gaponik, A. Eychmüller, 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.
- [128] 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.

- [129] B. Weisbuch, Claude and Vinter, *Quantum Semiconductor Structures: Fundamentals and Applications*. Academic Press, 1991.
- [130] P. S. Zory, ed., *Quantum Well Lasers*. Academic Press, 1993.
- [131] W. W. Chow and S. W. Koch, *Semiconductor-Laser Fundamentals*. Springer-Verlag Berlin Heidelberg, 1 ed., 1999.
- [132] S. Lu and A. Madhukar, "Nonradiative resonant excitation transfer from nanocrystal quantum dots to adjacent quantum channels," *Nano Letters*, vol. 7, no. 11, pp. 3443–3451, 2007.
- [133] 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.
- [134] A. H. Mueller, M. A. Petruska, M. Achermann, D. J. Werder, E. A. Akhadow, 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. 1039–44, 2005.
- [135] 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.
- [136] H. V. Demir, S. Nizamoglu, T. Erdem, E. Mutlugun, N. Gaponik, and A. Eychmüller, "Quantum dot integrated LEDs using photonic and excitonic color conversion," *Nano Today*, vol. 6, no. 6, pp. 632–647, 2011.
- [137] O. Jani, I. Ferguson, C. Honsberg, and S. Kurtz, "Design and characterization of GaN/InGaN solar cells," *Applied Physics Letters*, vol. 91, no. 13, p. 132117, 2007.
- [138] R. Dahal, B. Pantha, J. Li, J. Y. Lin, and H. X. Jiang, "InGaN/GaN multiple quantum well solar cells with long operating wavelengths," *Applied Physics Letters*, vol. 94, no. 6, p. 063505, 2009.
- [139] 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.

-
- [140] M. Brossard, C.-Y. Hong, M. Hung, P. Yu, M. D. B. Charlton, P. G. Savvidis, and P. G. Lagoudakis, "Novel Non-radiative Exciton Harvesting Scheme Yields a 15% Efficiency Improvement in High-Efficiency III-V Solar Cells," *Advanced Optical Materials*, vol. 3, no. 2, pp. 263–269, 2015.
- [141] D. Basko, G. C. Rocca, F. Bassani, and V. M. Agranovich, "Förster energy transfer from a semiconductor quantum well to an organic material overlayer," *European Physical Journal B*, vol. 8, pp. 353–362, 1999.
- [142] G. Heliotis, P. N. Stavrinou, D. D. C. Bradley, E. Gu, C. Griffin, C. W. Jeon, and M. D. Dawson, "Spectral conversion of InGaN ultraviolet microarray light-emitting diodes using fluorene-based red-, green-, blue-, and white-light-emitting polymer overlayer films," *Applied Physics Letters*, vol. 87, no. 10, pp. 1–4, 2005.
- [143] G. Heliotis, G. Itskos, R. Murray, M. D. Dawson, I. M. Watson, and D. D. C. Bradley, "Hybrid Inorganic/Organic Semiconductor Heterostructures with Efficient Non-Radiative Energy Transfer," *Advanced Materials*, vol. 18, no. 3, pp. 334–338, 2006.
- [144] S. Nizamoglu and H. V. Demir, "Excitation resolved color conversion of CdSe/ZnS core/shell quantum dot solids for hybrid white light emitting diodes," *Journal of Applied Physics*, vol. 105, no. 8, p. 083112, 2009.
- [145] R. Smith, B. Liu, J. Bai, and T. Wang, "Hybrid III-nitride/organic semiconductor nanostructure with high efficiency nonradiative energy transfer for white light emitters," *Nano Letters*, vol. 13, no. 7, pp. 3042–3047, 2013.
- [146] S. Lu, Z. Lingley, T. Asano, D. Harris, T. Barwicz, S. Guha, and A. Madhukar, "Photocurrent induced by nonradiative energy transfer from nanocrystal quantum dots to adjacent silicon nanowire conducting channels: Toward a new solar cell paradigm," *Nano Letters*, vol. 9, no. 12, pp. 4548–4552, 2009.
- [147] O. Seitz, L. Caillard, H. M. Nguyen, C. Chiles, Y. J. Chabal, and a. V. Malko, "Optimizing non-radiative energy transfer in hybrid colloidal-nanocrystal/silicon structures by controlled nanopillar architectures for future photovoltaic cells," *Applied Physics Letters*, vol. 100, no. 2, p. 021902, 2012.
- [148] A. Yeltik, B. Guzelturk, P. Ludwig Hernandez-Martinez, S. Akhavan, and H. Volkan Demir, "Excitonic enhancement of nonradiative energy transfer to bulk silicon with the hybridization of cascaded quantum dots," *Applied Physics Letters*, vol. 103, no. 26, p. 261103, 2013.

- [149] W. J. I. De Benedetti, M. T. Nimmo, S. M. Rupich, L. M. Caillard, Y. N. Gartstein, Y. J. Chabal, and A. V. Malko, "Efficient directed energy transfer through size-gradient nanocrystal layers into silicon substrates," *Advanced Functional Materials*, vol. 24, no. 31, pp. 5002–5010, 2014.
- [150] A. R. Clapp, I. L. Medintz, and H. Mattoussi, "Förster resonance energy transfer investigations using quantum-dot fluorophores.," *ChemPhysChem*, vol. 7, no. 1, pp. 47–57, 2006.
- [151] U. Resch-Genger, M. Grabolle, S. Cavaliere-Jaricot, R. Nitschke, and T. Nann, "Quantum dots versus organic dyes as fluorescent labels.," *Nature Methods*, vol. 5, no. 9, pp. 763–775, 2008.
- [152] H. A. Atwater and A. Polman, "Plasmonics for improved photovoltaic devices.," *Nature Materials*, vol. 9, no. 3, pp. 205–213, 2010.
- [153] S. Pillai, K. R. Catchpole, T. Trupke, and M. A. Green, "Surface plasmon enhanced silicon solar cells," *Journal of Applied Physics*, vol. 101, no. 9, p. 093105, 2007.
- [154] Y. Lee, C. Jung, J. Park, and H. Seo, "Surface Plasmon-Driven Hot Electron Flow Probed with Metal-Semiconductor Nanodiodes," *Nano Letters*, pp. 4251–4255, 2011.
- [155] S. Mubeen, G. Hernandez-Sosa, D. Moses, J. Lee, and M. Moskovits, "Plasmonic photosensitization of a wide band gap semiconductor: Converting plasmons to charge carriers," *Nano Letters*, vol. 11, no. 12, pp. 5548–5552, 2011.
- [156] Y. Tian and T. Tatsuma, "Plasmon-induced photoelectrochemistry at metal nanoparticles supported on nanoporous TiO₂.," *Chemical Communications*, no. 16, pp. 1810–1, 2004.
- [157] K. Yu, Y. Tian, and T. Tatsuma, "Size effects of gold nanoparticles on plasmon-induced photocurrents of gold-TiO₂ nanocomposites.," *Physical Chemistry Chemical Physics*, vol. 8, no. 46, pp. 5417–20, 2006.
- [158] S. Jin, E. Demarco, M. J. Pellin, O. K. Farha, G. P. Wiederrecht, and J. T. Hupp, "Distance-engineered plasmon-enhanced light harvesting in CdSe quantum dots," *Journal of Physical Chemistry Letters*, vol. 4, no. 20, pp. 3527–3533, 2013.
- [159] S. A. Crooker, T. Barrick, J. A. Hollingsworth, and V. I. Klimov, "Multiple temperature regimes of radiative decay in CdSe nanocrystal quantum dots: Intrinsic limits to the dark-exciton lifetime," *Applied Physics Letters*, vol. 82, no. 17, p. 2793, 2003.

-
- [160] C. De Mello Donegá, M. Bode, and A. Meijerink, “Size- and temperature-dependence of exciton lifetimes in CdSe quantum dots,” *Physical Review B*, vol. 74, no. 8, p. 085320, 2006.
- [161] D. Valerini, A. Cretí, M. Lomascolo, L. Manna, R. Cingolani, and M. Anni, “Temperature dependence of the photoluminescence properties of colloidal CdSe/ZnS core/shell quantum dots embedded in a polystyrene matrix,” *Physical Review B*, vol. 71, no. 23, p. 235409, 2005.
- [162] M. S. Gaponenko, A. A. Lutich, N. A. Tolstik, A. A. Onushchenko, A. M. Malyarevich, E. P. Petrov, and K. V. Yumashev, “Temperature-dependent photoluminescence of PbS quantum dots in glass: Evidence of exciton state splitting and carrier trapping,” *Physical Review B*, vol. 82, no. 12, p. 125320, 2010.
- [163] O. Labeau, P. Tamarat, and B. Lounis, “Temperature Dependence of the Luminescence Lifetime of Single CdSe/ZnS Quantum Dots,” *Physical Review Letters*, vol. 90, no. 25, p. 257404, 2003.
- [164] D. Kim, K. Okazaki, and M. Nakayama, “Temperature dependence of the energy transfer of exciton states in bilayer structures of CdSe/ZnS quantum dots,” *Physical Review B*, vol. 80, no. 4, p. 045322, 2009.
- [165] A. Efros, M. Rosen, M. Kuno, M. Nirmal, D. Norris, and M. Bawendi, “Band-edge exciton in quantum dots of semiconductors with a degenerate valence band: Dark and bright exciton states,” *Physical Review B*, vol. 54, no. 7, pp. 4843–4856, 1996.
- [166] P. Lavallard, M. Chamarro, J. Pérez-Conde, A. K. Bhattacharjee, S. V. Goupalov, and A. A. Lipovskii, “Exchange interaction and acoustical phonon modes in CdTe nanocrystals,” *Solid State Communications*, vol. 127, no. 6, pp. 439–442, 2003.
- [167] D. Oron, A. Aharoni, C. De Mello Donega, J. Van Rijssel, A. Meijerink, and U. Banin, “Universal role of discrete acoustic phonons in the low-temperature optical emission of colloidal quantum dots,” *Physical Review Letters*, vol. 102, no. 17, p. 177402, 2009.
- [168] J. Eilers, J. V. Hest, A. Meijerink, and C. D. M. Donega, “Unravelling the Size and Temperature Dependence of Exciton Lifetimes in Colloidal ZnSe Quantum Dots,” *Journal of Physical Chemistry C*, vol. 118, no. 40, pp. 23313–23319, 2014.
- [169] S. Brovelli, R. D. Schaller, S. A. Crooker, F. García-Santamaría, Y. Chen, R. Viswanatha, J. A. Hollingsworth, H. Htoon, and V. I. Klimov, “Nano-engineered

- electron-hole exchange interaction controls exciton dynamics in core-shell semiconductor nanocrystals,” *Nature Communications*, vol. 2, p. 280, 2011.
- [170] L. Biadala, B. Siebers, R. Gomes, Z. Hens, D. R. Yakovlev, and M. Bayer, “Tuning Energy Splitting and Recombination Dynamics of Dark and Bright Excitons in CdSe/CdS Dot-in-Rod Colloidal Nanostructures,” *Journal of Physical Chemistry C*, vol. 118, pp. 22309–22316, 2014.
- [171] C. Javaux, B. Mahler, B. Dubertret, A. Shabaev, A. V. Rodina, A. L. Efros, D. R. Yakovlev, F. Liu, M. Bayer, G. Camps, L. Biadala, S. Buil, X. Quelin, and J.-P. Herrier, “Thermal activation of non-radiative Auger recombination in charged colloidal nanocrystals,” *Nature Nanotechnology*, vol. 8, no. 3, pp. 206–212, 2013.
- [172] Y. Chen, T. Okuno, Y. Masumoto, Y. Terai, S. Kuroda, and K. Takita, “Spin relaxation in CdTe quantum dots,” *Physical Review B*, vol. 71, no. 3, p. 033314, 2005.
- [173] G. Morello, M. De Giorgi, S. Kudera, L. Manna, R. Cingolani, and M. Anni, “Temperature and size dependence of nonradiative relaxation and exciton-phonon coupling in colloidal CdTe quantum dots,” *Journal of Physical Chemistry C*, vol. 111, no. 16, pp. 5846–5849, 2007.
- [174] K. P. O’Donnell and X. Chen, “Temperature dependence of semiconductor band gaps,” *Applied Physics Letters*, vol. 58, no. 25, pp. 2924–2926, 1991.
- [175] Y. Varshni, “Temperature dependence of the energy gap in semiconductors,” *Physica*, vol. 34, no. 1, pp. 149–154, 1967.
- [176] G. Decher and J. B. Schlenoff, eds., *Multilayer Thin Films: Sequential Assembly of Nanocomposite Materials: Second Edition*. Wiley-VCH, 2012.
- [177] G. Decher, “Fuzzy Nanoassemblies: Toward Layered Polymeric Multicomposites,” *Science*, vol. 277, no. 5330, pp. 1232–1237, 1997.
- [178] Z. Tang, Y. Wang, P. Podsiadlo, and N. A. Kotov, “Biomedical applications of layer-by-layer assembly: From biomimetics to tissue engineering,” *Advanced Materials*, vol. 18, no. 24, pp. 3203–3224, 2006.
- [179] B.-S. Kim and J.-W. Choi, “Polyelectrolyte Multilayer Microcapsules: Self-Assembly and Toward Bimedical Applications,” *Biotechnology and Bioprocess Engineering*, vol. 12, pp. 323–332, 2007.

-
- [180] C. A. Constantine, K. M. Gattás-Asfura, S. V. Mello, G. Crespo, V. Rastogi, T. C. Cheng, J. J. DeFrank, and R. M. Leblanc, "Layer-by-layer biosensor assembly incorporating functionalized quantum dots," *Langmuir*, vol. 19, no. 23, pp. 9863–9867, 2003.
- [181] G. De Bastida, F. J. Arregui, J. Goicoechea, and I. R. Matias, "Quantum dots-based optical fiber temperature sensors fabricated by layer-by-layer," *IEEE Sensors Journal*, vol. 6, no. 6, pp. 1378–1379, 2006.
- [182] R. Kniprath, J. P. Rabe, J. T. McLeskey, D. Wang, and S. Kirstein, "Hybrid photovoltaic cells with II-VI quantum dot sensitizers fabricated by layer-by-layer deposition of water-soluble components," *Thin Solid Films*, vol. 518, no. 1, pp. 295–298, 2009.
- [183] J. De Girolamo, P. Reiss, M. Zagorska, R. De Bettignies, S. Bailly, J.-Y. Mevellec, S. Lefrant, J.-P. Travers, and A. Pron, "Layer-by-layer assembled composite films of side-functionalized poly(3-hexylthiophene) and CdSe nanocrystals: electrochemical, spectroelectrochemical and photovoltaic properties.," *Physical Chemistry Chemical Physics*, vol. 10, no. 27, pp. 4027–4035, 2008.
- [184] T. Franzl, D. S. Koktysh, T. A. Klar, A. L. Rogach, J. Feldmann, and N. Gaponik, "Fast energy transfer in layer-by-layer assembled CdTe nanocrystal bilayers," *Applied Physics Letters*, vol. 84, no. 15, pp. 2904–2906, 2004.
- [185] D. Kim, S. Okahara, M. Nakayama, and Y. Shim, "Experimental verification of Förster energy transfer between semiconductor quantum dots," *Physical Review B*, vol. 78, no. 15, p. 153301, 2008.
- [186] R. A. McAloney, M. Sinyor, V. Dudnik, and M. Cynthia Goh, "Atomic force microscopy studies of salt effects on polyelectrolyte multilayer film morphology," *Langmuir*, vol. 17, no. 21, pp. 6655–6663, 2001.
- [187] S. Pendlebury, P. Parbrook, D. Mowbray, D. Wood, and K. Lee, "InGaN/GaN quantum wells with low growth temperature GaN cap layers," *Journal of Crystal Growth*, vol. 307, no. 2, pp. 363–366, 2007.
- [188] L. J. Higgins, *Plasmon Mediated Energy Transfer in a Hybrid Quantum Well - Quantum Dot System*. PhD thesis, Trinity College Dublin, 2016.
- [189] W. W. Yu, L. Qu, W. Guo, and X. Peng, "Experimental Determination of the Extinction Coefficient of CdTe , CdSe , and CdS Nanocrystals Experimental Determination of the

- Extinction Coefficient of CdTe , CdSe , and CdS Nanocrystals,” *Chemistry of Materials*, vol. 125, no. 17, pp. 2854–2860, 2003.
- [190] J. J. Mock, D. R. Smith, and S. Schultz, “Local refractive index dependence of plasmon resonance spectra from individual nanoparticles,” *Nano Letters*, vol. 3, no. 4, pp. 485–491, 2003.
- [191] H. Chen, X. Kou, Z. Yang, W. Ni, and J. Wang, “Shape- and size-dependent refractive index sensitivity of gold nanoparticles,” *Langmuir*, vol. 24, no. 10, pp. 5233–5237, 2008.
- [192] J. N. Anker, W. P. Hall, O. Lyandres, N. C. Shah, J. Zhao, and R. P. Van Duyne, “Biosensing with plasmonic nanosensors,” *Nature Materials*, vol. 7, no. 6, pp. 442–453, 2008.
- [193] V. Amendola, O. M. Bakr, and F. Stellacci, “A study of the surface plasmon resonance of silver nanoparticles by the discrete dipole approximation method: Effect of shape, size, structure, and assembly,” *Plasmonics*, vol. 5, no. 1, pp. 85–97, 2010.
- [194] M. Grabolle, M. Spieles, V. Lesnyak, N. Gaponik, A. Eychmüller, and U. Resch-Genger, “Determination of the Fluorescence Quantum Yield of Quantum Dots: Suitable Procedures and Achievable Uncertainties,” *Analytical Chemistry*, vol. 81, no. 15, pp. 6285–6294, 2009.
- [195] L. V. Poulikakos, F. Prins, and W. A. Tisdale, “Transition from thermodynamic to kinetic-limited excitonic energy migration in colloidal quantum dot solids,” *Journal of Physical Chemistry C*, vol. 118, no. 15, pp. 7894–7900, 2014.
- [196] S. F. Wuister, C. De Mello Donegá, and A. Meijerink, “Luminescence temperature anti-quenching of water-soluble CdTe quantum dots: Role of the solvent,” *Journal of the American Chemical Society*, vol. 126, no. 33, pp. 10397–10402, 2004.
- [197] E. J. Mayer, N. T. Pelekanos, J. Kuhl, N. Magnea, and H. Mariette, “Homogeneous linewidths of excitons in CdTe/(Cd,Zn)Te single quantum wells,” *Physical Review B*, vol. 51, no. 23, pp. 17263–17266, 1995.
- [198] S. Rudin and T. L. Reinecke, “Temperature-dependent exciton linewidths in semiconductor quantum wells,” *Physical Review B*, vol. 41, no. 5, pp. 3017–3027, 1990.
- [199] A. M. Jagtap, J. Khatei, and K. S. R. Koteswara Rao, “Exciton-phonon scattering and nonradiative relaxation of excited carriers in hydrothermally synthesized CdTe quantum dots,” *Physical Chemistry Chemical Physics*, vol. 17, pp. 27579–27587, 2015.

- [200] G. M. Akselrod, F. Prins, L. V. Poulikakos, E. M. Y. Lee, M. C. Weidman, A. J. Mork, A. P. Willard, V. Bulovic, and W. A. Tisdale, "Subdiffusive Exciton Transport in Quantum Dot Solids," *Nano Letters*, vol. 26, no. 14, pp. 3556–3562, 2014.
- [201] S. F. Wuister, R. Koole, C. M. De Donegá, and A. Meijerink, "Temperature-dependent energy transfer in cadmium telluride quantum dot," *Journal of Physical Chemistry B*, vol. 109, no. 12, pp. 5504–5508, 2005.
- [202] P. T. K. Chin, C. D. M. Donegá, S. S. Van Bavel, S. C. J. Meskers, N. A. J. M. Sommerdijk, and R. A. J. Janssen, "Highly luminescent CdTe/CdSe colloidal heteronanocrystals with temperature-dependent emission color," *Journal of the American Chemical Society*, vol. 129, no. 48, pp. 14880–14886, 2007.
- [203] V. Amendola and M. Meneghetti, "Size Evaluation of Gold Nanoparticles by UV-vis Spectroscopy," *Journal of Physical Chemistry C*, vol. 113, no. 11, pp. 4277–4285, 2009.
- [204] T. Franzl, A. Shavel, A. L. Rogach, N. Gaponik, T. A. Klar, A. Eychmüller, and J. Feldmann, "High-rate unidirectional energy transfer in directly assembled CdTe nanocrystal bilayers," *Small*, vol. 1, no. 4, pp. 392–5, 2005.
- [205] B. Guzelturk, P. L. H. Martinez, Q. Zhang, Q. Xiong, H. Sun, X. W. Sun, A. O. Govorov, and H. V. Demir, "Excitonics of semiconductor quantum dots and wires for lighting and displays," *Laser and Photonics Reviews*, vol. 8, no. 1, pp. 73–93, 2014.
- [206] F. Liu, A. V. Rodina, D. R. Yakovlev, A. A. Golovatenko, A. Greulich, E. D. Vakhtin, A. Susha, A. L. Rogach, Y. G. Kusrayev, and M. Bayer, "Förster energy transfer of dark excitons enhanced by a magnetic field in an ensemble of CdTe colloidal nanocrystals," *Physical Review B*, vol. 92, no. 12, p. 125403, 2015.
- [207] Š. Kos, M. Achermann, V. Klimov, and D. Smith, "Different regimes of Förster-type energy transfer between an epitaxial quantum well and a proximal monolayer of semiconductor nanocrystals," *Physical Review B*, vol. 71, no. 20, p. 205309, 2005.
- [208] H. Wang, C. Zhang, W. Chan, C. Manolatou, S. Tiwari, and F. Rana, "Radiative lifetimes of excitons and trions in monolayers of the metal dichalcogenide MoS₂," *Physical Review B*, vol. 93, no. 4, p. 045407, 2016.
- [209] D. M. Samosvat, O. P. Chikalova-Luzina, and G. G. Zegrya, "Nonradiative resonance energy transfer between quantum dots," *Journal of Experimental and Theoretical Physics*, vol. 121, no. 1, pp. 76–95, 2015.

- [210] R. Baer and E. Rabani, "Theory of resonance energy transfer involving nanocrystals: The role of high multipoles," *Journal of Chemical Physics*, vol. 128, no. 18, p. 184710, 2008.
- [211] P. L. Hernandez-Martinez, A. O. Govorov, and H. V. Demir, "Generalized theory of Förster-type nonradiative energy transfer in nanostructures with mixed dimensionality," *Journal of Physical Chemistry C*, vol. 117, no. 19, pp. 10203–10212, 2013.
- [212] 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.
- [213] O. Ambacher, D. Brunner, R. Dimitrov, M. Stutzmann, A. Sohmer, and F. Scholz, "Absorption of InGaN single quantum wells determined by photothermal deflection spectroscopy," *Japanese Journal of Applied Physics*, vol. 37, no. 3 A, pp. 745–752, 1998.
- [214] C. Jordan, J. F. Donegan, J. Hegarty, B. J. Roycroft, S. Taniguchi, T. Hino, E. Kato, N. Noguchi, and A. Ishibashi, "Carrier-density dependence of the photoluminescence lifetimes in ZnCdSe/ZnSSe quantum wells at room temperature," *Applied Physics Letters*, vol. 74, no. 22, p. 3359, 1999.
- [215] L. Kappei, J. Szczytko, F. Morier-Genoud, and B. Deveaud, "Direct observation of the Mott transition in an optically excited semiconductor quantum well," *Physical Review Letters*, vol. 94, no. 14, p. 147403, 2005.
- [216] K. Fujiwara, N. Tsukada, and T. Nakayama, "Observation of free excitons in room temperature photoluminescence of GaAs/AlGaAs single quantum wells," *Applied Physics Express*, vol. 53, no. 8, pp. 675–677, 1988.
- [217] J. Fouquet and A. Siegman, "Room-temperature photoluminescence times in GaAs/Al_xGa_{1-x}As molecular beam epitaxy multiple quantum well structure," *Applied Physics Letters*, vol. 46, no. 3, pp. 280–282, 1985.
- [218] E. D. Palik, *Handbook of Optical Constants of Solids*. Academic Press, 1985.
- [219] 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,” *International Conference on Transparent Optical Networks*, no. 1, pp. 1–4, 2015.
- [220] D. M. Ledwith, A. M. Whelan, and J. M. Kelly, “A rapid, straight-forward method for controlling the morphology of stable silver nanoparticles,” *Journal of Materials Chemistry*, vol. 17, no. 23, p. 2459, 2007.
- [221] V. D. Karanikolas, C. A. Marocico, and A. L. Bradley, “Dynamical tuning of energy transfer efficiency on a graphene monolayer,” *Physical Review B*, vol. 91, no. 12, p. 125422, 2015.
- [222] V. D. Karanikolas, C. A. Marocico, and A. L. Bradley, “Tunable and long-range energy transfer efficiency through a graphene nanodisk,” *Physical Review B*, vol. 93, no. 3, p. 035426, 2016.
- [223] A. Raja, A. Montoya-Castillo, J. Zultak, X.-X. Zhang, Z. Ye, C. Roquelet, D. A. Chenet, A. M. van der Zande, P. Huang, S. Jockusch, J. C. Hone, D. R. Reichman, L. E. Brus, and T. F. Heinz, “Energy transfer from quantum dots to graphene and MoS₂ : The role of absorption and screening in two-dimensional materials,” *Nano Letters*, 2016.
- [224] F. Prins, A. J. Goodman, and W. A. Tisdale, “Reduced dielectric screening and enhanced energy transfer interactions in single and few-layer MoS₂,” *Nano Letters*, vol. 14, no. 11, pp. 6087–6091, 2014.
- [225] L. Biadala, Y. Louyer, P. Tamarat, and B. Lounis, “Band-edge exciton fine structure of single CdSe/ZnS nanocrystals in external magnetic fields,” *Physical Review Letters*, vol. 105, no. 15, p. 157402, 2010.
- [226] D. E. Blumling, S. McGill, and K. L. Knappenberger, “The influence of applied magnetic fields on the optical properties of zero- and one-dimensional CdSe nanocrystals,” *Nanoscale*, vol. 5, no. 19, pp. 9049–56, 2013.
- [227] L. Biadala, F. Liu, M. D. Tessier, D. R. Yakovlev, B. Dubertret, and M. Bayer, “Recombination Dynamics of Band Edge Excitons in Quasi-Two-Dimensional CdSe Nanoplatelets,” *Nano Letters*, vol. 14, pp. 1134–1139, 2014.
- [228] F. Liu, A. V. Rodina, D. R. Yakovlev, A. Greilich, A. A. Golovatenko, A. S. Susa, A. L. Rogach, Y. G. Kusrayev, and M. Bayer, “Exciton spin dynamics of colloidal CdTe nanocrystals in magnetic fields,” *Physical Review B*, vol. 89, no. 11, p. 115306, 2014.

- [229] D. E. Blumling, T. Tokumoto, S. McGill, and K. L. Knappenberger, "Temperature- and field-dependent energy transfer in CdSe nanocrystal aggregates studied by magnetophotoluminescence spectroscopy," *Physical Chemistry Chemical Physics*, vol. 14, no. 31, pp. 11053–11059, 2012.
- [230] Z. Lin, T. Kerle, T. P. Russell, E. Schäffer, and U. Steiner, "Structure formation at the interface of liquid liquid bilayer in electric field," *Macromolecules*, vol. 35, pp. 3971–3976, 2002.
- [231] J. Kim, L. J. Cote, F. Kim, and J. Huang, "Visualizing graphene based sheets by fluorescence quenching microscopy," *Journal of the American Chemical Society*, vol. 132, no. 1, pp. 260–267, 2010.