ENVIRONMENTAL SENSING USING SEMICONDUCTOR QUANTUM DOTS

Submitted in fulfilment of the requirements of the Materials Science Part II
Examination

by

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I, the undersigned, do hereby declare that all works within this thesis are my own, unless were otherwise indicated and that the thesis conforms to the word and page limits as set out in the Examination Regulations for the Honour School of Materials Science Part II

Signed:…………………………………….

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Abstract

The focus of this project was to develop the necessary equipment and techniques to allow the epifluorescence microscope in the Photonic Nanomaterials Group to continuously record spectral from a single semiconductor nanocrystal while a liquid or gas environment surrounding the nanocrystal is altered. The ability to do so is useful for a two broadly defined reasons:

- Such a technique will allow further insights into the physical processes that govern the fluorescence instabilities observed in colloidal semiconductor quantum dots and allow developments that improve the performance of these important new materials.
- The characterisation of spectral instability variation with surrounding environment change may lead to the development of novel use of colloidal nanocrystals as nanoscale sensors.

I will describe the design and construction of a device that allows photoluminescence spectra from single semiconductor nanocrystals to be monitored in a changing gas environment. Then the performance of the device and some initial results will be presented. I include a novel analysis of fluorescence line width variation when the fluorescence peak is shifted. I was also highlight the challenges faced in conducting photoluminescence experiments in liquids.

Acknowledgements

I would like to express my gratitude for the limitless encouragement and advice given to me throughout my Part II year by all the members of the Photonic Nanomaterials Group. Specifically, I would like to express my sincere thanks to both Simon Fairclough and Benny Sher because without their support with experimental work I am certain this project would not have been possible. I am grateful for the whole Group’s friendly support and advice. I would also like to extend my thanks to two of the technical staff within the department, Laurie Walton and Radka Chakalova for their advice and help with some of the novel manufacturing challenges that I encountered during this project. Finally I would like to thank my supervisor, Dr Jason Smith, for his teaching and advice throughout the year.

Contents

1. Background

1.1 CdSe Nanocrystals

In his 1996 paper Alivisatos describes Quantum Dots as; “Fragments of semiconductor consisting of hundreds to many thousands of atoms- with the bulk geometry and with surface states eliminated by enclosure in a material that has a larger band gap.”[1]

A colloid is a liquid in which a solid particle of diameter between 1nm and 100nm is dispersed in it. Colloidal Semiconductor Nanocrystals have been around since the mid to late1980s. A wholly invented material they were the result of scientists at Bell Laboratories in the US attempting to create a material to spatially modulate electrons. Nanocrystals prior to this had been manufactured through lithographic or self assembly methods and there was great scepticism that a wet chemistry method for manufacture could be found [2]. The quantum dots produced by the colloidal method differ greatly in their properties from the quantum dots produced by other methods. Firstly epitaxial self assembled quantum dots and lithographically defined quantum dots are both grown on a substrate. They may then be left on the substrate or have a matrix grown around them. This differs substantially from the colloidal quantum dots, which are grown in a liquid and are essentially free from their inception.

Colloidal semiconductor nanocrystals are more cheaply and easily produced than many other types of nanocrystals [3]. Cadmium Selenide colloidal nanocrystals have for a long time been used for studies of such structures because they are the very straight forward to grow. Nanocrystals are semiconductor crystallites ranging in size from one to tens of nanometres in diameter, which is smaller than the bulk Bohr exciton diameter in CdSe (12.2nm [4]). Despite their small size nanocrystals retain the bulk crystallography [1]. They exhibit properties that are intermediate between the bulk material and atoms or clusters of atoms that do not maintain the bulk crystallography [5]. The main characteristic of nanocrystals is quantum confinement, resulting in the size dependence of the optical properties.

The Nanocrystals that we will use throughout this report are CdSe/ZnS Core-Shell Nanocrystals manufactured by Evident Inc of the USA that are sold under the brand name Evidot. Figure one shows a core-shell nanocrystal, which is a nanocrystal with a central core of one material, usually of a smaller band gap, surrounded by a shell of another material, which usually has a larger band gap [3]. Cadmium Selenide (E_g=1.74eV), a II-VI semiconductor, is the constituent of Evidot cores and the shell or capping layer is Zinc Sulphide (E_g=3.54eV). It is also important to note that the conduction band edge of the shell material, ZnS, is higher in energy than that of CdSe (i.e. its electron affinity is lower) and the valance band edge of ZnS is lower than that of CdSe. This results in improved confinement of the exciton and enhanced luminescence. On top of the layer of ZnS is an organic capping layer that functions as a passivating layer.

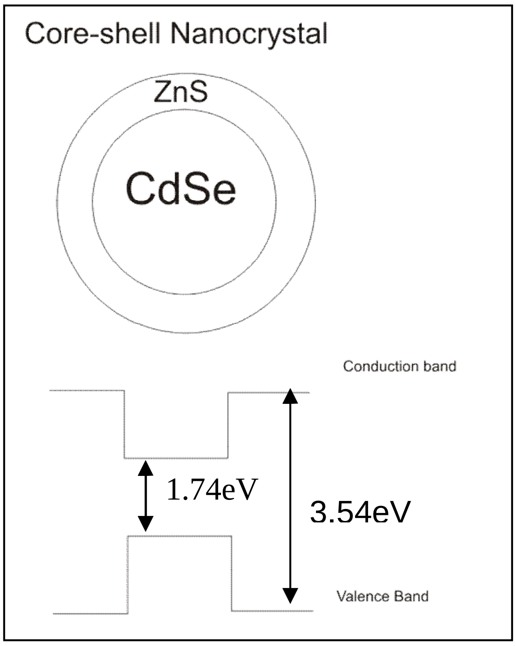


Figure1 Schematic of a core shell nanocrystal and its band structure.

Semiconductor nanocrystals exhibit photoluminescence, which means they are excited by absorbing a photon and then can they can relax from the excited state by emitting another photon. Semiconductor nanocrystals are used or have been proposed for use in a wide variety of applications due to this and other properties. These include OLED [6], Quantum Dot solar cells [7], Lasers [8], fluorescent tags in Biosensing and in vivo imaging [9-11] and as single photon emitters for Quantum Information Processing [12].

1.2 Manufacture of Colloidal NCs

In any study of semiconductor quantum dots it is important that they are of uniform size and shape and have a crystal structure that is consistent with the bulk as well as a consistent surface chemistry. This is because these variables affect the electrical and optical properties of the nanocrystal [13]. Fortunately for our experiments we have a ready supply of dots with such consistent properties from the commercial company Evident. Recently many more firms are offering nanocrystals for sale.

The standard method for producing a colloid of nanoscale crystallites of CdSe is by the thermal decomposition of precursor molecules, which contain the Cadmium and Selenium species that constitute the nanocrystal [2, 3] Control of the nanocrystals size and shape can be achieved through the control of the temperature, the concentration of precursors and the concentration of the coordinating solvent [3]. The precursor molecules are introduced into a reaction vessel heated to around 200°C, this provides the energy to decompose the precursor molecules but is sufficiently low to avoid crystal defects which would reduce the nanocrystals efficiency. The major challenge in producing nanocrystals is to prevent the agglomeration and control the Ostwald ripening of the crystals during the manufacturing: for this reason a coordinating solvent is included. Care is required in choosing a solvent that will sufficiently coordinate the Nanocrystal to prevent agglomeration or ripening but allow the crystal to grow [14]. This method is referred to as TOP/TOPO synthesis in reference to the coordinating solvents tri-*n*- octylphosphine oxide (TOPO) and tri-*n*-octylphosphine (TOP) [13] which are commonly used. The coordinating solvents are also important after growth has stopped and the nanocrystals are returned to lower temperatures. At the lower temperatures the surfactants are more strongly bound to the surface and can, dependant on the surfactant allow the nanocrystal to dissolve in a wide variety of solvents.

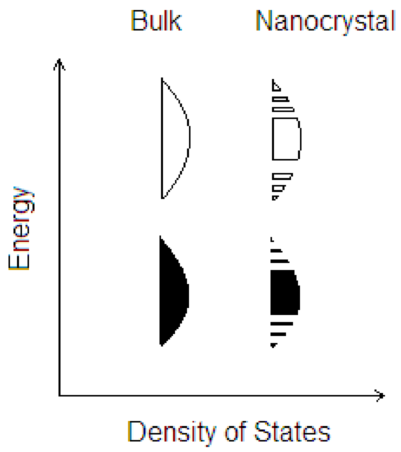
When producing core-shell nanocrystals such as those that we will use, the organic layer is temporarily removed and the wide band ZnS is grown locally epitaxial on the

CdSe core surface. In general such a layer is not thicker than 1.3 monolayer as defects due to lattice mismatch become abundant above such thicknesses [14].

The primary focus in early synthesis research has led to manufacturing methods that produce nanocrystal with narrow size distribution (<5rms), low crystal defect concentration and good control over particle size. Recently improvements to this technique have been reported in literature [15-17]. The improvements in these techniques mainly focus on the reduction of fluorescence intermittence.

1.3 Quantum confinement

The purpose of producing small sized semiconductor crystalline particles is to confine excited charge carriers in three dimensions. Quantum dots are sometimes referred to as zero dimension quantum systems as the carriers have zero dimensions in which to move. The effects of quantum confinement in semiconductor nanocrystals are that the nanocrystals have discrete energy levels rather than continuous band. Another effect of quantum confinement is that these energy levels, and therefore the optical properties are dependant on the size of the nanocrystal.



Schematic comparison between Density of States for a Bulk Semiconductor and a Semiconductor Nanocrystal (After Alivisatos 1996)

Figure 2

If we work out the density of states for a bulk semiconductor we see a continuous distribution however for a quasi-zero dimensional structure such as a quantum dot we observe delta functions for the density of states. This gives discrete energy levels that maybe occupied for by an electron and results in the artificial atom like behaviour.

Bloch's Theorem is used when describing quasi particles in bulk semiconductors. In such a case we regard the material as an infinite repeating periodic potential with perfect translational symmetry and can then describe the particle with a planar wave.

In small crystallites with a finite number of atoms the infinite repeating periodic potential approximation is no longer valid. Two approximations are used when working out energy spectra due to confinement, the weak confinement regime and the strong confinement limit. The weak confinement approximation is valid when the radius of the crystallite is small but larger than the Bohr radius of the exciton and the strong confinement case is when the crystal radius is smaller than the Bohr radius. In

CdSe the Exciton Bohr radius is 4.9nm [5]. The nanocrystal which we are interested in are of a similar if slightly smaller size that the exciton Bohr radius. Therefore the equation that best expresses the energy of the band gap for the lowest energy exciton in CdSe has been found to be a modified version of the Strong Confinement regime;

$$E = E_g + \frac{\pi^2\hbar^2}{2\mu a^2} - 1.786\frac{e^2}{\varepsilon a}$$

In this equation E_g is the band gap of the semiconductor the term proportional to $e^2 / \varepsilon a$ describes the effective Coulomb between the electron and the hole.

1.4 Single Nanocrystal Photoluminescence Spectroscopy

Nanocrystal ensembles exhibit inhomogeneous broadening of the emission spectral line. This gives a Gaussian line shape for the spectra, with a function of the form;

$$S(\omega) = ae^{\frac{-(\omega-\omega_0)^2}{2c^2}}$$

This is a result of averaging of the individual emission spectra which vary in peak wavelength as a result of size and shape distributions, defects, Stark shift as a result of the nanocrystals individual electric field environment. To examine the properties of Nanocrystals it is therefore important to examine spectral information of individual nanocrystals and any luminescence features described from now on are features of single nanocrystal spectroscopy unless otherwise stated. [18, 19].

All single nanocrystal exhibits a similar emission line shape. Firstly there is a narrow peak, which is homogeneously broadened, and a longitudinal optical (LO) phonon peak, which is clearly observable at low temperatures [19]. The homogeneous broadening observed in the main peak means that it can be fitted with a Lorentzian function (Figure 3);

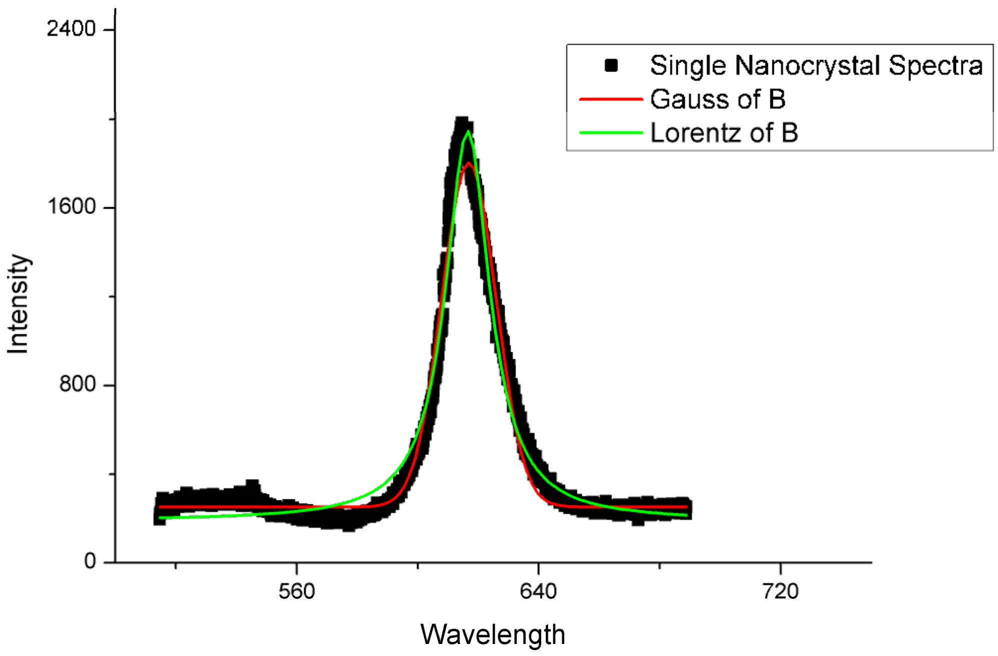
$$I(\omega) = A\frac{\Gamma^2}{(\omega - \omega_0)^2 + \Gamma^2}$$

This line shape is usually found in the emission spectra taken from single atoms and results from emission from discrete energy levels as opposed to broad bands[5] [20]. The line width results from the Heisenberg uncertainty principle;

$$\Delta E \Delta t \geq \frac{\hbar}{2}$$

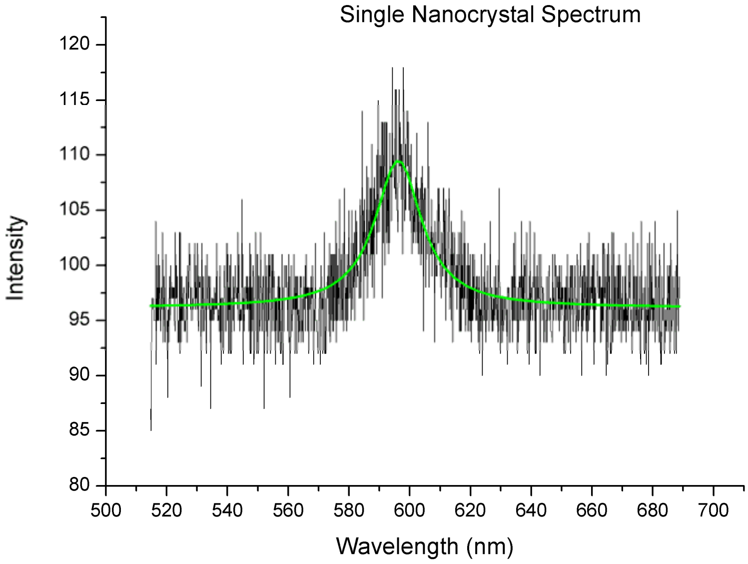
The scattering of the quantum state of the exciton over time is called the dephasing time. As this has a finite value it is not possible to have a discrete energy.

Figure3 Typical single Nanocrystal Spectrum



In fact line broadening occurs due in single nanocrystals due to inhomogeneous processes over time[18] and it is possible by using a shorter integration time to obtain spectra that more closely follow a Lorentzian line shape as can be seen when comparing figure three and figure four. Figure three shows a spectrum that is integrated for 10 seconds while figure four shows a line shape that is closer to the Lorentzian function because the integration time was 0.2 seconds.

Figure 4



The uncertainty in the energy of the bandgap gives the line width by the relationship;

$$\Delta E = -\frac{hc}{\lambda^2}\Delta\lambda$$

1.5 Fluorescence instabilities

Due to their efficient and tuneable Photoluminescence great numbers of potential applications for colloidal nanocrystals have been proposed in fields as diverse as biological labelling and optoelectronics. The major inconvenience for those working in these areas is the instabilities observed in the photoluminescence. The large research effort that has been made into characterising these instabilities has realised much information about the physics that causes these effects. Blinking is the first instability that I will outline as it receives much coverage in the literature. The others being spectral drift, blueing and bleaching.

1.5.1 Blinking Mechanisms

The unexpected phenomenon of blinking was first reported by Nirmal et al[21] in 1996 and is the switching of a nanocrystal between a bright, emitting, state and a dark, non-emitting, state[22] (figure 5). The dark state is long lived and the nanocrystal can remain off for a number of minutes before switching back on, this obviously would not be the case if it was due to a photo-bleaching effect. The mechanism for this process has been widely researched and we now know that the bright state is that of an uncharged nanocrystal while the dark state is a charged nanocrystal [23].

As shown in the schematic diagram figure 6 in a charged nanocrystal the additional charge carrier provides a non radiative recombination route by which the exciton relaxes through an Auger process, where the energy of recombination is transferred to the additional charge carrier [22].

Charging of the nanocrystal is thought to be a result of ejection of one of the two carrier, either electron or hole, from an exciton in the nanocrystal core into either a surface trap state or the surrounding matrix [22]. The electron-hole pair is now spatially separated so may not recombine resulting in the long lived dark state. This may either occur by the thermionic emission of the carrier, tunnelling or an Auger processes if two excitons are present in the nanocrystal (figure7).

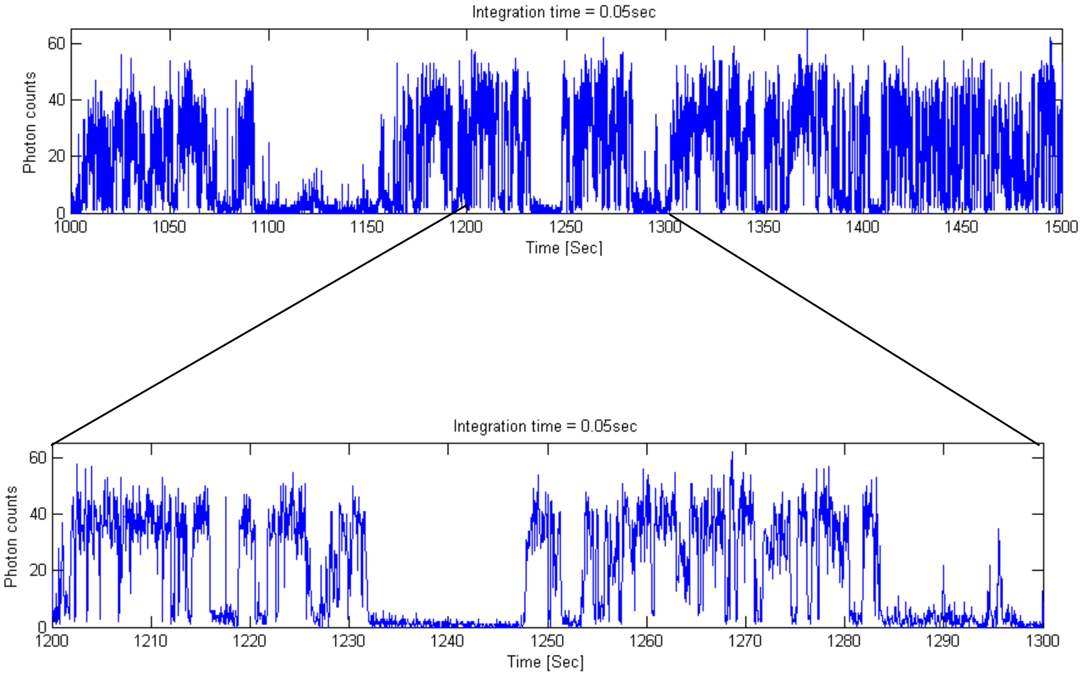


Figure 5- Blinking time trace from Benny Sher showing on and off states or varying times

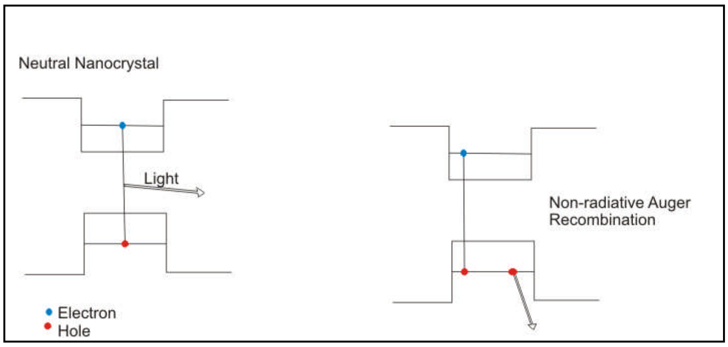


Figure 6-Schematic showing the processes of exciton relaxation in the on state in a neutral nanocrystal and the off state in a charged.

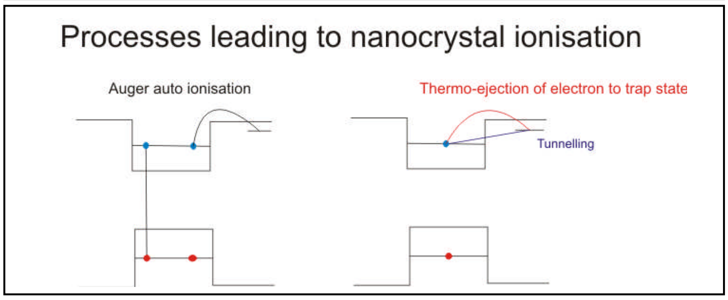


Figure 7- Schematic showing the processes leading to the off state in nanocrystals

1.5.2 Spectral Drift

Spectral Drift is the name given to phenomena where the luminescence peak from a single nanocrystal randomly moves around. These spectral drifts can contribute to line width broadening and we observe increasing line widths with increasing integration time [18]. Spectral drift is a result of changes in the immediate environment surrounding the nanocrystal. The Quantum Confined Stark Effect results in a reduction in the band gap when an electric field is applied to the nanocrystal. The Quantum Confined Stark Effect has been demonstrated in single CdSe nanocrystals [24] and spectral shifts due to this process have been report of an order of magnitude larger than the spectrum line width at room temperature [21].

These random spectral drifts are then attributed to the Quantum Confined Stark Effect as it is believed to occur due to changing electric fields around the nanocrystal [25]. The fields surrounding nanocrystals can change when charge carriers trapped in sites on or near the nanocrystal surface are given sufficient energy to move [4]. This explains the observation of decreasing line width with reduced excitation power [4] as the excess energy from the excitation can be absorbed by the charge carriers located on the surface or in the matrix, which gives these charge carriers sufficient energy to move around. Neuhauser et al [26] report the correlation between Blinking and spectral diffusion that would corroborate this, as the off periods end with the return of a charge carrier this may be a result of an ionisation event in close proximity to the quantum dot or a rearrangement of surface charges. The local electric field surrounding the nanocrystal will now be different so the emission will be altered due to the QCSE.

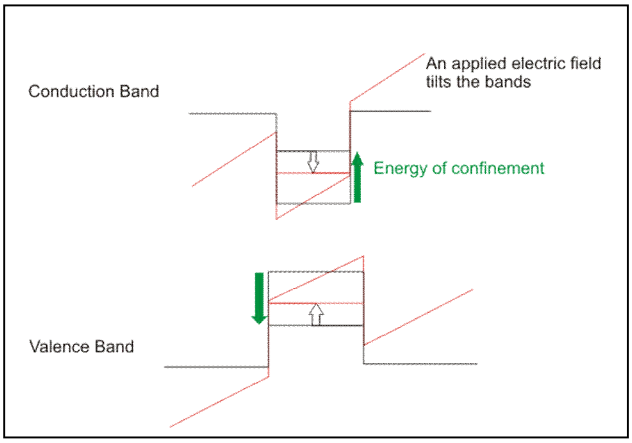


Figure 8- Schematic of the Quantum confined stark effect. Notice the reduction in the confinement energy in the band diagram in the electric field

1.5.3 Blueing

Blueing is a non random and non reversible shift to the blue of the photoluminescence spectrum of a nanocrystal [27]. Shifts in the emission wavelength of up to 40nm to the blue have been reported in CdSe/ZnS core-shell nanocrystals [27]. It is the result of photo oxidation of the nanocrystal, which decreasing the size and increasing the confinement energy, which then results in bluer photoluminescence. Oxidation of the CdSe core in a core shell nanocrystal requires oxygen to diffuse through the ZnS capping layer. It is hypothesised that this is done along grain boundaries which are there as a result of the over growing of a ZnS layer having multiple nucleation sites so ZnS layer is polycrystalline [27]. Alternatively the ZnS layer itself is oxidised resulting in a porous structure that slows the CdSe core to be oxidised.

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2. Literature Review

2.1 Modification of Photoluminescence Phenomena

Recently there have been a few papers reporting modification of blinking behaviour by alteration of the surrounding environment of the nanocrystal. Two of these papers report on modification by liquids [1][2] and one by gas [3]. In the paper by Fomenko et al it is reported that blinking behaviour can be almost entirely suppressed by propyl gallate solution, they also report that other ligands can also suppress blinking [1]. In addition to blinking suppression this paper also reports a 5 fold reduction in fluorescence lifetime [1]. This paper hypothesises that the reduction in blinking is as a result of the saturation of surface trap sites. From the previously discussed auger model of blinking [4] we can see that such saturation would lead to such suppression. In their 2004 paper Hohng and Ha [2]demonstrate a similar suppression of blinking. In this case the thio moiety β-mercaptoethanol (BME) was suggested as the agent of blinking reduction and it is hypothesised that as an electron donor it also binds with surface trap states to prevent the movement of an electron from the core into the surface trap state[2]. In both cases [1, 2] the cessation of blinking activity is first observed upon the introduction of a buffer solution with an appropriate concentration of the stated ligands, the change is reversible by the introduction of a buffer solution without the ligands that, it is hypothesised, causes the ligands to return to solution and the trap sites to become unblocked. A further similarity that exists between the Fomenko [1] and Hohng[2] papers is that both used Streptavidin functionalised Quantum dots from the commercial manufactured Quantum Dot Corp. that are then tethered onto a glass or quartz substrate that has been treated with Biotinylated BSA.

The Streptavidin-Biotin interaction is one of the strongest non-covalent bonds known. The reason for these nanocrystals for these studies is the ease of acquiring Quantum dots that are conjugated to Streptavidin and the strong Avidin-biotin interactions that is widely understood and used in Biology[5], which allows the Nanocrystals to remain in position when the surrounding buffer solution is altered.

In the 2001 paper by Koberling[3] the change in ensemble fluorescence intensity of CdSe/ZnS quantum dots between measurements taken in an Argon environment to those in an Oxygen environment is explained by an increase in blinking in the Oxygen atmosphere. The oxygen is hypothesised to create additional trap states which lead to shortening of the on times but leaves the off times unchanged.

2.2 Optical Sensing/Microprobes

Since the start of the millennium a large effort has been made to produce nanoscale sensors [6, 7][8-11]. The range of applications that have been suggested for such a system is varied. The methods that have been proposed by literature of going about sensing using nanostructures are also varied. Specifically I will focus on environmental sensing using florescence instabilities of semiconductor quantum dots, however it may be useful to quickly familiarise ourselves with other proposed novel sensing methods and, perhaps more importantly, the applications of such techniques and their wider significance. What can be immediately seen from nearly all of the papers referenced at the start of this section is that a nanoscale sensor would be very useful for biological application. Yi Cui et al describe, in their 2001 paper how a functionalised Silicon Nanowire can be used to measure Calcium ion concentrations. Calcium ions are used in biological systems to bring about muscle contraction, protein secretion and other biological processes. The measure of their concentrations within cells may help to understand these processes more fully [11]. Despite demonstrating conclusive results that Calcium ion concentration or at least presence could be measured I am sceptical about the claimed usefulness of such a device as a biosensor. In the paper they suggest that it could be used for array based or in vivo measurements. As the measurement was made by measuring the change in conductance across the Nanowire, which would undoubtedly require a macroscopic set up I find in vivo applications unlikely.

In their 2008 paper Bo Tang et al describe a Nanobiosensor for Glucose and again the high sensitivity and potential for in vivo measurement of such a device or system are touted[10].

Dyadyusha et al suggest using emission quenching of quantum dots as a novel approach to biosensing [12]. This method requires a quantum dot functionalised with DNA. A gold particle with the complimentary DNA sequence may then be introduced and emission is quenched as a result of the gold particle being brought into close proximity of the quantum dot.

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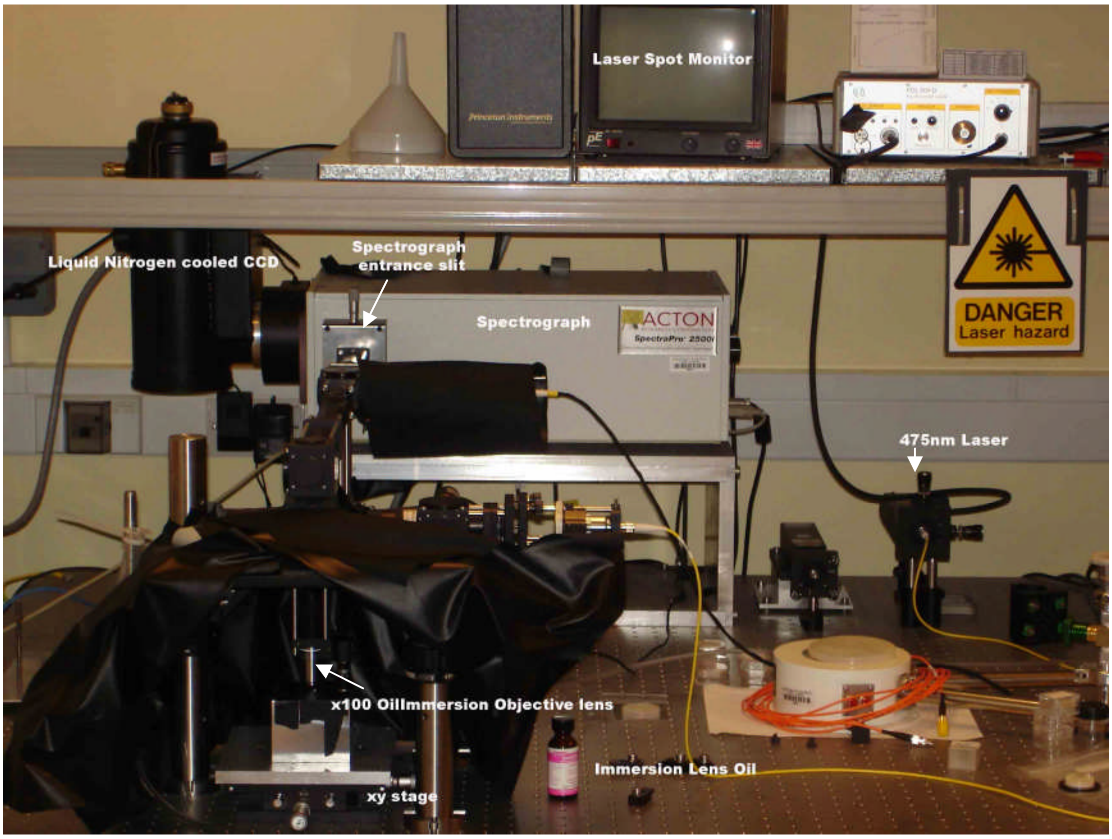
3. Experimental and Equipment Design

The aim of this project is to investigate the possibility of using nanocrystals as sensors. I have identified the possibility of using fluorescence instabilities, as described in the introduction, as being a likely candidate for such an application due to their dependence on the local environment and surface chemistry of the nanocrystals. Such fluorescence instabilities are only obvious in the spectra of single quantum dots due to averaging and inhomogeneous broadening effects observed in the ensemble spectra. Therefore it is important to be able to measure the spectra from a single nanocrystal, which, the Photonic Nanomaterials Group already has a method for doing. All spectra from single nanocrystals are slightly different, due to size distribution, variations in shape, each nanocrystals immediate electronic environment and small variations in surface chemistry. To be sure those variations in the observed in the emission spectra are due to environmental change and not due to variation between nanocrystals it is important to continuously examine the emission from a single nanocrystal while the surrounding environment is in someway altered. It is then hoped that it will be possible to correlate this environmental change to an alteration in the emission behaviour.

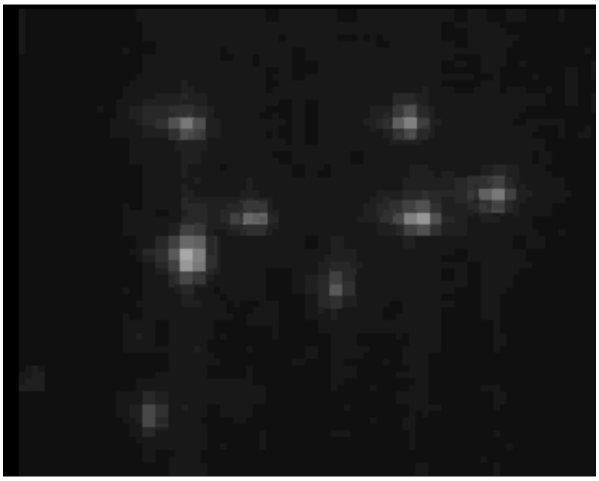
3.1 Imaging Single Nanocrystals

As I have mentioned the Photonic Nanomaterials Group (PNG) has developed a method for examining the Photoluminescence from Nanocrystals. Whether we are interested in spectral data or blinking time traces, such as the one provided by Benny Sher (Figure5) in the introductory section to this report, the sample preparation is the same. The process involves the spin casting a diluted solution of nanocrystals onto a fused silica substrate. The fused silica is used as a substrate as it has low auto fluorescence and the spin casting is used to create a thin film so that nanocrystals are spatially separate so that their emission may be examined individually. The nanocrystals arrive from their manufacturer dissolved in the organic solvent toluene. This solution is too concentrated to use for the spin casting as spatial separation of the nanocrystals adequate for single nanocrystal photoluminescence experiments is not achieved so further dilution is required. The dilution to the supplied solution is made using chloroform and the addition of Poly (methyl methacrylate) (PMMA) and Hexadecylamine (HDA) ligands. PMMA is a synthetic polymer that is added to form a matrix on the surface of the substrate when the dilute solution is spun cast. The thin film provides some level of protection to the nanocrystal from the environment while ensuring that it remains secured to the substrate. The nanocrystals are supplied capped with long chain amines similar to HDA in structure. When the commercial solution is diluted the concentration of these amines also decreases and as a result they dissolve off the surface of the nanocrystal. The HDA ligands are added to the solution to replace any surface ligands which dissolve off the nanocrystal. This is important because if the ligands are stripped from the nanocrystal it may agglomerate with other nanocrystal also the emission efficiency of the nanocrystal will be reduced because the ligands bond to surface traps which play an important role in Auger processes described elsewhere in this report.

The substrates are examined through a home made epifluoresence microscope, shown in the photograph figure 9, which uses standard optical lab equipment. Excitation is provided by a blue laser (475nm), which is usually used in continuous wave mode for these experiments. Collection and excitation is made through the same high numerical aperture lens. The output signal is separated from the excitation using a beam splitter and a filter. The output then enters the spectrograph (Acton SpectraPro 2500i). We can switch between a mirror and a diffraction grating in the spectrograph to allow direct imaging mode and spectroscopy mode respectively. There is a highly sensitive liquid nitrogen cooled CCD (Princeton Instruments Spec 10:100B) attached to the spectrograph for displaying the output on a computer.



Above; Figure 9 Photograph of Microscope



Left; Figure 10 Image of Nanocrystals from CCD camera when using the system in image mode with a mirror in the spectrograph.

When the mirror is in place in the spectrograph light collected from the specimen is directed on to the CCD. The software is then set up appropriately for imaging. As you can see from the above image, figure 10, when used in this set up there is light being collected from a number of nanocrystals concurrently. To take a spectrum from a single nanocrystal when observing such a situation one must first narrow the slit width on the entrance to the spectrograph so that light from only a column wide enough that only light from one nanocrystal enters the spectrograph. We then use the software to bracket only a select number of pixels in the horizontal direction on the CCD. The mirror is then replaced with a diffraction grating and the software is set up to regard the input as spectral data.

The pixel pitch of the CCD is 25µm and the magnification of the optics when using the x100 objective is x93.75. From this we can work out the resolution of the microscope is 0.27µm or 270nm on the substrate surface. In the image taken above the nanocrystals which are <10nm in diameter appear in some cases to be several pixels across in size. It is important to note that the nanocrystals themselves are fluorescing due to the excitation by the laser. As a result the light emitted can be detected by adjacent pixels. The size of the spot of light collected is also diffraction limited (d), the resolution is given by;

$$d = \frac{0.6\lambda}{NA}$$

In this case the NA of the lens is 1.3 and the wavelength of light emitted by the fluorescing nanocrystal is 600nm. This gives the diffraction limit of 277nm. It is important also that when preparing sample the nanocrystals are sufficiently dispersed so that individual nanocrystals can be recognised. Ideally individual nanocrystals would be identified by a Hanbury Brown and Twiss set up[1, 2]. Such a set up involves the use of two Avalanche Photo Diodes to conduct photon anti bunching experiments. In general our sample preparation technique tends to provide single quantum dots that are suitable for observation the majority of the time and this can be verified without using this method. Instead it is possible to verify a nanocrystal is spatially separate from its neighbours by observing the nanocrystal in the imaging mode and ensuring that the nanocrystal demonstrates blinking behaviour with the nanocrystal going fully dark. In this case “fully dark” during “off” events is when only the background count should be visible. To verify a single nanocrystal is observed one can recording an emission spectrum from the nanocrystal and fitting a Lorentzian function to the spectrum.

Obviously from the method outlined above it is important that the nanocrystals remain very still as a movement of a few hundreds of nanometres will move the nanocrystal out of the bracket or slit defined to collect the nanocrystals emission.

3.2 Developing the Techniques to study Nanocrystals in Gas/Liquids

The current microscope set up has certain dimensional limitations that must be accommodated when designing a system so that measurements can be taken from single nanocrystals in a controlled gas or liquid environment. Firstly it is impractical to operate some or all of the optics within a controlled gas atmosphere due to the size of the optics bench and other equipment and obviously it is important that the optics are kept isolated from any liquids. So therefore it is important that the device contain the liquid or gas but allow the liquid or gas to come into contact with the surface on which the nanocrystals are dispersed. The device must also fit into the space below the microscope objective. The dimensions of this space are length and width of 165mm and height 98mm. It is also important to note that the high numerical aperture objective lens that is used to collect sufficient light from such small particles has a working distance of around 0.25mm. This puts the restraint that the objective lens must be able to come within 0.1mm of the top surface of the coverslip.

Due to the size constraints associated with the short working distance of the microscope objective lens I decided that the best method would be to image through the substrate and to contain the liquid on the underside of the substrate. I also thought that a thinner substrate such as a coverslip, with thickness ≤130μm would allow easier imaging of the nanocrystals with the short working distance of the lens. I therefore decided to investigate using a standard glass coverslip as the substrate and image through this while containing the liquid beneath it. Fused silica is used due to its low auto fluorescence, which results from the fused silica's regular crystal structure. Glass has higher auto fluorescence due impurities included during manufacturing. The Fused silica substrates are considerably thicker than the 130µm thick cover glass so the background is very similar. I have found that by using a glass coverslip and focusing on the underside using an oil immersion lens with a special low auto fluorescence immersion lens oil I can greatly increase the signal from the nanocrystal, from ~800 to ~4000 counts per second, with very small increase in background signal (figure11). This is important because photoluminescence measurements can be taken using a lower power excitation, this leads to a more stable spectrum with less instabilities.

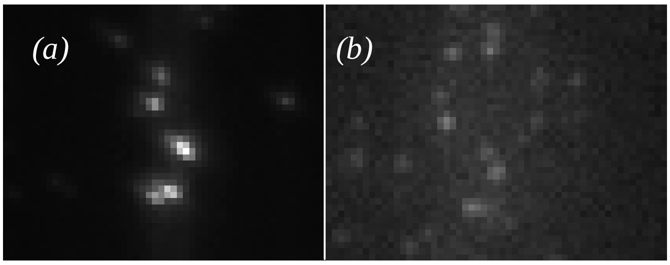


Figure 11; Image (a) is using the 100x oil immersion objective lens. Image (b) is through the 60x lens.

The increase in signal due to the change in objective lens from x60 to x100 oil immersion is due partly to the increase in magnification but also due to the increase in Numerical aperture associated with using an oil immersion lens (figure 12). The original x60 objective lens used in the system has a numerical aperture of 0.7. This is a high numerical aperture lens and this is to increase the light collected by the objective. The oil immersion lens used has a numerical aperture of 1.3 due to the high refractive index ($n \approx 1.4$) or the immersion lens oil. High numerical aperture lenses tend to have a reduced working distance. In the case of the oil immersion lens the working distance is ~0.23mm.

$$NA = n\sin\theta$$

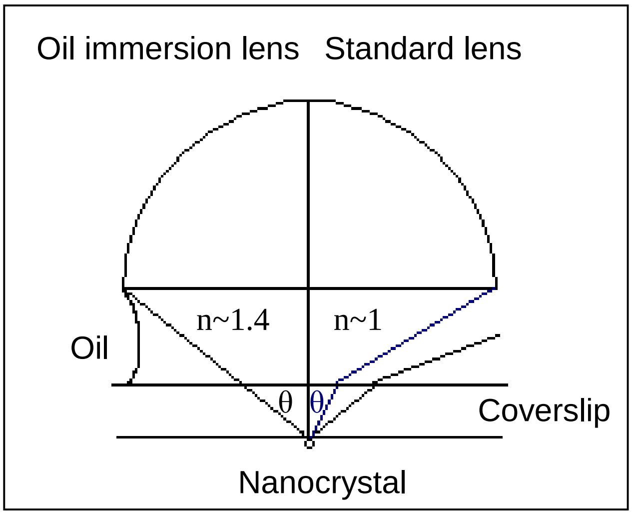


Figure 12; Schematic diagram comparing the angle, θ, for an Oil Immersion lens and a normal lens. The increase in θ and the increase in n results in a larger Numerical Aperture for the Oil immersion lens.

The light collection is proportional to the solid angle, which is the square of the NA. The light collected by the two objects can be compared thus;

$$\left(\frac{1.3}{0.7}\right)^2 = 3.4$$

This can account somewhat for the five fold increase in the intensities of light collected. The rest of the increase maybe accounted for by the increase in excitation power due to the increase in magnification of the optics.

As mentioned above the oil immersion objective lens has a working distance in the region of 0.23mm, it is very important that the lens can approach the substrate unimpeded within this distance. The oil immersion lens has dimensions similar to those of a regular microscope objective. Obviously an objective with a larger working distance is available but such a lens would have a smaller numerical aperture and would therefore impact the strength of the signal that is detected. Therefore the most important consideration while designing the device was to allow the microscope with the working distance of less than one quarter of a millimetre to image the substrate surface where the nanocrystals are positioned.

3.3 Design Process

When conducting the photoluminescence experiments it is important that the substrate and any other material surrounding the substrate do not make a significant contribution to the noise of the system. This requires making the system from a low auto fluorescence material. When laying out the criteria for the initial design the following were identified as most important;

- accommodate the dimensional limitations
- containing the fluid and/or gas
- using low auto fluorescence materials
- Mechanical stability.

Criteria that were less important were also considered at this stage, for example the ability to switch rapidly between environments.

There were three iterations of the design in total. The first two were unsuccessful and a return to the design process was required. During the third iteration a successful device was manufactured. The two unsuccessful designs will be outlined briefly before the description of the working device.

The first design iteration made use of the material that was used in the existing system; fused silica substrates were placed on glass slide to observe them. Glass proved suited to the design of such a device due to its low auto fluorescence and impermeableness while also offering a good degree of chemical inertness, which would allow a variety of environments to be investigated.

The first design used a 250μm diameter hypodermic needle that was to be accommodated in a channel cut into a glass slide using a diamond wheel that was 380μm wide and 500μm. Unfortunately this needle provided insufficient flow rate for fluids, and other manufacturing problems due to its small size. So it was decided to move to a needle of 500μm diameter so a wider channel was required in the glass. No diamond wheels were available of sufficient width so two channels were cut next to one another length ways in the glass coverslip (Figure 13(a)). This design then called for the glass coverslip to be placed on top of the channel and then to be held down on top of the glass by a piece of PTFE so create a seal with an aluminium plate on top that was attached to another aluminium plate behind the glass by a screw in each corner (Figure 14). Unfortunately it was not possible to ensure that the resultant channel was sufficiently deep to accommodate the new larger needle. Eventually a sufficiently deep and wide channel was produced by using an epoxy resin to glue two halves of a glass slide onto of the slide with a gap sufficiently wide to accommodate the needles for introducing and extracting the liquid (Figure 13(b)). However still manufacturing a non leaking seal was proving difficult and despite numerous attempts and design alterations a working model could not be produced. Also the narrow channel width did not give a very large area in which experiments could be carried out.

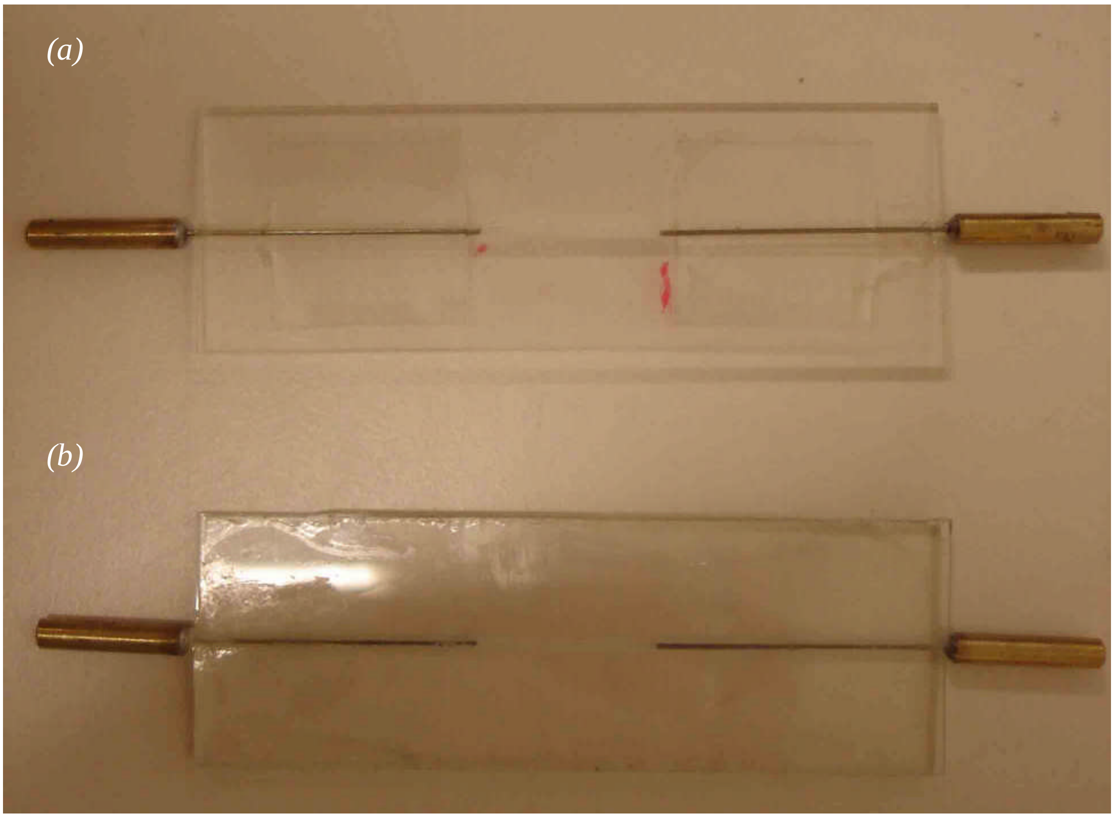


Figure 13 (a) is the device built using a channel cut with a diamond saw into the glass slide with the two 500µm diameter hypodermic needles glued in place. Figure 13 (b) is the next iteration of the design with the two halves of the slide glued on top of the slide to make the channel. Again the hypodermics glued into the channel with homemade brass adaptors soldered on can be seen.

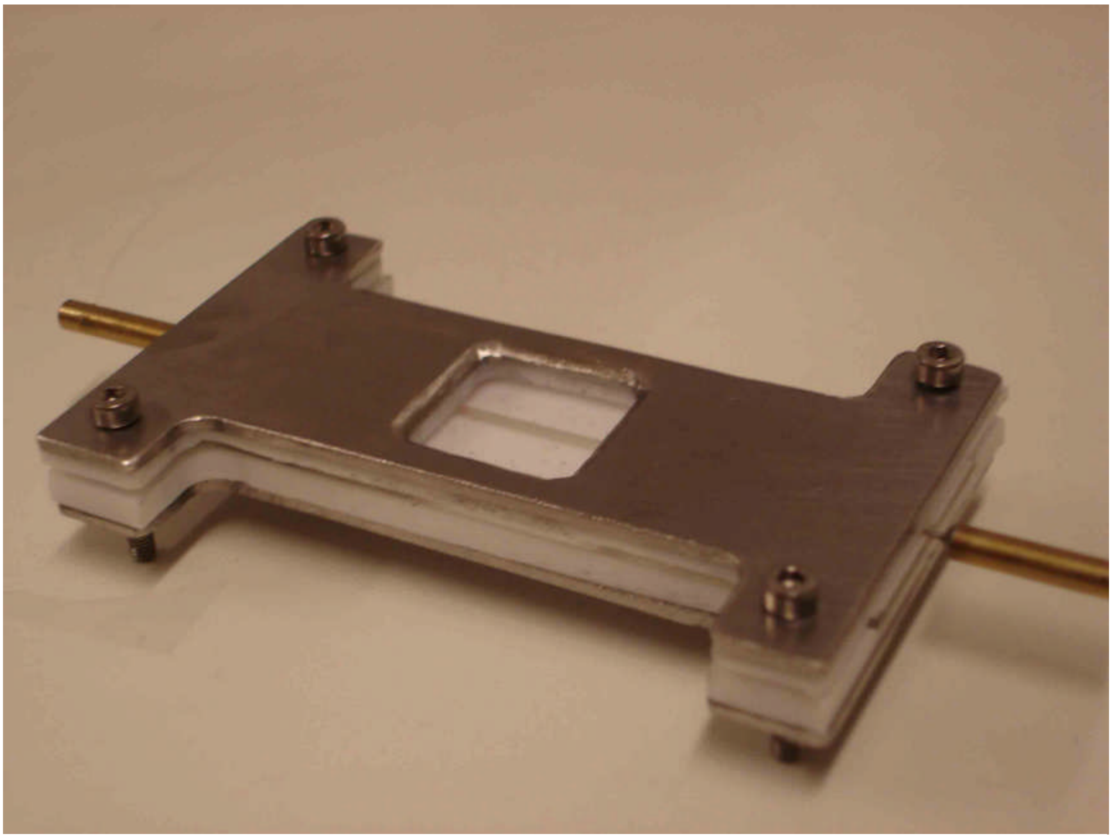


Figure 14; Complete view of one of the unsuccessful devices. In place can be seen the aluminium clamping plates and white PTFE seal material. The window for the objective lens can be seen in the top aluminium plate.

The obvious challenge here was manufacturing the device from very brittle and hard glass. A change in the material from which the device was being manufactured was required. While experimenting with a late iteration of the glass based micro fluidics device it was noted that the spectrum obtained from a nanocrystal showed very little background despite the presence of a piece of PTFE, used in the design to prevent the glass from cracking as the aluminium plates are screwed together. The shapes required for such a device are more straight forwards to fabricate in PTFE, a highly workable and chemically inert polymer commonly sold under the trade name Teflon. Further work was conducted to investigate the possibility of using PTFE using the PTFE shapes from the clamp of the previous device. After these trials proved successful a device from PTFE in which a liquid could be contained and a coverslip mounted was designed and manufactured. This proved very successful and the functioning model that is in use today was designed and produced. The final device is shown in Figures 15-17.

The device was manufactured from a solid block of PTFE that is 32mm square with a height of 20mm. It incorporates a well that is 14mm long and 10mm wide and 3mm deep to contain the fluid. On top of this a glass coverslip is situated. A further piece of 3mm thick PTFE is situated on top of this and is screwed down. This ensures the seal around the coverslip is good to prevent leakage and that the coverslip is flat so that the nanocrystals remain in focus. Into the top piece of PTFE a window the same size as the well was cut and then further material was removed to allow the objective lens to approach the glass. There are then two holes 2mm in diameter through the sides of the device into the well. This allows two large diameter hypodermic needles into the well. One is used for introducing liquids or gases and the other for removing them. The 2mm outside diameter stainless steel hypodermic needles soldered onto brass adapters with an outside diameter of 3mm. The 3mm internal diameter PVC hose that can attach onto the gas supply or onto syringes can also fit onto the brass adapters. The whole device has four holes in each corner that allow 2.5mm diameter screws to pass through vertically so the device can be clamped down onto a 3mm thick aluminium plate. The aluminium plate then bolts onto the microscopes xy stage at the four 8mm threaded holes located at the four corners of the stage.

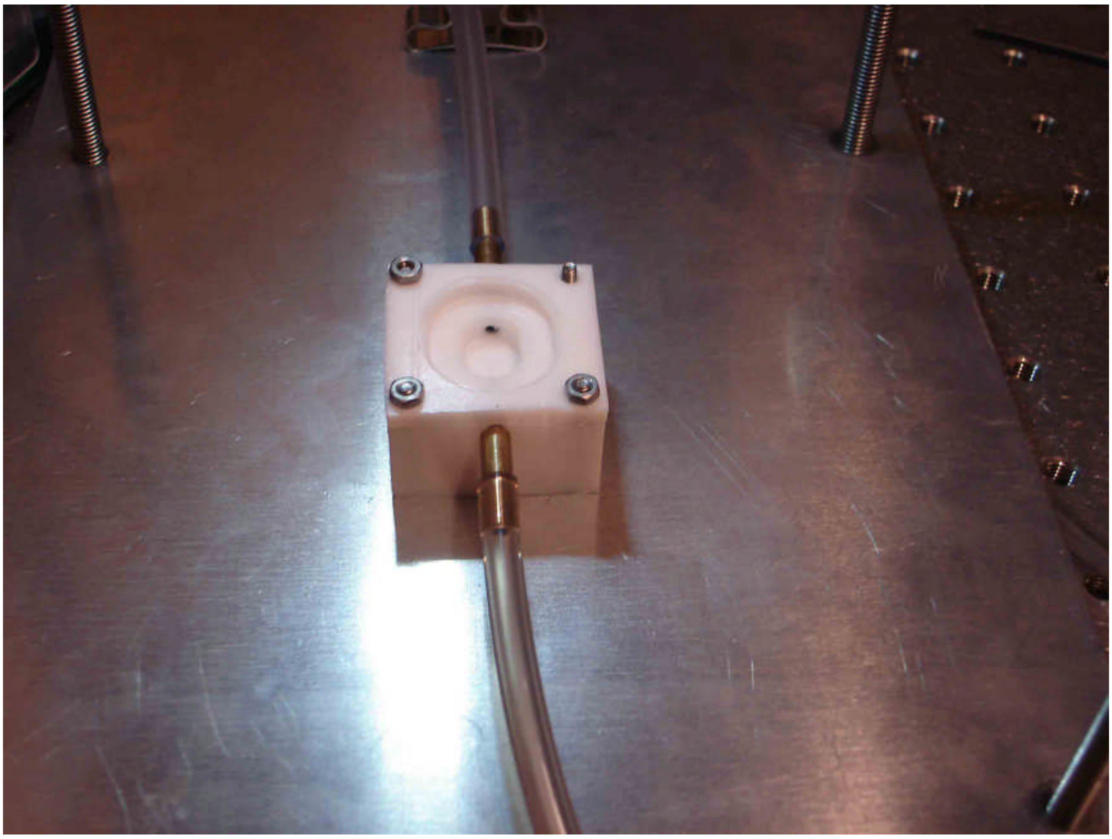
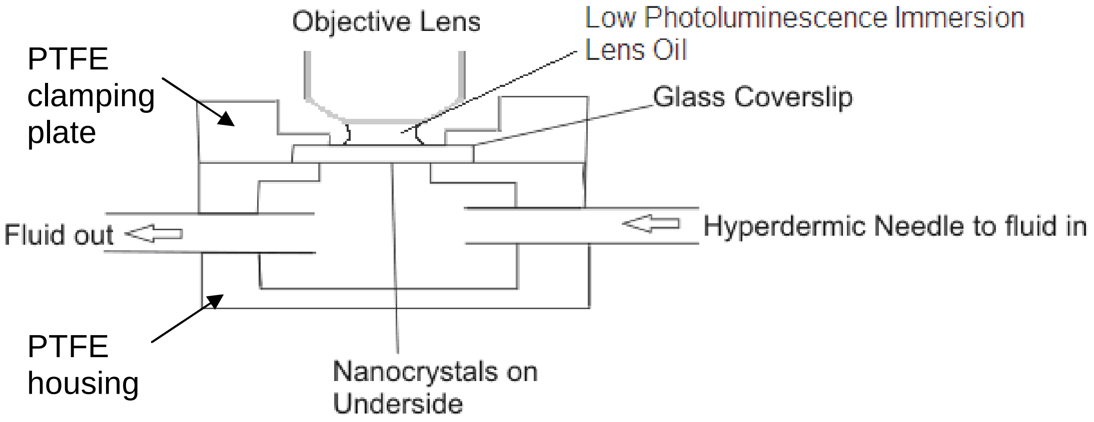


Figure 15, Image of the final device attached to input and output hoses and bolted down onto backing plate.

Figure 16; Schematic of final device



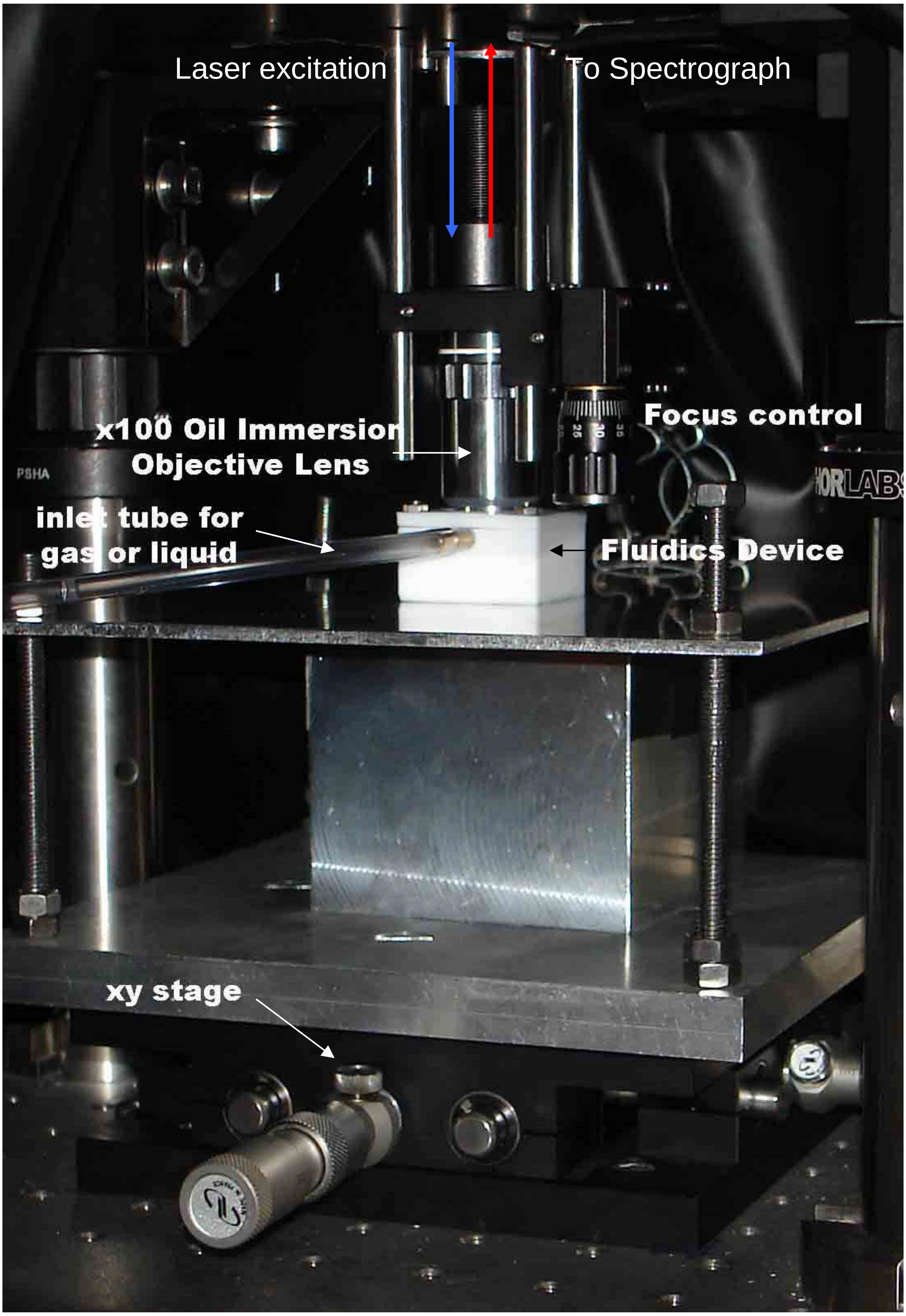


Figure 17Final device in position on microscope xy stage with x100 Oil Immersion Objective in place.

3.4 Experiments

Once a successful design had been settled upon and manufactured the emphasis of the investigation was then moved on to tethering the nanocrystal onto the glass coverslip substrate. Initially this proved to be quite simple as a similar method to that used for dispersing the nanocrystals onto the fused silica substrates could be used to attach the nanocrystals to the larger glass coverslip surface. The only difference between the two methods being small tweaks to concentrations to ensure the correct dispersion of quantum dots on the surface was achieved. Therefore single nanocrystal spectra from the set up were reasonably straight forwards to acquire while using cover glasses in the device. This proved that mechanically the device was sufficiently stable and the design afforded sufficient access to the objective lens.

The next stage was the measurement of nanocrystals in a changing surrounding medium or medium other than air. To allow the fullest interaction of the nanocrystal and the surrounding medium experiments were conducted without using PMMA in the dilution that is dispersed onto the glass coverslip. This was very successful and I was able to observe nanocrystals without the presence of a PMMA matrix without any loss in signal strength.

As mentioned elsewhere in this report, fluorescence instabilities in nanocrystals are heavily dependant on the surface chemistry of the nanocrystal. As has also been mentioned the surface ligands have a large effect on this [3, 4]. Therefore initial efforts were made to remove or add ligands to the nanocrystals while the photoluminescence measurements were being taken. This involved the introduction of an organic solvent with a varying concentration of HDA ligands in. However, observation of the nanocrystal when introducing a liquid into the device was not possible. The likely explanation was that they dissolved from the substrate surface. This was also the case with the presence of a PMMA matrix. To prevent the dissolution the nanocrystal a further layer of PMMA was spin cast over the nanocrystal layer but this also had little effect. A range of polar and non polar solutions was tested in an attempt to find a solvent that would not dissolve the nanocrystals. However in every case the nanocrystals were removed from the surface. When examining the two literature examples where single nanocrystals photoluminescence are observed in a liquid both use nanocrystals functionalised with Streptavidin bonded strongly to biotin molecules attached to the substrate surface [3, 4]. After consultation with a Sonia Contera from the Oxford University Biophysics lab and further literature research this technique appears to be successfully employed in a variety of single molecules studies. Unfortunately in the time available I was unable to investigate this avenue for tethering nanocrystals to glass in a liquid but it appears to be have been used successfully in the past[3, 4].

Although the nanocrystals do not stay in position when a liquid is introduced they are attached to the glass substrate sufficiently for the gas environment to be altered around them. We know that Oxygen is extremely electro negative and that when it is present it plays a part in the charge carrier dynamics of the surface traps [5], we also know that these trap states play an important role in the fluorescence instabilities observed in nanocrystals[6] so I conducted a brief study using the equipment described above on the fluorescence instabilities in an oxygen atmosphere and in an atmosphere without oxygen, in this case Helium. The results of this study and analysis form the remainder of the thesis.

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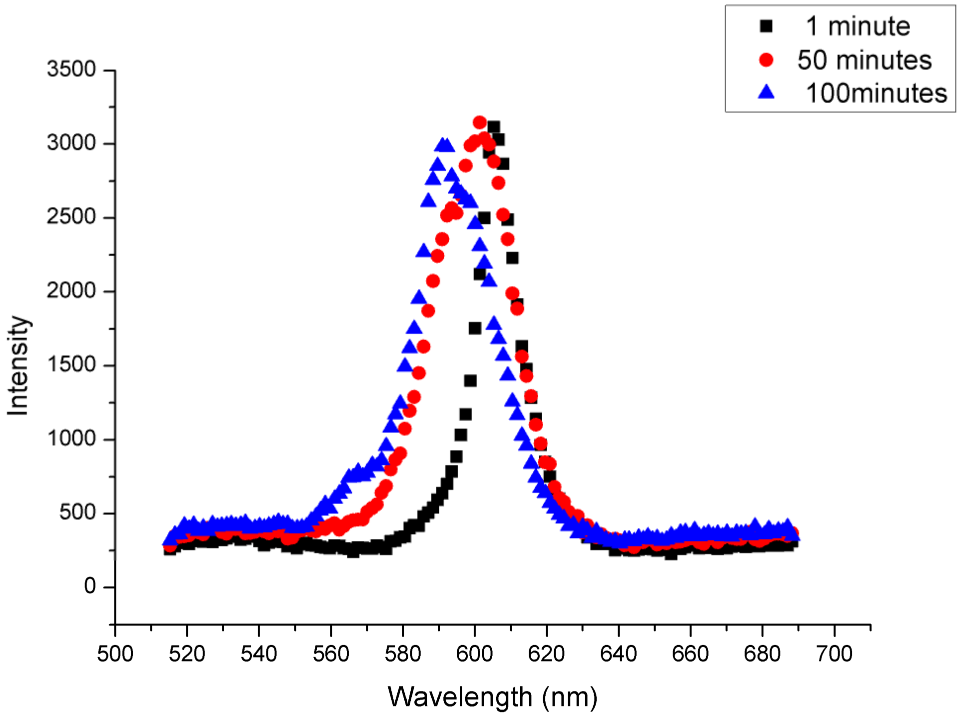
4. Results and Discussion

4.1 Blueing Experiments

Successive spectra were taken from an Evidot 600 Nanocrystal in air over a 100 minute period. The better signal that that is now collected allows series of spectra over a longer time period to be recorded. Previously series of up to 10 minutes could be recorded. Samples of three of the spectra are shown in figure 18.

Figure 18: Graph showing three sample spectra taken over a during a 100 minute



A Lorentzian was then fitted to the spectra and the peak emission wavelength was found from the fitted function. The emission wavelength was then plotted for the nanocrystal every 5 minutes for the 100 minute period.

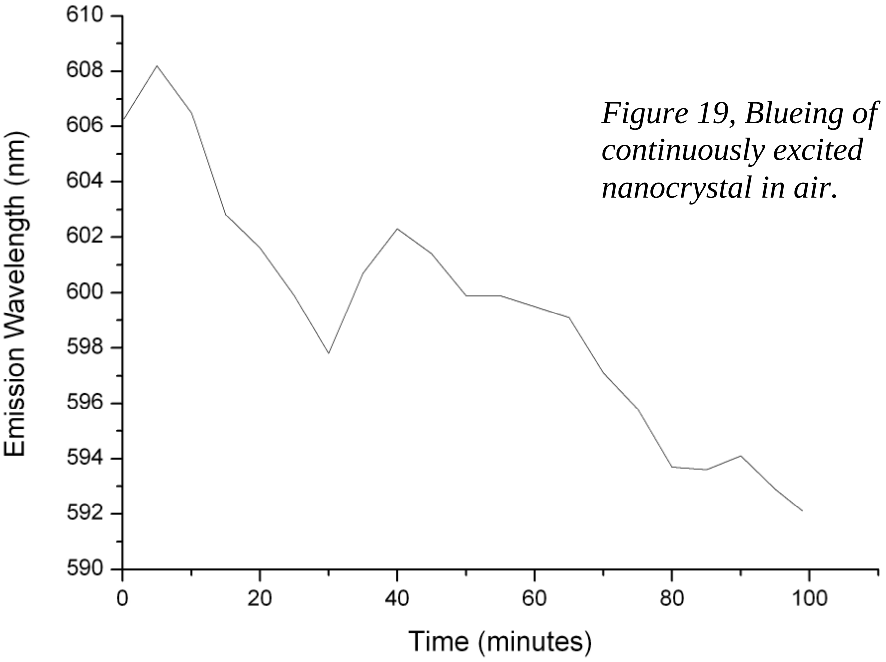


Figure 19, Blueing of a continuously excited nanocrystal in air.

We can see from the above graph (figure 19) that over time there is a shift towards the blue of the peak. This is a result of photo induced oxidation of the nanocrystal which takes place under the laser excitation. This results in a decrease in particle size and improved confinement of the exciton. There is an increase in the band gap between associated with the decrease in particle size, which results in shorter wavelength light being emitted from the nanocrystal as a result of photoluminescence. This observation is consistent with those made by van Sark et al[1].

To demonstrate the device and investigate the role of the environment in the blueing process an experiment with a changing gas environment was settled upon. The blueing property of the nanocrystals will be observed and because blueing is a result of photooxidation so should cease in the absence of oxygen. The device is able to switch the surroundings of the nanocrystal between air and an atmosphere which contains no oxygen while continuously recording spectral data. By conducting an experiment where the blueing of the nanocrystal is controlled by the switching of the gases surrounding the nanocrystal is, in some ways, more challenging than observing variations in the shorter term fluorescence instabilities. The greater challenge arises because the device must remain still for a long period of time, over 100 minutes, and movements of ~5µm could move the nanocrystal out of the few pixels that has been bracketed for light collection or could move the nanocrystal out of the focal plane. The inert gas atmosphere used when taking spectra in the absence of Oxygen will test the seals on the device. It was decided to use helium as the inert gas atmosphere as there is a ready supply in the laboratory.

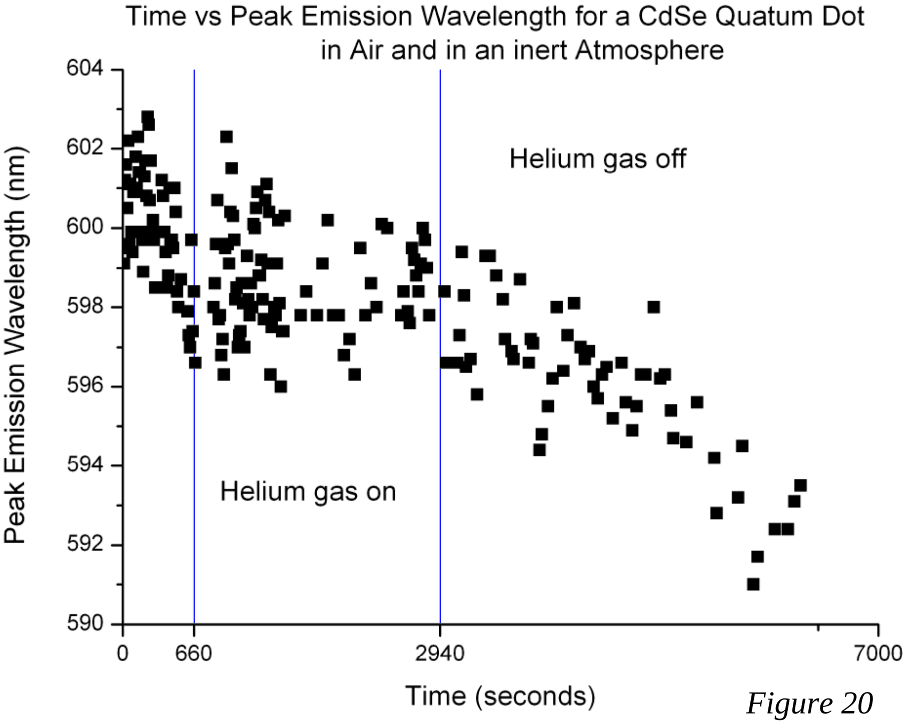


Figure 20

The above graph (figure 20) was produced by recording a series of spectra from a single nanocrystal over 100 minutes. Initially the nanocrystal is in air then, after 11 minutes, in an inert helium atmosphere. After 49 minutes the Helium was disconnected and air allowed into the system.

It was a great success for the system that the single Nanocrystal could be monitored continuously for 100minutes even with the changing environment. This demonstrates excellent stability in the system.

During the initial 11 minutes in air the emission peak wavelength is moving toward the blue. This blueing effect is stopped by flushing the system with Helium gas and the emission peak wavelength remains constant for the next 38 minutes showing that some component of air is required for blueing. In both Air and Helium there is a certain amount of noise attributed to changes in the immediate emission conditions of the nanocrystal, specifically the local electric field. After 49 minutes of the total experiment time (38 minutes in helium) the helium gas was switched off and air was introduced into the system and the shift towards the blue begins again for the remaining 56 minutes of the experiment. In their 2002 paper van Sark et al [1] show blueing behaviour in air and not in nitrogen, and suggest photo induced oxidation is responsible for the blueing our result supports this.

During the periods when the Nanocrystal is in air the processes of blueing is occurring. We can see from the first graph in which the nanocrystal is in air for 100minutes that a blue shift of 16nm occurs over the 100minute period. This gives a blueing rate of 0.16nm min^{-1}. In the second graph the nanocrystals peak moves from a maximum value of 602.8nm to a minimum value of 591nm. This gives 11.8± 2.2nm during the 105minute period. During this period the nanocrystal is exposed to the air for 56 minutes in the longer second period and for the initial 11 minute period combined this is 67minutes. On average this nanocrystal experiences a blueing rate of 0.17±0.03 nm min^{-1}. In a 2001 paper van Sark et al report blueing rates of 40nm in one minute [2].the likely explanation for the difference is that our nanocrystals are sourced from a commercial company and the nanocrystals used in this study were manufactured by the research group. The commercial nanocrystals have a well formed ZnS shell and organic capping layer. In this paper[2] they also report that the nanocrystals are completely photo bleached after being excited for only 70s in air, while we can still observe the commercial nanocrystal for up to 100 minutes with little loss in intensity.

While examining the second graph it would also appear that there is initially an immediate increase in the variation of the peak wavelength after the switch between air and helium. Then during the period when the atmosphere is Helium there is a decrease in the variation in peak wavelength. It is highly possible that this observation is coincidental and the current data is insufficient to prove a trend. What is seen however is an increase in variation due to a change from air to helium, then a reduction in variation after prolonged exposure to helium. If we were required to account for the initial increase then reduction in variation after the prolonged exposure to helium it may be attributed to the reversal of oxygen adsorption onto surface traps initially resulting in a rapidly changing electronic environment around the nanocrystal result in changes to the band gap as a result of the quantum confined stark effect. After the prolonged exposure of the nanocrystal to helium the traps could be depleted of oxygen so this effect is no longer occurring and variations are due to other ionisation events due to the laser excitation changing the surrounding medium. This could be investigated further by recording a series of switches between air and helium or another inert gas atmosphere.

4.2 Experiments to Correlate Spectral Drift to Environment

In this experiment four 10 second data sets were taken from a Nanocrystal. The spectra were integrated for 0.5seconds each. The shorter integration time was used because the line widths are thinner and the spectral jumps are more clearly recorded. The peak wavelength was plotted against time to attempt to see if there is any correlation between the spectral diffusion behaviour and the surrounding environment. Koberling et al discussed the relationship between Oxygen and blinking activity in the 2001 paper [3]. It is suggested that oxygen acts to increase the number of traps, which in turn increase charging activity, reducing on times while leaving off times unaffected[3]. It is thought that as the nanocrystal charges and uncharges the local electrical environment will change which will result in spectral diffusion due to QCSE. If this hypothesis is correct we may expect that there would be an increase in the jumps in peak wavelength in a series of spectra taken in air compared with a series of spectra taken in a Helium atmosphere.

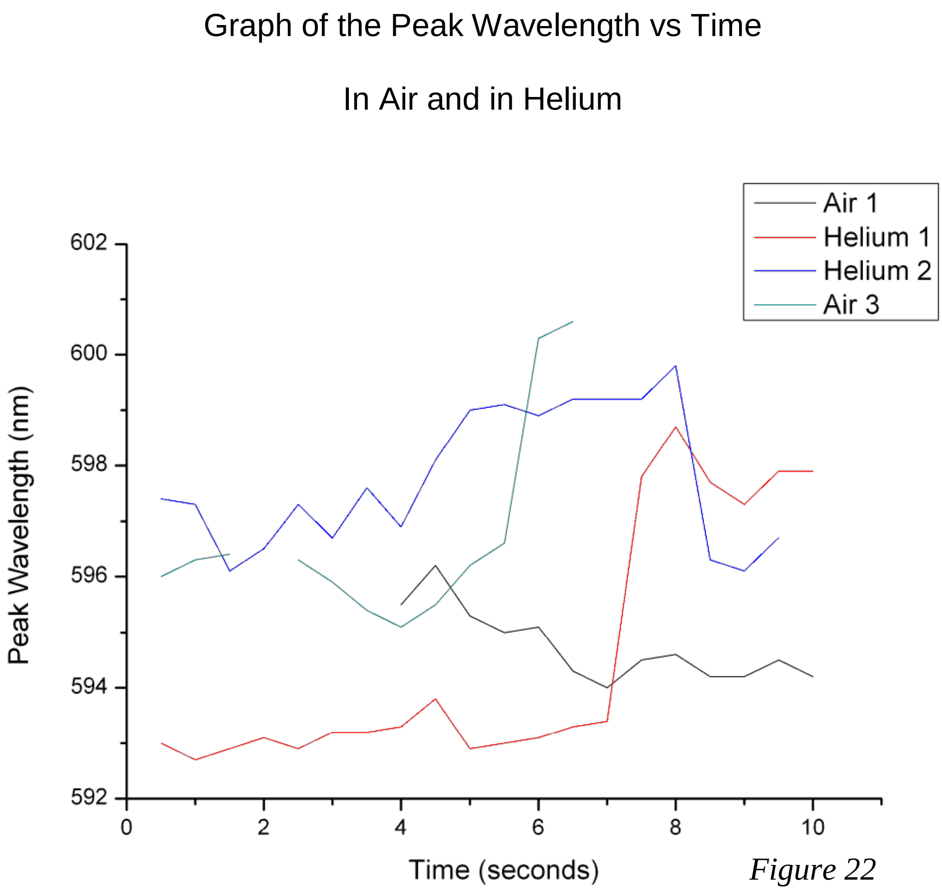
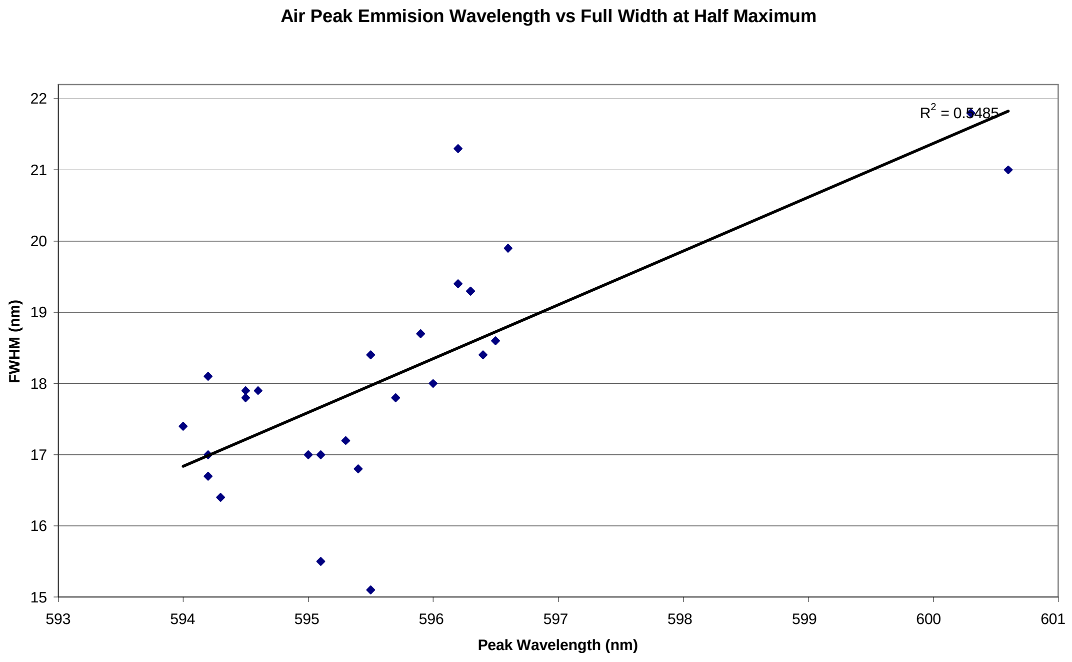


Figure 22

We can see from the above graph (figure 22) that there is no distinct behaviour attributed to the nanocrystal when it is in air or helium regarding spectral jumps. This could be because the data is insufficient this is because each spectra requires a curve to be fitted. One 10 second series of spectra integrated for 0.5s requires that 20 spectra be fitted with curves. However what we can notice from the data is that the two lines for the nanocrystal in Air are discontinuous while the two lines for the nanocrystal in Helium are continuous. This is because the nanocrystal experienced prolonged blinking events while in the air but not in the Helium. Although not rigorous due to the small data set size this result would support the result in the Koberling paper [3] that oxygen modifies blinking activity in nanocrystals.

4.3 FWHM Variation with Peak Wavelength

Another piece of spectral information that can be found when fitting Lorentzian functions to the acquired spectra is the Full Width at Half Maximum (FWHM). This value is a description of how much the emission wavelength varies during the integration time (0.5s) and the homogeneous line width. The FWHM therefore provides information about the dephasing rates and on the rapid drift. The broadening due to dephasing is homogeneous broadening and maintains the Lorentzian function the broadening due to rapid drift distort the line shape from a Lorentzian function. The Full Width Half Maximum for the spectra acquired during the experiment above was recorded when fitting peaks to the data.


Air Peak Emmision Wavelength vs Full Width at Half Maximum

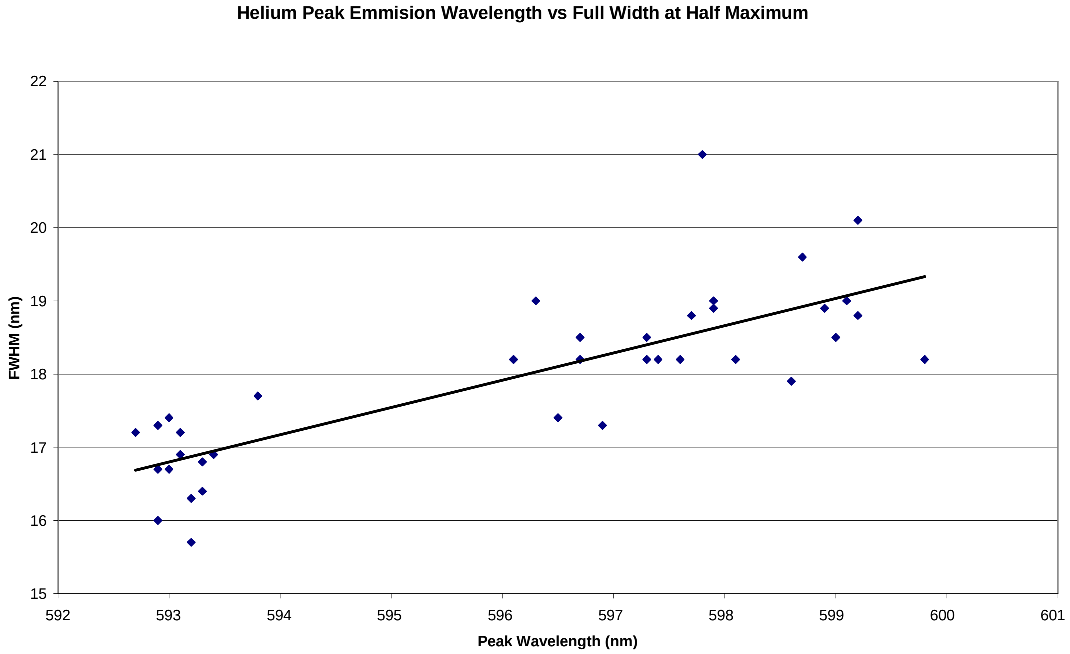


Figure 22 (a) Graph showing the variation of FWHM with the variation in peak wavelength of a nanocrystal in air. (b) shows the same data for the same nanocrystal in Helium

Pearson Product Moment Correlation Coefficient was used to test the correlation between two sets of data taken from these successive spectra. The data was the full width at half maximum (FWHM) and the Emission Peak Wavelength. The Pearson Coefficient (r) was found for the various set and is displayed in the table. Pearson Coefficient is worked out using the following formula;

$$r = \frac{\sum (x-\bar{x})(y-\bar{y})}{\sqrt{\sum (x-\bar{x})^2 \sum (y-\bar{y})^2}}$$

Gas Environment Surrounding Nanocrystal	Pearson Coefficient (r)
Air	0.74
Helium	0.80
All	0.72

The Pearson Product Moment Correlation Coefficient or Pearson Coefficient varies from 1 to -1 for perfect correlation to negative correlation with 0 representing no correlation between data sets. From the numbers for the Pearson Coefficient for our two conditions we can see that there is a strong positive correlation between the FWHM and the Peak Wavelength and the correlation is strongest between data in the same condition than between all the data. As the correlation between the Full Width Half Maximum and the Peak Wavelength were demonstrated by the Pearson Coefficients the FWHM and Peak were plotted on scatter plots for Air and for Helium and a line was fitted to demonstrate the positive correlation.

We can see from the both graphs that there is a trend for FWHM to increase for lower energy transitions. We would expect this to be the case as energy is related to wavelength by the equation;

$$E = \frac{hc}{\lambda}$$

Since a constant dephasing time gives a constant energy width (ΔE) rather than a constant $\Delta\lambda$ we can convert to this using the equation ;

$$\Delta E = -\frac{hc}{\lambda^2}\Delta\lambda$$

In the case when the energy change is the same size but the emission is longer wavelength the $\Delta\lambda$ will be also be larger. However the difference between the minimum and maximum FWHM is over 30% while the variation in wavelength is only 1.2%.

The change in the energy of these transitions over such as short period of time is due to the Quantum Confined Stark Effect [4, 5]. The equation relating the electric field experienced by the nanocrystal to the corresponding change in the energy of the exciton is give by[4];

$$\Delta E = \alpha(\varepsilon_{\text{int}} + \varepsilon_{applied})^2$$

So if we assume that the line width is a result of small spectral drifts during the integration time, then we can alter this expression to give [4];

$$\Delta(\Delta E) = 2\alpha(\varepsilon_{\text{int}} + \varepsilon_{applied})\Delta\varepsilon_{\text{int}}$$

This accounts for the larger FWHM at longer wavelengths [4]. From the Quantum Confined Stark Effect we know the longer wavelengths are a result of the nanocrystal being in a larger total electric field ($\varepsilon_{\text{int}} + \varepsilon_{applied}$). Therefore we expect to see a larger $\Delta(\Delta E)$ when the same small change in the local field is experience by a nanocrystal in a larger total field. The $\Delta(\Delta E)$ is the change in the energy during the integration and when it is larger we observe a broader peak [4].

The small change in the local field, $\Delta\varepsilon_{\text{int}}$ in the above expression, is likely to be the result of changes in the local electric environment experienced by the nanocrystal. Small changes in local electric fields are possible due to the movement of charge carriers between surface trap states on the nanocrystal [5] or due to local ionisation events due to the excitation laser. So our data would suggest that this small change to local field ($\Delta\varepsilon_{\text{int}}$) is larger for the nanocrystal which is experiencing a large Quantum Confined Stark Effect in air than in the inert Helium atmosphere. It is possible that the increase in line width is due to more movements of the charge carriers between surface trap states during the integration of the peak. This may be a result of one or two of the following processes; the presence of oxygen results in more surface traps [3], alternatively oxygen mediates the jumping of carriers between the states. In the case where there are more trap sites on the nanocrystal surface the traps would be less separated spatially. If the traps are closer together this could allow more tunnelling between trap states or a higher probability of jumps due to other processes, such as thermal promotion of charge carriers over the potential barriers between trap states.

A further contributing factor may be changes in the homogeneous line width. The emission peak shape for a single nanocrystal is described by a Lorentzian function [6];

$$I(\omega) = A\frac{\Gamma^2}{(\omega-\omega_0)^2+\Gamma^2} \qquad \text{(Equation 1)}$$

Where Γ is the dephasing rate, which is the rate at which the quantum state of the exciton is scattered, and gives half the line width. Dephasing rate is related to the total dephasing time (T_2) by the equation [6];

$$\Gamma = \frac{1}{T_2}$$

So an increase in the FWHM is an increase in Γ and a decrease in T_2. It is possible that the surface induced dephasing for the nanocrystal when in air is different than when in a Helium atmosphere. Dephasing is accelerated by the interaction of the electron or hole with other particles outside of their confined system. When the nanocrystal experiences the QCSE the modification of the nanocrystal band structure will also result in a shift in the charge carrier wave functions.

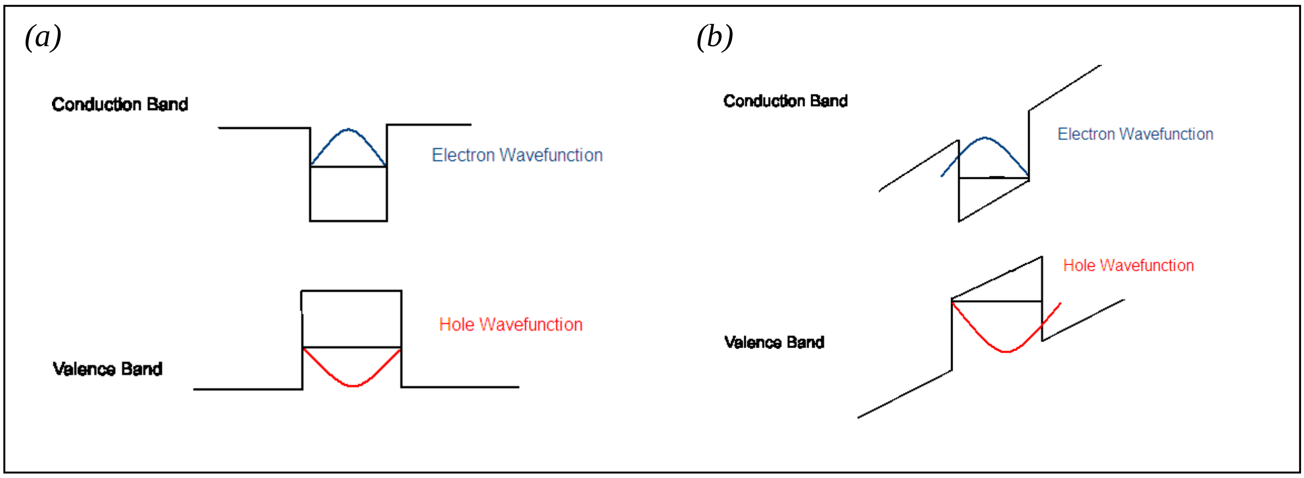


Figure 23; Diagram (a) shows the electron and hole wave functions in a nanocrystal in the absence of an electric field. (b) Shows the electronic band structure and wave functions of hole and electron modified by the QCSE due to an applied electric field.

We can see from the diagram that, on average, the electron and hole spend more time at or near the surface of the nanocrystal in the nanocrystal in an electric field. We also know that charge carriers reside on the surface of the nanocrystal in the trap states. Spending more time in close proximity to these other charge carriers will reduce the dephasing time and therefore increase dephasing rate (Γ). When plotting the Lorentzian line shape of the spectra we use Equation 1. In this equation the dephasing rate Γ also gives the half width at half maximum of the line.

It may be possible to fit different line shapes to these spectra to separate the effects of rapid spectral drift events and the dephasing effects. As mentioned before, the homogeneous broadening effects that result from the dephasing effects produce a line width that is best fit by a Lorentzian function. While in the case of the rapid spectral shift they produce inhomogeneous broadening of the spectrum. This produces a spectrum that is best fitted with a Gaussian function. Further data and more in depth analysis of the spectral line shape may be able to find which of these two explanations or if a combination of both is in fact occurring.

References

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5. Summary and Further Work

Obviously a large portion of time when conducting this project was dedicated to the design, manufacture and testing of a suitable device for conducting the single nanocrystal photoluminescence experiments in a changing environment. The experiments conducted on the nanocrystal in a gas have proved to be successful, if limited by time constraints. The mechanical stability is excellent and the improved light collection allows monitoring of nanocrystals for 10 times longer than previously. Now that the equipment is in place further work to characterise the behaviour of single nanocrystals in oxygen and in an inert gas may prove to be interesting. Such work could have implication for the further understanding of the spectral instabilities of nanocrystals. Broadly speaking the furthering of our understanding of these phenomena would be very useful. The majority of applications in which colloidal nanocrystals are used or would be useful in require them to have stable luminescence. Studies in various gas atmospheres may shed light on the mechanisms that lead to these instabilities that are observed in colloidal nanocrystals and help to design nanocrystals that are more efficient.

The primary goal of this project was to investigate the use of nanocrystals as sensors. The advantage of this would be the small size of the nanocrystals would be able to investigate variations in local environment down to a very small scale. This project has moved towards that goal in some respects;

- The ability to measure spectra continuously while switching between gas environments has been achieved
- Changes in fluorescence instabilities between gas environments have been seen.

Further work to allow the device to be used with changing liquid environments or changing between liquid and gas environments is required. This work involves tethering the nanocrystals to the glass coverslip. As mentioned earlier this has been done by Hohng et al[1] using the interaction between biotin and Streptavidin. Streptavidin coated nanocrystals are available from commercial sources due to their use as biological tags. The further work that would need to be done would be to work out a process for coating the cover slips with biotin and a method for dispersing the nanocrystals onto the substrate in a manner that is suitable for single nanocrystal photoluminescence experiments. After this work has been completed experimenting with a variety of liquids can take place to see their effects on the fluorescence instabilities of the nanocrystals.

References

[1] S. Hohng, T. Ha, **2004**, *J. Am. Chem. Soc.*, *126*, 1324.

6. Project Management

The focus of the project was to develop the necessary equipment and techniques to allow the epifluorescence microscope in the Photonic Nanomaterials Group to continuously record spectral data while a liquid or gas environment surrounding the nanocrystal is altered. This additional function should allow further insights into the physical processes that govern the fluorescence instabilities observed in colloidal semiconductor quantum dots and allow the possibility that nanocrystals could be used as sensors to be explored.

The task that was identified early in the project as critical to the progression was that before any design work could be done was that I must be familiar with the operation of the home made microscope that is used for single nanocrystal photoluminescence experiments. To achieve this object I received training from a Graduate Student in the research group, Benny Sher. Once familiar with the operation of the microscope the design work could begin in earnest.

The first stage in the design process was to draw up a list of the features that it would be desirable for a device to have. This was done in conjunction with other members of the group who work on the fluorescence instabilities of nanocrystals. The features that were identified were to be able to conduct the Photoluminescence experiments in;

- Gases
- Liquids
- In both liquids and gases while on the cryostat

The experience of using the microscope had by this stage allowed me to understand the requirements of the system for conducting the photoluminescence experiments and these needs were defined as;

- Low noise (auto fluorescence)
- Mechanically stable
- Within dimensional constraints of the microscope
- Allow the microscope to capture sufficient light from the Nanocrystal

With the desirable features and the requirements in mind I set about designing the device. Initially I focused primarily on designing a device that would allow the experiments to be done in a liquid. Once the design process was underway it became apparent that a device that was compatible with the cryostat would not be possible. The feature of compatibility with the cryostat was not present in any designs.

Initial iterations of the device were built and were completed slightly behind the ambitious schedule that was initially laid out. The first schedule underestimated the time to manufacture the device. Primarily because of little experience in working with some of the materials and machines required to make parts such as the 500µm square channel in a glass microscope slide. That part specifically had to be remade many times until an adequate method for producing it was found. As the report suggests the first and second iterations took several months to complete and were not at all successful. This hampered the other aspects of the investigation, specifically the tethering of the nanocrystals in liquids.

Eventually a new design allowed a functioning device to be produced and work on the tethering of the nanocrystals could begin. The tethering of the nanocrystals to the substrate surface to allow the experiments to take place in liquids was to prove difficult. This was particularly time consuming because the loss of signal coincided with the introduction of a liquid into the device. As I mentioned in the earlier in the report light collection from the nanocrystals is highly dependent on mechanical stability and it is possible that the introduction of a liquid could move the microscope out of alignment. Therefore this possibility of de-focussing or de-alignment had to be examined during every experiment with an alternative nanocrystal tethering method to ensure that the loss was due to the nanocrystals being removed from the surface and not due to other factors. It is possible that the introduction of a liquid could deform the 130µm thick coverslip sufficiently to move it out of focus or could move the device sufficiently that the nanocrystals are no longer in focus or the substrate could move so the objective lens is above a region on the substrate that has no nanocrystals on it.

The interest of having a device for the study of nanocrystal photoluminescence in a liquid meant that a lot of time was invested in trying various solutions to the tethering problem. This included experiments with the spin casting process, attempting to use different solvents as the introduced liquid and substantial literature research into other tethering methods. Research in the literature led us to the biotin-Streptavidin interaction. Streptavidin conjugated quantum dots were sourced but unfortunately due to time constraints I was unable to investigate the coating of the cover slips with biotin.

The last stage of the project was testing the device with Helium gas. This proved to yield some interesting data. Obviously this data demonstrates the device functioning with a varying environment which was the aim of the project. I did have some time to take some initial data after completing the device and this was presented in the report.

PROJECT MANAGEMENT FORM 1

Part II Project Description Form

After discussion with your supervisor YOU should complete this form and send a copy to Sarah Johnson (Academic Adminstrators' Secretary) by Friday of 0th week of Michaelmas Term.

Name: Luke Hanson Pettengell College: Mansfield

Address for correspondence: Mansfield College, Mansfield Road, Oxford, OX1 3TF

Contact telephone number: 22717

Title of project: Environmental sensing using single Semiconductor Nanocrystals.

Supervisor: Jason Smith

What are the objectives of the project in order of priority?
Measure Photo Luminescence from Single NCs in Various Liquids:
Design a container compatible with current equipment and techniques.
Construct the container.
Test the containers and techniques.
Carry out PL study on single NCs in various liquids.
Use single NC photoluminescence to sense environment.

List the major milestones that must be accomplished in order to meet the objectives of the project
Learn to carry out PL studies on single NCs
Find appropriate method for fixing NCs in place
Design container
Build container
Select interesting liquids and carry out PL measurements.

Are you working essentially on your own or as part of a team? If you are part of a team what is your role, and to what extent is the success of your project dependent on other members of the team?
I am using the same apparatus as a post graduate student but our projects are different.

What resources (equipment, materials, technician support etc.) will you need?

Do you require any training to meet your objectives, e.g. in the use of specific experimental equipment or software, and how are you going to obtain that training?
Benny Sher will be teaching me how to use the microscope and spectrometer.

Complete the following plan for your entire project as you see it now. List each major task down the left hand column, and for each one draw a horizontal line to indicate the period you expect to allocate to it. For example, the final task, writing your thesis, is shown as occupying mid-April to mid-June.

Task	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun
Learn to measure PL of single NCs	xxxx								
Find Appropriate method for fixing NCs in place	Xx								
Design container	xx	Xxx							
Manufacture container		xxxx	Xxx						
Select interesting liquids and carry out PL measurements				xxxx	Xxx	xxxx			
Writing up							xxxx	xxxx	xxxx

Has your supervisor completed a *Risk Assessment Form* about your project yet? Yes

Your signature: Your supervisor's signature:
Date: Date:

PROJECT MANAGEMENT FORM 2

1st Part II Project Analysis Form

Complete this form and send a copy to Sarah Johnson (Academic Administrators' Secretary) by Friday of 6th week of Michaelmas Term

Name: Luke Hanson Pettengell

Title of Project as given in your Project Description: Fluorescence instabilities in semiconductor nanocrystals (Environmental sensing using single semiconductor nanocrystals).

Refer back to the project plan in your Project Description and list the goals you set for this term. Comment briefly on the extent to which you have achieved them.
Learn to measure PL of single Nanocrystals. I am able to use the current experiment to do this.
Find appropriate method for fixing NCs in place. A number of methods that may be suitable have been identified. The experiment must be constructed to test absolutely their suitability.
Design container. A design has been finalised.
Construct container. Manufacturing of components for the system has begun.

Identify clearly any difficulties you have encountered. Are they surmountable in the time available?

State any refinements, modifications or replacements of the original objectives for your Part II project:
An additional objective has been added; use single NC photoluminescence to sense environment.

Are you intending to change the title of your project? If so, state the new title:
Environmental sensing using single semiconductor nanocrystals.

Have the training needs you identified in the Project Description been met, and have you identified any further training requirements? Yes

Tick the appropriate box. Do you have

	None	Some	Sufficient
Results	X		
Analysis of results	X		

Do you have any other comments you wish to make?

After looking at the project plan in your Project Description complete the following project plan for the remainder of your Part II.

Task	Dec	Jan	Feb	Mar	Apr	May	Jun
Find Appropriate method for fixing NCs in Place		xx					
Manufacture container	Xxxx						
Select interesting liquids	xxxxx	xx					
Work on method for taking PL measurements in Liquid		xxxx					
Carry out PL measurements for a variety of liquids		xx	xxxx	xxxx	xxxx		
Writing up					xxxxx	xxxxx	xxxxx

General comments by the supervisor:

Your signature:
Date:

Your supervisor's signature:
Date:

PROJECT MANAGEMENT FORM 3

2nd Part II Project Analysis Form

Complete this form and send a copy to Sarah Johnson (Academic Administrators Secretary) by Friday of 6th week of Hilary Term

Name: Luke Hanson Pettengell

Title of Project: Fluorescence instabilities in semiconductor nanocrystals (Environmental sensing using single semiconductor nanocrystals).

Refer back to the project plan you made last term and list the goals you set for this term. Comment briefly on the extent to which you have achieved them.

The previous Project Management Form I had listed the goal of finishing my micro fluidics device by the end of December. Although this device was finished in early January it did not function as intended and the numerous and repeated redesigns since have also failed to operate in a useable manner. I am currently nearing completion on the manufacture of a dramatic redesign that I am confident that using the lessons learnt from earlier iterations will work.

I have been very successful in measuring fluorescence from single nanocrystals attached to the bottom surface of a cover slip, and using an oil immersion objective lens. This will serve me well when the fluidics device is complete

Identify clearly any difficulties you have encountered. Are they surmountable in the time available?

I have experienced great difficulty in manufacturing a working device for taking the PL measurements in a liquid. It is a problem that I am still working on. As a result of not having a system for performing PL measurement in a liquid I have been unable to advance my investigations in the tethering of single NCs to the observation surface. This is a problem as to take measurement the NCs must not move and I will be changing the surrounding liquid and if tethering is insufficient the NCs maybe washed away making measurements impossible.

State any refinements, modifications or replacements of the objectives you set for your Part II project:

As a result of the great engineering challenges faced in producing a working system. I am being more conservative and pragmatic in the objective of the project. I would judge the project to be an unqualified success if I was able to demonstrate a measurable alteration in a measured spectrum/ blinking statistics upon the change in a surrounding liquid environment. Additionally it would be very useful to have designed and built a working system and method for performing PL measurements in the liquid that could be used in further investigations.

Are you intending to change the title of your project? If so, state the new title:
Environmental sensing using single semiconductor nanocrystals

What is the title of the talk you will give to the Department?
Environmental sensing using single semiconductor nanocrystals

Have all your training needs for this project now been met?
Yes

Tick the appropriate box. Do you have

	None	Some	Sufficient
Results	x		
Analysis of results	x		

Do you have any other comments you wish to make?

General comments by the supervisor: