

Cranfield University

Hannah Catherine Gardner

**The Influences of Post-Preparative
Treatments on Luminescence from
CdTe Nanoparticles**

School of Applied Sciences

PhD

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CRANFIELD UNIVERSITY

School of Applied Sciences

Nanotechnology Centre

PhD Thesis

2008

HANNAH CATHERINE GARDNER

**The Influences of Post-Preparative Treatments on
Luminescence from CdTe Nanoparticles**

Supervisor: Dr Steve Dunn

This thesis is submitted in fulfilment of the requirements for the degree of doctor of philosophy.

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Abstract

Nanotechnology has seen an explosion of research interest in recent years. Nanoparticles are finding applications in an ever growing list of applications. To further develop these applications an understanding of the properties of a nanoparticle is needed. This thesis presents an investigation of the photoluminescent properties of CdTe nanoparticles as a function of various post-preparative treatments.

Changing the inter-particle distance is found to cause photoluminescence wavelength shifts. These shifts are determined by the amount of energy transferred between nanoparticles. The effects of inter-particle distance are seen when a suspension is diluted, re-concentrated or deposited as a thin film. In a thin film format similar effects are seen if the number of layers in a thin film is increased.

Changing the temperature of either a thin film or suspension of nanoparticles produces both reversible and irreversible photoluminescence wavelength shifts. The reversible changes are mainly found to be due to the presence of thermally activated trap states within the nanoparticles.

Finally, formation of a thin film via the layer-by-layer deposition method is studied. A real time *in-situ* analysis technique is used to monitor the whole deposition process. The deposition is found to take place in a series of stages with nanoparticles becoming either strongly or loosely bound to the surface. Optical waveguide lightmode spectroscopy is found to be an extremely useful technique for monitoring this thin film deposition as it allows researchers the opportunity to quickly and easily characterize individual experimental setups.

Keywords:

Layer-by-layer, Photoluminescence, Quantum dot, Temperature, Thin film

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List of Abbreviations

AFM	Atomic force microscope
AUC	Analytical Ultra Centrifuge
DDA	Dodecylamine
FWHM	Full width at half maximum
IR	Infra-red
ITO	Indium tin oxide
LBL	Layer-by-layer
LED	Light emitting diode
NLED	Nanostructured light emitting device
OLED	Organic light emitting diode
OWLS	Optical waveguide lightmode spectroscopy
PAni	Polyaniline
PDDA	Polydiallyldimethylammonium chloride
PEI	Polyethylenimine
PLL	Poly-L-Lyseine
PMMA	Polymethylmethacrylate
PNIPAM	Poly(<i>N</i> -isopropylacrylamide)
PPV	Poly(para-phenylene vinylene)
rms	Root mean square
SEM	Scanning electron microscope
TBP	Tributylphosphine
TGA	Thioglycolic acid
TOP	Trioctylphosphine
TOPO	Trioctylphosphine oxide
UV	Ultra violet
UV-Vis	Ultra violet – visual spectroscopy
WLI	White light interferometer
XPS	X-ray photoelectron spectroscopy

Author Publications

Journal Papers:

- 1) A Photoluminescence Study of Film Structure in CdTe Nanoparticle Thin Films. H. C. Gardner, D. E. Gallardo, S. Dunn, A. Eychmüller and N. Gaponik. *Journal of Nanoscience and Nanotechnology*, 2008, **8**, 2578-2581.
- 2) Red shift for CdTe Nanoparticle Thin Films and Suspensions During Heating. S. Dunn, H. C. Gardner, C. Bertoni, D. E. Gallardo, N. Gaponik and A. Eychmüller. *Journal of Nanoscience and Nanotechnology*, 2008, **8**, 2544-2548.
- 3) Degradation of Photoluminescence in CdTe Nanoparticles due to Cl₂ Contamination, H. C. Gardner, B. Patel, C. Bertoni, D. E. Gallardo and S. Dunn. *Advanced Materials Research*, 2008, **31**, 150-152.
- 4) In-situ kinetic analysis of self-assembled nanoparticle and polyelectrolyte thin films, H. C. Gardner, R. Horvath, S. C. Dunn and J. J. Ramsden
Submitted to *Langmuir*.

Conference proceedings:

1) Temperature Shifted Photoluminescence in CdTe Nanocrystals. Hannah C. Gardner, Diego E. Gallardo, Cristina Bertoni, Steve Dunn. Proceedings of SPIE, Nanophotonics, 2006, 6195, 10.1117/12.661233.

2) Influences of the Surrounding Materials on CdTe Nanoparticles within Self-Assembled Thin Films. H.C. Gardner, C. Bertoni, D.E. Gallardo, S. Dunn and M.G. Cain. Technical Proceedings of the 2007 NSTI Nanotechnology Conference and Trade Show, 2007, 1, 395.

Oral presentations given at:

1) SPIE Photonics Europe, 3rd -7th April 2006, Strasbourg, France

2) Thin Films 2006, 11-15th Dec 2006, Singapore

3) International Conference on Materials for Advanced Technologies 2007 (ICMAT) MRS, 1st – 6th July 2007, Singapore

Poster presentations given at:

1) 6th International Conference on Materials for Microelectronics and Nanoengineering. (MFMN 2006) 29th - 31st Oct 2006, Cranfield, UK

2) IOP Nanoscale Physics and Technology: the Interface with Medical and Biological Sciences. 26-27th March 2007 Southampton UK.

1. Introduction

1.1 Context

After Richard Feynman's infamous "There is plenty of room at the bottom" speech(1) there has been an explosion in the amount of research into the various forms nanotechnology. Many university courses(2,3), journals(4,5) and companies(6) have been founded. "Nanotechnology" and "nano" have become buzzwords and are applied to numerous products irrespective it seems of whether or not the said product actually contains any nanotechnology(7). This research explosion has been followed by a rapid increase in media interest. Not all of it good(8). But what is this nanotechnology? And why is it useful?

Nanotechnology is, by definition, technology on a nanometre (or 10^{-9}m) scale. This size regime is the same order of magnitude as large molecules such as a DNA double helix which has a diameter of approximately 2nm. When reduced to this size, the physical and chemical properties of materials change. There is also a change in the priority of physical phenomenon. This means that researchers have an entirely new set of tools to work with and an entirely new set of problems to understand. The applications of these new tools are seemingly limitless.

The fast growing nature of nanotechnology means that almost as soon as something is published it is obsolete. However, Madou(9), Poole(10) and Foster(11) provide good introductions to this very broad field.

1.2 Motivation

A quantum dot or semiconductor nanoparticle is one of the many new tools available to researchers. The properties and applications of these nanoparticles are discussed in Chapter 2. The motivation behind this thesis is to build a greater understanding of these novel materials.

To do this we will look at how the nanoparticles interact with one another in suspension and thin film forms. One of the most common post-preparative treatments of CdTe nanoparticles is their deposition as a thin film thus this is looked at in greater detail. Finally, to gain an insight into how the nanoparticles may be affected by the environment they face within their many applications we also look at the effects of changing the temperature of suspensions and thin film.

1.3 Thesis Structure

The thesis is split into 8 Chapters. Chapters 4 - 6 are self contained Chapters on a particular topic; they each include an introduction to the topic, any necessary experimental information and a results and discussion section. The remaining Chapters are general and apply to all of the topics discussed.

Chapter 2 gives a brief general introduction into the background and previously published literature surrounding this thesis. The Chapter explains what nanoparticles are and what makes them special. Next, the synthesis and refining of CdTe nanoparticles is discussed. Several current applications of semiconductor nanoparticles are highlighted with particular attention given to the fields of biomedical and photonic technologies. Finally, different

methods of depositing thin films from suspensions are discussed and an explanation is given as to why the technique used in this report was chosen.

Chapter 3 is a general methodology providing information on the generic techniques used throughout the thesis and the chemicals and instrumentation employed to achieve them.

Chapter 4 covers the manipulation of nanoparticles by dilution of suspensions and deposition of thin films. Before the nanoparticles can be used in any way they must first be processed into a useable format. As the nanoparticles used throughout this report have been produced by wet chemical synthesis the main usable forms are suspensions and thin films. This Chapter therefore looks at the factors affecting the nanoparticles as they are manipulated in these ways. The interaction between the nanoparticles is studied.

Chapter 5 looks in more detail at the layer-by-layer deposition method. Thin films of nanoparticles and three different polyelectrolytes are produced. Differences between the thin films are used to develop a proposed mechanism of deposition. The deposition is then studied in greater detail using an *in-situ* real time analysis technique.

Chapter 6 looks at the effects of heating and cooling both suspensions and thin films. Samples are repeatedly heated and cooled (temperature cycled) within the temperature range 293K-358K. Temperature changes are one key environmental factor that nanoparticles are likely to face within their various applications. It is therefore important to study how these changes affect the particles in order to assess their feasibility for proposed applications.

Chapter 7 is a general conclusion Chapter bringing together knowledge from each of the above Chapters.

Chapter 8 gives details of some unusual observations made throughout this thesis work and provides suggestions for future work topics within this area.

2 Background Literature

2.1 A Brief History of Nanoparticles

Today nanoparticles can seem to be magic or miraculous materials as they provide solutions to seemingly endless problems. A look at the content pages of the most respected general science journals such as Nature(1) or Science(2) reveals that, even in these non-specialist journals, nanoparticles are a hugely influential topic. Many specialist journals such as “Nano letters”(3), “Nanotechnology”(4), “Nature Nanotechnology”(5) and “Small”(6) have been founded to expand the available space for publishing in this discipline.

Publishing on nanomaterials is no longer restricted to the scientific community. Numerous newspaper articles (7,8) and popular-science books(9,10) are available to the interested non-scientist. Richard Turton's *The Quantum Dot*(11) made the bestsellers lists and nanotechnology now has its own *For Dummies* title(12). Nanoparticles have even become the domain of science fiction writers with Michael Crichton's *Prey*(13) focussing on the perceived terrors of uncontrolled nanotechnology. In his 1995 futuristic sci-fi book, *The Diamond Age*(14), Neal Stephenson describes “fabricules” nanotechnology which when applied to the surface of gloves allows them to dig into dirt and yet be clean again moments later. The reason for this intense interest is that nanotechnology and nanoparticles, in their various forms, are proving to have applications in areas as different as catalysis(15) and consumer electronics(16) or medicine(17) and security(18). This recent

nanoexplosion would lead you to think that nanoparticles are new materials. They are not. Of course, the specialized nanoparticles being employed in many modern applications are new. But nanoparticles themselves are not. In fact they have been known to be used in hair-dyes as early as Greco-Roman times. Scientists following an ancient recipe for hair-dye used by the Romans found the active ingredients to be PbS nanoparticles(19). A 2006 transmission electron microscope study showed that nanotechnology had been commonly used in 17th century India, albeit unwittingly, when blacksmiths developed *Damascus Steel* swords which were known for their strength, sharpness and flexibility. Analysis conducted by Riebold *et al*(20) at Dresden University showed the steel used in the swords contained carbon nanotubes!

2.2 Nanoparticle Nomenclature

Nanoparticles, nanocrystals and colloidal quantum dots are popular terms for semiconductor particles that have all three spatial directions measurable in the nanoscale and which exhibit exciton confinement. Although by definition nanoscale encompasses everything from 1nm to 100nm the particles are generally in the lower end of this range, 2 – 10nm. These terms can become confusing as sometimes they are used interchangeably(21,22) but they can also have different meanings; for example Murray *et al*(23) only use the term nanocrystals for structures with well-characterised crystalline cores and define nanoparticles as being amorphous or having multi-domain cores. For simplicity, throughout the rest of this thesis only the term nanoparticle is used

(except when referring to work by other researchers) and is used to mean a highly-crystalline, electron-confined semiconductor nanostructure.

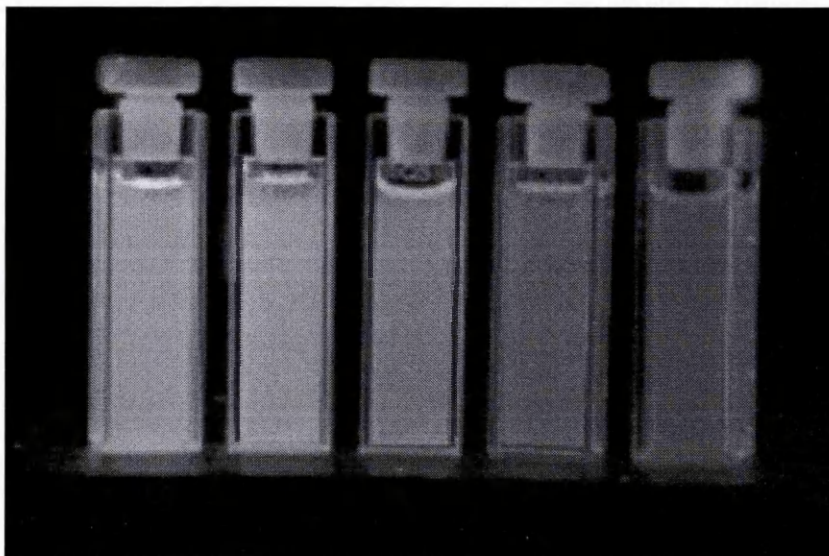


Figure 2.1: Different sized nanoparticles displaying different optical properties. Image is reproduced with permission from Phillips(24).

2.3 Size Quantisation

An exciton is a paired conduction band electron and valence band hole. In a nanoparticle the radius of the particle (a) is smaller than or comparable to the wavelengths of the electrons and holes and the Bohr radius (a_B) of the exciton. This confines the exciton to within the nanoparticle and is also known as size quantisation. Early reports on size quantisation by Efros and Efros(25) and Ekimov and Onushchenko(26) started the research interest into nanoparticles. Confining electrons in this way changes the energy spectrum of the nanoparticle; discrete atom-like energy bands are formed. When the

nanoparticle is in a strong confinement regime, $a \ll a_B$, the energy of the absorbance spectrum bands (E_{nl}) are given by the expression(27):

$$E_{nl} = E_g + \frac{\hbar^2}{2\mu a^2} \chi_{nl}^2$$

Equation 2.1: The quantised absorbance bands in a nanoparticle

Where E_g is the band gap of the bulk material; $\hbar$ is the reduced plank's constant; μ is the electron hole reduced mass; a is the area of the nanoparticle and χ_{nl} are the roots of the Bessel function(28). The absorbance of a nanoparticle is at higher energy than the absorbance of the bulk semiconductor. Since the area of the nanoparticle is a denominator in equation 2.1 decreasing the area of the nanoparticle will increase the value of the variable in the equation and increase the energy of the absorbance band. Thus the nanoparticle exhibits size selective optical properties. Figure 2.2 shows the change in absorbance wavelength (size of nanoparticle increases a to h) and Figure 2.1 shows a change in photoluminescence (the size of the nanoparticle is increased left to right).

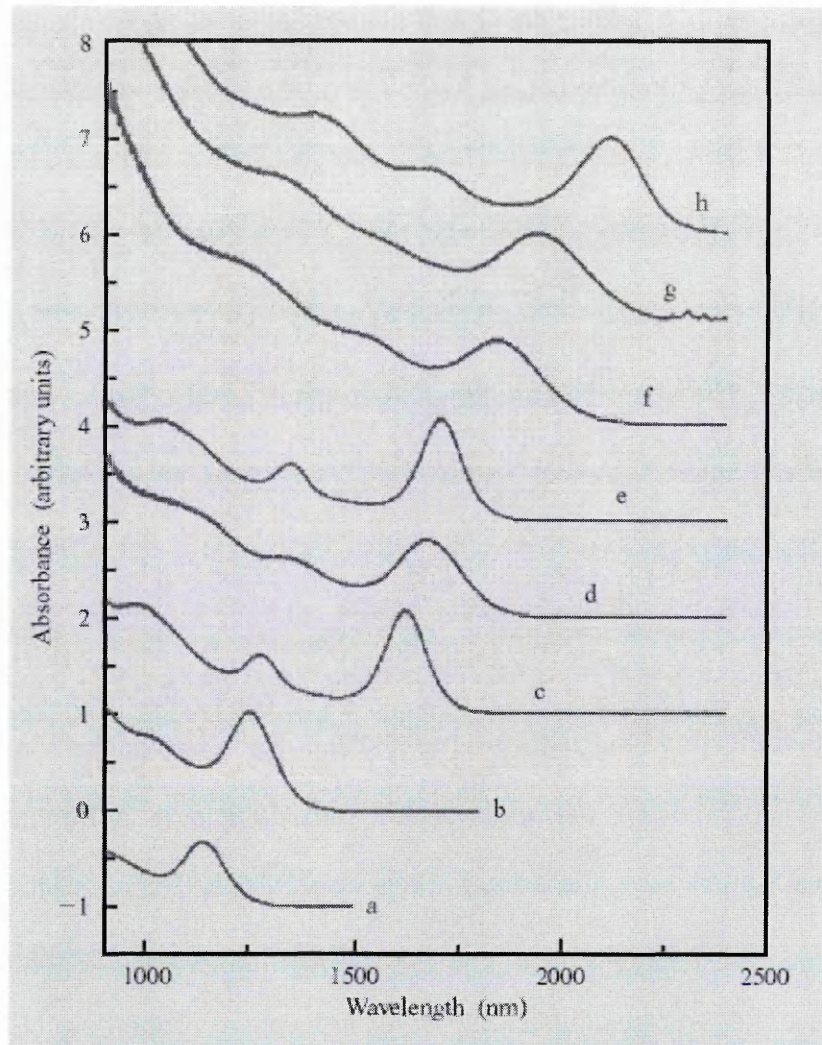


Figure 2.2: The changes in absorbance wavelength as the size of nanoparticles are increased. The smallest particles are shown in spectrum **a** and the largest in spectrum **h**. The image is taken from Murray *et al* (29).

2.4 Synthesis of Nanoparticles

2.4.1 Desirable Nanoparticle Properties

For use in any application nanoparticles need to be of a high quality. Desirable properties in a nanoparticle are high stability, high crystallinity and

high quantum yield. The ability to select the size of nanoparticles and ensure a narrow size distribution is also important along with the option of controlling the surface properties of the particle. Colloidal chemical synthesis provides a method of reaching all these targets. Cadmium chalcogenide nanoparticles display high quantum yields. Wuister *et al*(30) achieved a 40% quantum yield by controlling the synthesis reaction time in the production of CdTe nanoparticles. High crystallinity is important as defects can allow non-radiative recombination reducing the quantum yield. Higher yields have been obtained by passivating or capping the nanoparticle. Hines and Guyot-Sionnest(31) reported a 50% yield and Bao *et al*(32) an 85% yield.

2.4.2 Controlling the Size Distribution

Since the size of a nanoparticle directly affects its optical properties it is important to develop synthetic methods that allow control over both size and size distribution.

A study by LaMer and Dinegar(33) in 1950 investigated the mechanism of formation of monodisperse hydrosols. Examining the decomposition of sodium thiosulfate in hydrochloric acid they found that the concentration of sulfur builds up until a critical concentration is reached when self-nucleation occurs. This nucleation reduces the sulfur concentration and further nucleation is halted as the critical concentration is no longer reached. Therefore, to obtain monodisperse colloids of nanoparticles it is important to control the rate of addition of reagents. If the concentration of reagents is allowed to reach a critical concentration and then is quickly reduced - no further nucleation will take place. Growth of all the nanoparticles will take

place at similar rates. If the growth after nucleation is large compared with the nucleation stage then the nanoparticles will become more uniform with time. This is known as focussing the size distribution.

Ostwald ripening(23,34) also improves the monodispersity of nanoparticles. Ostwald ripening occurs naturally during the synthesis procedure and is seen as a second growth stage. The high surface energy of the smaller nanoparticles promotes their breakdown. Subsequent material is then deposited onto the remaining larger nanoparticles. A long growth stage at high temperature allows Ostwald ripening to occur.

2.4.3 Wet Chemical Synthesis

The desire to produce nanoparticles with the properties outlined in Section 2.4.1 has led to a vast amount of research and several synthetic techniques. Nanoparticles can be produced from both group II-VI and group III-V compounds and the wavelength of emission can be tuned from the ultra violet (UV) to the near infra-red (IR)(35). Figure 2.3 shows the approximate wavelengths of emission that can be achieved using various II-VI combinations. The variance within each compound is the wavelength change that is determined by the nanoparticle size.

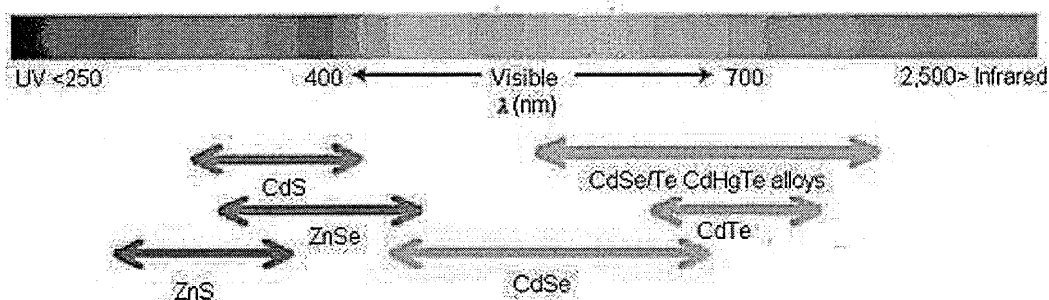


Figure 2.3 Emission wavelengths of various nanoparticle materials.

Prior to 1993 nanoparticles were mainly synthesised via aqueous routes(36,37) but the nanoparticles produced had poor crystallinity and low uniformity in both size and shape having a root mean square (rms) greater than 15%(38,39). However, in 1993 and 1994 Murray *et al*(39) and Bowen Katari *et al*(40) developed highly cited organometallic syntheses of cadmium chalcogenides. Trioctylphosphine (TOP) or tributylphosphine (TBP) and trioctylphosphine oxide (TOPO) were used as high-boiling coordinating solvents. Cadmium and chalcogenide precursor reagents were added by injection to hot TOPO. This rapid introduction of the reagents followed La Mer's(33) guidelines to produce homogenous nanoparticles by keeping the nucleation stage short. This simple method provided high quality monodisperse nanoparticles with a rms of less than 5%.

Talapin *et al*(41) adopted a different method of controlling the size distribution. Dodecylamine (DDA) was dissolved in TOP and Me_2Cd and Te powder are added. The reaction temperature is carefully raised to 200°C. No hot injection method is used, instead, the DDA acts as a size-regulating and stabilizing agent. The tellurium powder dissolves slowly allowing the

nanoparticles to grow very slowly at high temperatures producing high quality crystallinity and very low defect density.

Recently Sapra *et al*(42) developed a novel synthesis route using olive oil as the co-ordinating solvent. This eliminates the need for the toxic TOP. As the popularity of nanoparticles increases (see Section 2.5) low cost, simple and less toxic production methods are likely to become more conventional.

The nanoparticles used throughout this thesis have been prepared by Gaponik *et al*(43). H_2Te was reacted with $\text{Cd}(\text{Cl})_4 \cdot 2.6\text{H}_2\text{O}$ under a N_2 atmosphere in the presence of thioglycolic acid (TGA) - used as a stabilising capping agent (see Section 3.1). The precursors were then refluxed at 100°C in open air conditions. The reflux time was determined by the size of the nanoparticle desired and the thiol present. For 5nm CdTe nanoparticles with a TGA capping layer a reflux time of 2-3 days was required.

2.4.4 Refining the Nanoparticles

The monodispersity of the nanoparticles in each of the methods discussed can be refined by size selective precipitation(39,41). A solvent that is miscible with the main solvent used in the synthesis but is not compatible with the capping layer of the nanoparticles is used. As this miscible non-solvent is slowly added to the suspension of nanoparticles it reduces the energetic barrier to aggregation and destabilises the suspension thus the nanoparticles begin to precipitate. Larger particles experience stronger attractive forces which makes them agglomerate and precipitate out of solution before the

smaller particles(39). Size fractions of nanoparticles can then be collected by filtering or centrifuging.

Due to the large surface area to volume ratio of the nanoparticles, factors affecting the surface of the nanoparticle have a pronounced effect on their physical properties. At the surface of the nanoparticle substantial repositions in the atomic positions occur causing energy levels within the forbidden energy gap of the bulk solid(44). Surface traps that allow non-radiative recombination greatly decrease the quantum efficiency of luminescent nanoparticles. The problem can be avoided by passivation where a capping material is added – surface atoms are bonded to another material of higher band gap and energy levels inside the band gap are eliminated. Ideally passivation should remove all the surface defects without causing a strain.

Bowen Katari *et al*(40) used x-ray photoelectron spectroscopy (XPS) to examine the surface of CdSe nanoparticles. They found that Cd atoms on the surface are bound to the stabilizing ligand TOPO whilst Se atoms are unbound and become oxidised on exposure to air. If TOPO is removed neither site is passivated and exposure to air oxidises both Cd and Se. This oxidation caused degradation of the nanoparticle over time.

2.4.5 Coating Nanoparticles

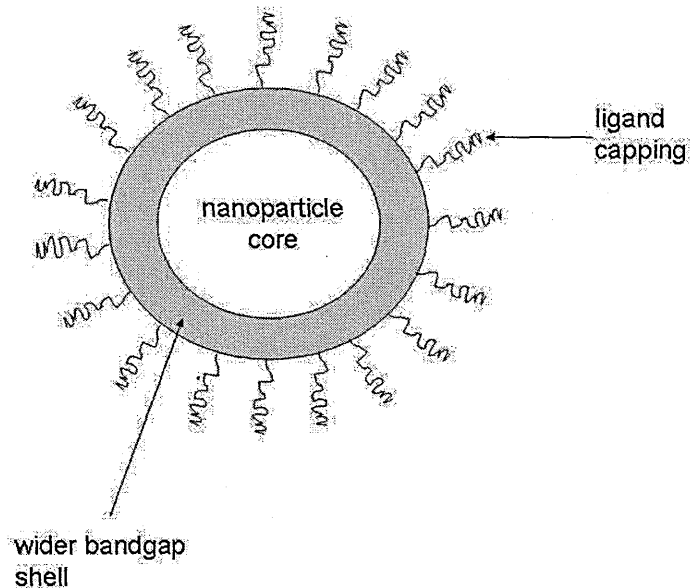


Figure 2.4: Schematic of a core - shell nanoparticle. The shell of the nanoparticle is made from a material with a wider band gap which confines the holes to the core of the nanoparticles reducing surface traps.

Several research groups have investigated coating nanoparticles in a shell of wider band gap material(45). This has the effect of confining the holes to the core of the nanoparticle and greatly improves the quantum yield. Peng *et al*(46) grew shells of CdS onto CdSe nanoparticles. The shells have a uniform thickness of up to 3 monolayers 23-39Å and are grown epitaxially onto the core. They found a change in the photoluminescence quantum yield with thickness of shell, reaching a maximum at just below 3 monolayers giving a quantum yield of 50%.

Hines and Guyot-Sionnest(31) grew (CdSe)ZnS nanoparticles confirmed by XPS following Bowen Katari's(40) method for CdSe nanoparticles and injecting Zn/S/TOP solution into the reaction vessel after the initial formation of nanoparticles. This results in a 50% quantum yield and nanoparticles that are stable for months.

2.5 Current Applications of Nanoparticles

2.5.1 Diagnostics and Biomedical Applications

Perhaps the most popular current use of semiconductor nanoparticles is their use in biomedical and diagnostic applications. Alivisatos(47) and Michalet *et al*(48) provide good reviews of this rapidly growing field.

Capping a nanoparticle with an isolating or biologically recognised shell(45,49) allows the nanoparticle to interact with biological systems. The small size of the nanoparticle coupled with a specifically designed shell means entry into a cell is possible. Consequently nanoparticles are now replacing the traditional organic dyes in cellular labelling of both live(49,50) and fixed(47,48) cells. Nanoparticles offer the advantage of multiple colour labelling and extended visualisation under continuous illumination(48,51). Near-IR emitting nanoparticles have also found applications in *in vivo* deep tissue imaging. The nanoparticles allow deeper image penetration than the existing IR dyes(51).

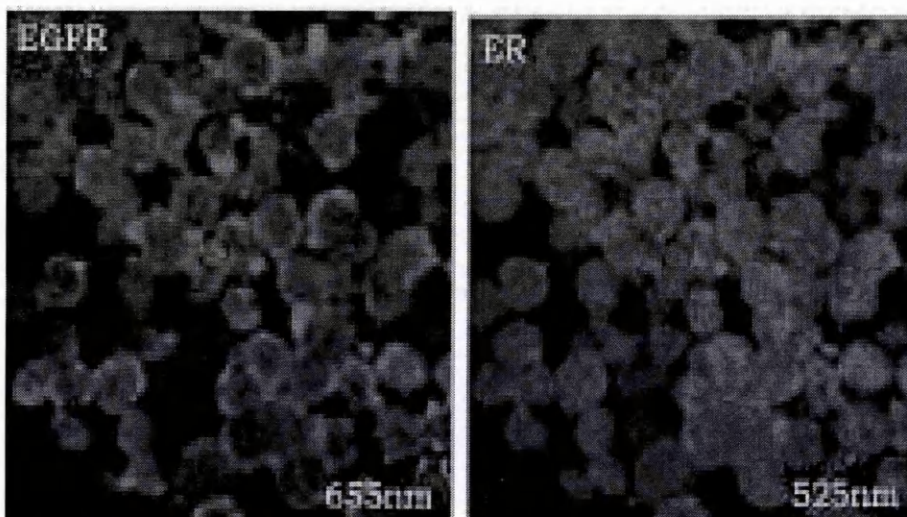


Figure 2.5: Nanoparticles as biomedical diagnostic tools. Bio conjugated nanoparticles are used to highlight breast cancer cells(52).

An example of how popular nanoparticles are becoming in the biological field can be found in cancer research(53). Luminescent nanoparticles have been used to confirm the presence of cancer cells, to image cancer cells, to monitor and track the development and spread of cancers and even to provide therapeutic treatment. Figure 2.5 shows an example of how useful the nanoparticles can be. The images are taken from a 2007 paper by Yezhelyev *et al*(52). The cells being imaged are MCF-7 human breast cancer cells, nanoparticles of different colours are capped with antibodies for particular oncoproteins expected to be found within the cell. The red nanoparticles are designed to detect, EGFR, a cell membrane surface antigen whilst the green nanoparticles detect, ER, a nuclear hormone receptor. The complete cell can then be imaged at different wavelengths, 655nm for the red and 525nm for the green, to simultaneously detect the presence of both biomarkers. Figure 2.6 is taken from the same paper and

shows a schematic of how the different nanoparticles can be used to image different parts of the cell.

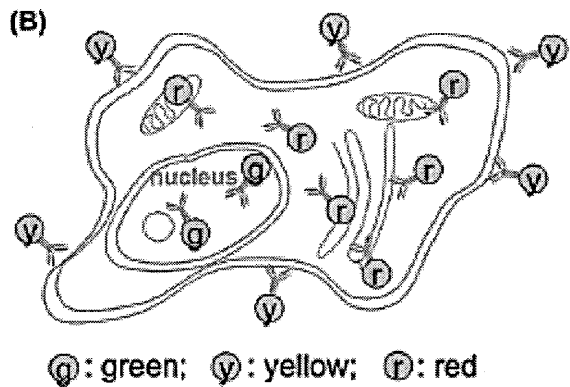


Figure 2.6 Nanoparticles imaging different parts of a cancerous cell(52).

Gao *et al*(54) and Pellegrino(55) have used nanoparticles to track cancer cells, monitor the development of the cells and gain information about the cancer’s invasiveness. Finally the Halas group at Rice university(56,57) have developed a cancer treatment using gold/silica nanoshells. The shells absorb light in the near IR region. The region of the electromagnetic spectrum provides efficient transmission through human tissue. As the shells absorb the light they undergo a temperature increase and whilst only small this temperature increase is toxic to the surrounding cells. The researchers have conducted *in vitro* studies on human cancer cells and *in vivo* studies on tumours in mice; both produced therapeutic results.

2.5.2 Nanostructured Light Emitting Devices

Another major area of interest in photoluminescent and electroluminescent nanoparticles is their incorporation into optoelectronic devices. Organic light emitting diodes (OLEDs) and nanostructured light emitting devices (NLEDs) aim to be a competing technology for the likes of liquid crystal displays providing low-cost, wide-angle, full-colour and large-area displays. Figure 2.7 shows electroluminescence from a NLED produced by Gallardo et al(58) operating in open-air conditions and Figure 2.8 shows a schematic of the different layers incorporated into an NLED.



Figure 2.7: Electroluminescence from a NLED. Image from Gallardo(58).

Although NLEDs have been produced without organic components there have been many cases of NLEDs being formed from semiconductor nanoparticles and polymers. Hybrid NLEDs combine the advantages of OLEDs(59) such as low cost and mechanical flexibility with the advantages of

semiconductor nanoparticles. Colvin *et al*(60) created hybrid devices from CdSe nanoparticles and poly(para-phenylene vinylene) (PPV) and found a voltage tuneable luminescence. At low voltages, emission from the CdSe layer occurs and the colour depends on the size of the nanoparticles used in the device. At high voltages, luminescence from the polymer occurs and is green. However the external quantum efficiency of the device is low 0.001 – 0.01%.

In 1997 Schlamp *et al*(61) improved the external quantum efficiency to 0.22% using CdSe nanoparticles capped with CdS shells and PPV. Several of their devices showed simultaneous luminescence from both nanoparticle and polymer layers, this changed to just nanoparticle emission as the nanoparticle layer was thickened. At higher voltages from 6-8V the polymer electroluminescence increased indicating that at higher fields a higher fraction of electrons reach the PPV before recombining.

Gaponik *et al*(62) produced a CdTe and polyaniline (PAni) NLED with a turn on voltage of ~2.5V (much lower than the 4V seen in previous work(60,61)). Comparing devices with and without PAni they found that above 4V the devices with PAni show higher external quantum efficiency, this occurs below the turn on voltage of the polymer emission. The polymer nanoparticle composite allows direct electrical connection of the PAni and CdTe, PAni then behaves as a hole-transporting layer.

Gao *et al* 2000(63) investigated NLEDs with various sizes of nanoparticles and found that both the stability and efficiency of luminescence increases with nanoparticle size. The turn on voltage, however, decreases with increasing nanoparticle size. Gao suggests this is because the electron

energy state is closer to the work function of Al in the larger particles, as the particle size decreases the electron state shifts to higher energies. Thus the efficiency of electron injection decreases with particle size. This group also synthesized devices containing layers of two different size nanoparticles. They found that luminescence always occurred from the nanoparticle layer closest to the hole injecting indium tin oxide (ITO) electrode. Showing electrons are the majority carriers.

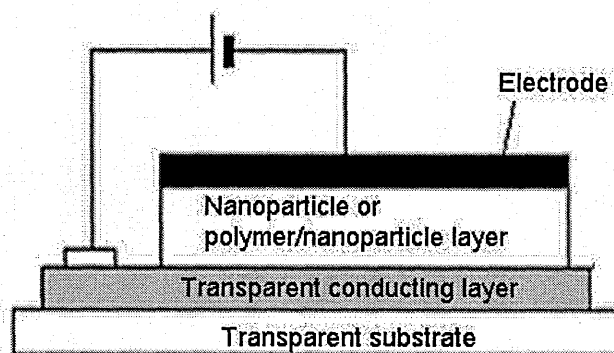


Figure 2.8: Schematic of a NLED. The luminescent nanoparticles are sandwiched between two electrodes.

2.5.3 Photovoltaics

According to the Earth Policy Institute(64) the worldwide production of photovoltaics has been rising by an average of 48% per year since 2002 making solar energy the world's fastest growing energy source. The main challenges in photovoltaic research are to increase the energy conversion efficiency of the devices and to decrease the cost of manufacturing them.

Traditional single crystal silicon solar cells are efficient but are also expensive(65).

Increasing the efficiency of photovoltaics is achieved by increasing the energy absorbed by the cell and decreasing the energy lost to exciton recombination. The tuneable nature of the band gap in semiconductor nanoparticles allows higher efficiency photon absorption by careful selection of the nanoparticles used. Using a mixture of differently sized nanoparticles allows both a high photon capture rate and capture of high energy photons. Thus provides an enhancement of the energy absorbed without the complications of achieving this through multi-junction cells(66). Nanorods have been shown to accelerate the carrier mobility(67) and in doing so reduce the energy lost to recombination. But nanoparticles can also increase the efficiency of photovoltaic devices in a third way, by providing multiple excitons per photon absorbed. When the energy of the absorbed photon is much higher than the band gap of the semiconductor multiple excitons can be formed(68). This does not usually happen in bulk semiconductors because the energy dissipates away as heat before multiple excitons can form. In nanoparticles the quantized energy states slow the heat loss and allow more time for excitons to form. Nozik has reported a 300% quantum yield when the energy of the photon is approximately four-times that of the semiconductor band gap(69,70).

Nanoparticles can be used in photovoltaic devices in several ways: as nanoparticles arrays(71), as hybrid nanoparticle-dye sensitized Grätzel cells(72) and as hybrid organic-nanoparticle devices(73). Gallagher *et al*(74,75), working as part of the European funded initiative *FULLSPECTRUM*,

provide another novel example of how nanoparticles can be used to improve the efficiency of photovoltaics. A spectral concentrator or converter is fabricated using a thin film of nanoparticles. Attached to the top surface of a traditional solar cell, the nanoparticles absorb the incoming light and red shifts its wavelength before emitting at a wavelength more suited to the band gap of the solar cell. This allows the mismatch between a silicon solar cell's band gap and the solar (AM1) spectrum to be bridged. Whatever the method of inclusion nanoparticles are sure to play a very important role in the future of solar energy.

2.6 Photoluminescence

Luminescence is the process in which substances emit photons. Excitation to a higher energy state has occurred then, as the system relaxes to a lower energy state, electromagnetic radiation is emitted. In photoluminescence excitation has occurred by absorption of a previous photon. The time period between excitation and emission is usually very short, in the order of ten nanoseconds.

Most of the results reported in this thesis involve measuring the photoluminescence of a suspension or thin film. Photoluminescence and absorption spectra of a typical CdTe suspension are shown in Figure 2.9. The photoluminescence peak maximum is ~630nm and the spectrum shows a full width at half maximum (FWHM) of 59nm. This is quite a broad spectrum and shows that the nanoparticles in this sample are of various diameters. Smaller nanoparticles emit at higher energy or shorter wavelengths and larger

nanoparticles emit at longer wavelengths. The absorption spectrum shows a featureless curve suggesting that the nanoparticles in this sample have a broad size distribution or are agglomerated into small clusters(76).

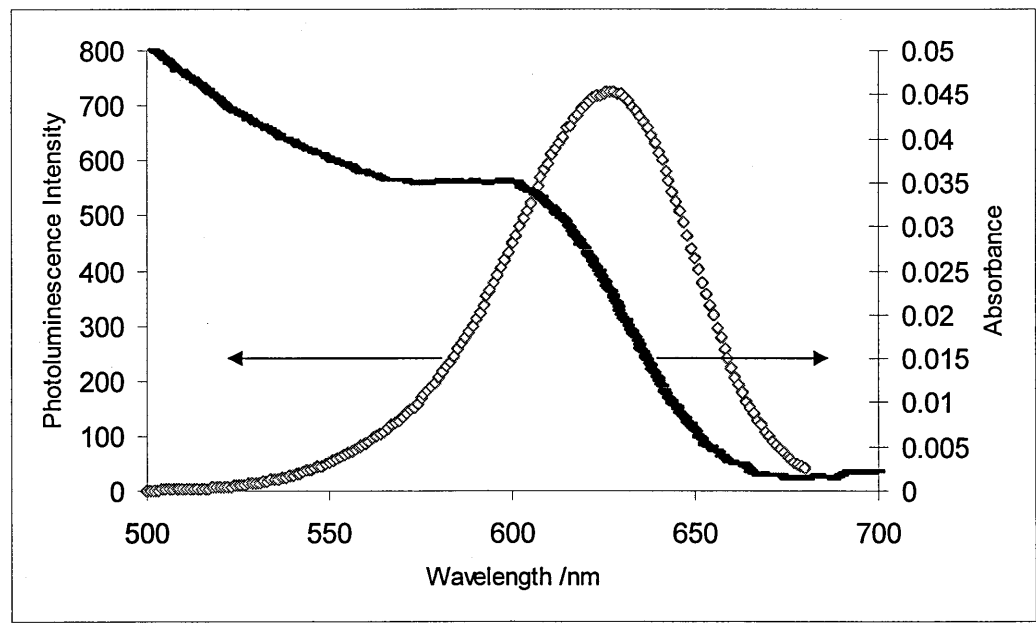


Figure2.9: Photoluminescence and absorbance spectra of a suspension of CdTe nanoparticles.

2.7 Thin film Deposition

Much of this thesis involves discussion of thin films of nanoparticles. It is therefore important to look at how these thin films are deposited. Chapter 5 studies the formation of thin films by a layer-by-layer (LBL) deposition method. As an introduction we should first look at the alternative methods of producing thin films.

There are many methods of creating thin films and choice between them is made by considering: the material to be deposited; the substrate to be deposited on; the required quality; the quantity of thin films required, e.g. commercial versus laboratory scale, and any cost restrictions. The nanoparticles used in this thesis have been produced by wet chemical methods (see Section 2.4.3) and are provided in an aqueous suspension form. Our choice of deposition methods is therefore limited to: spin coating, dip coating, spray coating, Langmuir-Blodgett deposition and LBL deposition.

2.7.1 Spin Coating

Spin coating is used to apply thin film coatings to flat substrates. It is commonly used when processing silicon wafers for micro electro mechanical devices. A solution or sol is applied to the substrate which is then rotated at high speed. Centrifugal force ensures a uniform layer of the coating. Excess deposition material is spun off the edge of the substrate and the machine must be cleaned regularly. The solvent used is volatile so the coating dries quickly allowing subsequent layers or further processing to follow. The layer thickness is controlled by the solution or sol composition, the spin speed and the spin time. Advantages of spin coating are that it is a quick, easy and cheap method. Disadvantages are that scale-up of the substrate size can be difficult, wastage of solution is high and drying steps must be included if multiple layers are required.

2.7.2 Spray Coating

Spray coating involves spraying a fine mist of material onto the substrate. Any size or shape of substrate can be used. The technique can include anything from a simple pump or gas powered bottle to a sophisticated ultrasonic or electron enhanced spraying machine. Figure 2.10 shows a ultrasonic liquid atomization sprayer from Sonotek(77).

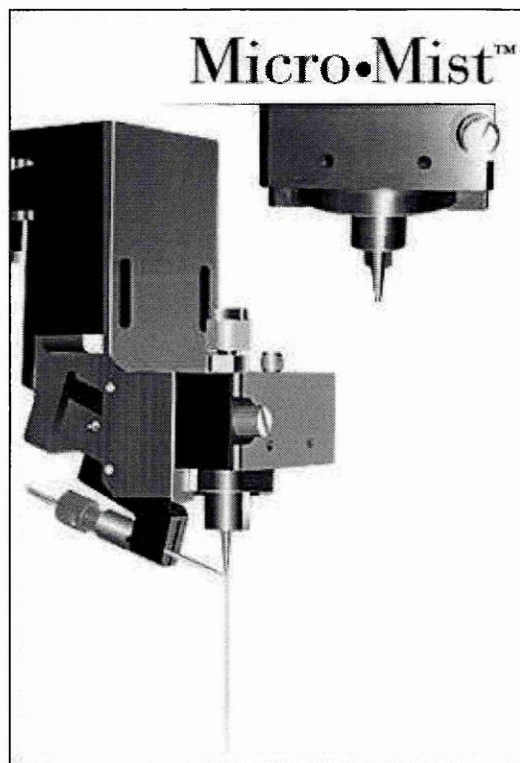


Figure 2.10: MicroMist from Sonotek

Spray coating is used extensively in industry as it is fast, easy to scale-up and can be very precise. A wide range of materials can be deposited and deposited on. A disadvantage of the technique is that wastage of the deposition material is often high due to overspray. In a laboratory it can be difficult to emulate the precision seen in industry without expensive

automation technology. Finally, if the material to be deposited included nanoparticles containing cadmium there would be the additional safety risk of having created airborne particles and deposition would have to take place in an enclosed environment.

2.7.3 Langmuir-Blodgett

Langmuir-Blodgett (LB) deposition is a very popular technique for depositing thin films of organic molecules. The technique was developed in the late 1910s and early 1920s by the Nobel prize winning Irving Langmuir(78) and applied by Catherine Blodgett in 1935(79). The LB technique works by first creating a monolayer of the material to be deposited on the surface of a LB trough. A substrate is then inserted and withdrawn through the monolayer and material is transferred from the trough to the surface of the substrate. Figure 2.11 shows a picture of a LB trough. Petty provides an excellent introduction to the physics and chemistry behind LB films(80).

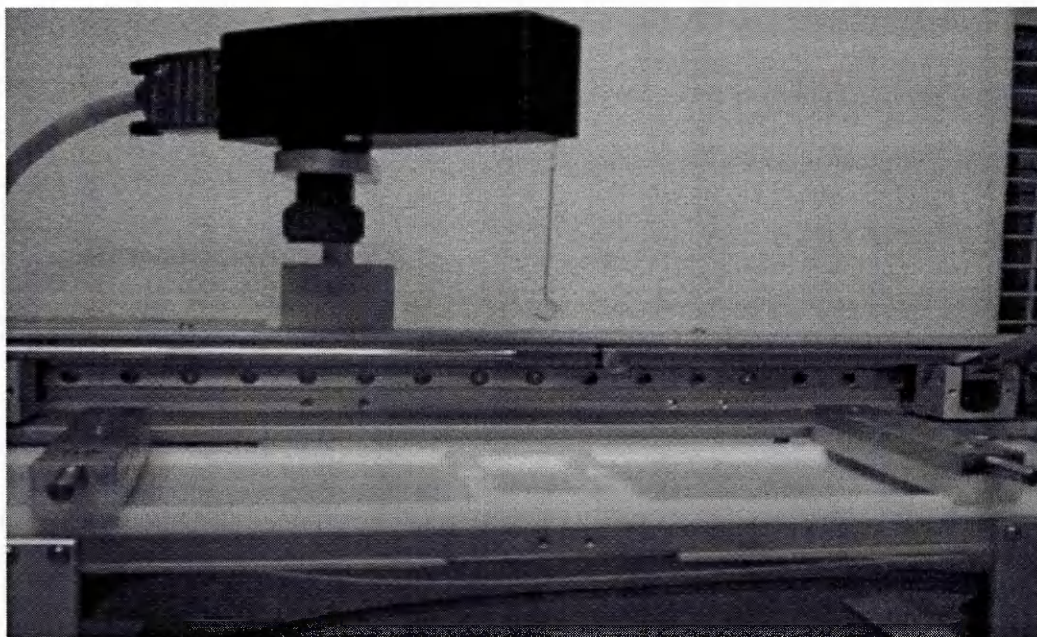


Figure 2.11: Langmuir-Blodgett trough.

The monolayer formation relies on the amphiphilic nature of the molecules. Thus to form a suitable monolayer for LB deposition we are limited to certain types of molecules. Careful consideration needs to be given to the size of the head group and the length of the hydrocarbon chain. If the chain is too short micelles will form instead of monolayers and if the chain is too long the material will crystallize⁽⁸⁰⁾. Non-amphiphilic molecules can and have been⁽⁸¹⁾ deposited by the LB technique, but they first need to be attached to a suitable amphiphile.

Once a monolayer is formed the dividing beam of the LB trough (see Fig. 2.11) is used to ensure the molecules are in a solid state phase. Material can then be transferred onto a substrate Figure 2.12 shows a schematic of this. Thin films can be deposited in several different film orientations by changing the direction of the first deposition stroke. In Figure 2.12 the substrate is being withdrawn from the trough, this means the first layer

deposited has the hydrophilic head groups attached to the substrate. Once completely withdrawn the substrate and monolayer could be re-inserted into the trough and a bi-layer would form. If the first layer was instead deposited by inserting the substrate into the trough a monolayer with the hydrophobic parts of the molecule attached to the substrate would form. Dual LB troughs also exist to enable alternate layers of two different molecules to be built up; the substrate is lowered through one part of the trough then transferred underwater to the second part. Langmuir-Schäfer deposition involves lowering the substrate horizontally towards the trough surface until the substrate just touches the hydrophobic tail of the molecules. In this method the material is transferred as a complete film.

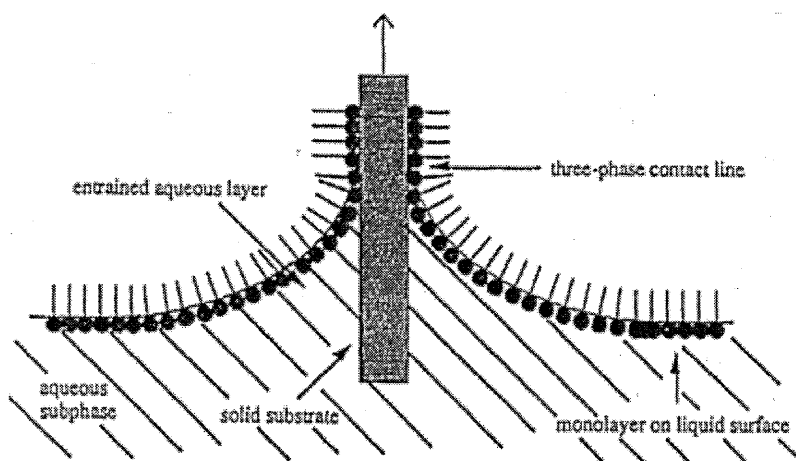


Figure 2.12: LB film deposition. Adapted from Petty(80).

Advantages of the LB technique are that it is well established, well understood and allows precise control of the number, orientation or thickness of the layers deposited. After the first layer has been deposited the technique

can proceed relatively quickly but is still very slow when compared to spray coating. Disadvantages of the technique are that there are some limitations on the materials that can be deposited and the initial trial and error of new setups can be complicated. Also, the strength of the film is dependent on Van der Waals forces which are weaker interactions than the electrostatic attraction seen in the next Section.

2.7.4 Dip Coating and Layer-by-layer Deposition

Dip coating is a simple procedure where a substrate is dipped into a solution of the material to be deposited and a layer is formed on the surface of the substrate. The LBL method is an advanced version of dip coating.

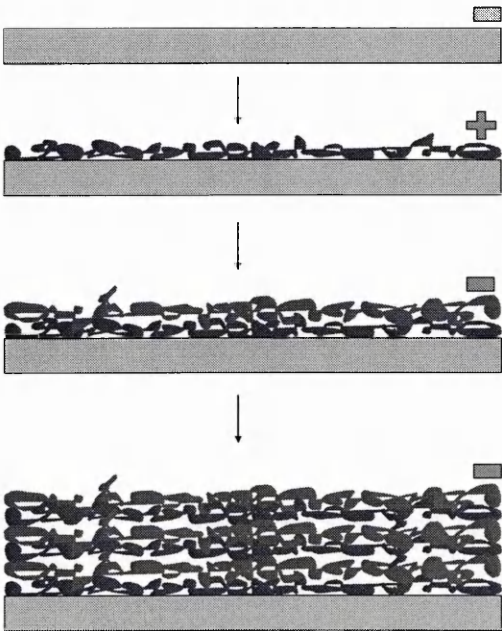


Figure 2.13: A schematic of the build-up of layers during the LBL process.

The cationic polyelectrolyte is shown in blue and the anionic polyelectrolyte in red. The surface charge at each stage is shown in green.

The LBL deposition process is a self-assembly technique commonly referenced as being introduced by Decher(82). The process works by using electrostatic charges to form attractive forces between different polyelectrolytes. Figure 2.13 shows a schematic of how the layers are built up during a LBL deposition process and Figure 2.14 shows the structures of some of the commonly used polyelectrolytes. A polyelectrolyte is a polymer containing electrolyte groups; when in aqueous or polar solvents the electrolyte group can dissociate to form a charged species. Of the polyelectrolytes shown in Figure 2.14 PEI, PDDA and PAH form positive polymers and PAA and PSS form negative polymers. In the first step of LBL deposition a charged substrate is immersed into a solution of oppositely charged polyelectrolyte. Due to electrostatic attraction the polyelectrolyte then forms a monolayer on the surface of the substrate. As the polyelectrolyte has multiple charges a charge reversal occurs on the surface; that is, enough polyelectrolyte is adsorbed to match and over-compensate the charge of the substrate therefore changing the charge of the newly created surface. This charge reversal is essential to the process as it allows further monolayers to be deposited. If the charge of the surface was not changed it would not be possible to deposit a layer of oppositely charged material. If the charge of the surface was only matched by the new polyelectrolyte therefore neutralising the surface charge then any further deposition attempts would be much less efficient as there would not be the same electrostatic incentive. The charge reversal also acts as a control; changing the surface charge prevents the deposition of more than one layer of polyelectrolyte in a single step as the deposited polymer will repel further deposition of polyelectrolytes

with the same electrostatic charge(83,84). A washing and sometimes also a drying(85) stage is employed to remove excess particles and prevent contamination. In the second step the substrate is immersed into a solution of oppositely charged polyelectrolyte and a second monolayer adsorbs. The washing and drying steps are repeated and one bi-layer is now complete. The process can be repeated until the desired number of layers has been deposited.

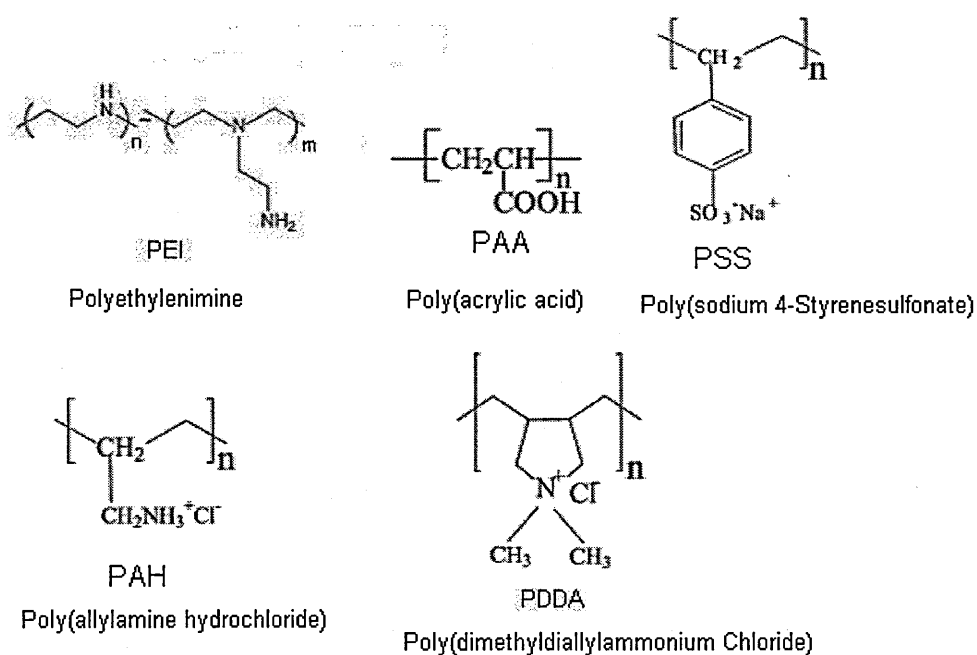


Figure 2.14: Structures of some common polyelectrolytes

There are many advantages to the LBL method perhaps the main one is its versatility. Any polyelectrolyte can be used(87). Figure 2.14 shows the structure of some commonly used electrolytes(86,87). Therefore, just by changing the polyelectrolyte and the number of depositions it is possible to control, at the nanometre scale, the thickness and architecture of the film. The LBL technique is mostly substrate insensitive(82); providing a substrate

has a charged surface it can be used for LBL. The substrate does not need to be pre-treated. The inherent surface charges in glass or on an ITO coated substrate are enough to perform LBL. Although, if a substrate has only a small amount of surface charge, charge multiplication can occur during the first few layers(88). The simplicity of LBL means no specialist equipment is needed. Being easy to automate also makes the technique a rapid and reliable method of producing high quality thin films. A disadvantage of the technique is that the mechanism of deposition is less well understood than that in LB. The technique is also limited to molecules with electrostatic charges, but this limitation is less restrictive than in LB.

2.7.5 Choice of Deposition Method

In this thesis the material to be deposited was aqueous suspensions of CdTe nanoparticles capped with TGA and the main substrate used was glass. The deposition method chosen was LBL. The methods of spin and spray coating were discounted due to the high wastage of material inherent in these techniques. Whilst LB has been used to deposit nanoparticles(81) there is more literature, and therefore knowledge, available on using LBL for these types of nanoparticles. The TGA capping of the nanoparticles makes their surface negatively charged thus miscible with polar solvents such as water. The nanoparticles would therefore need to be adapted before use with the LB technique. The particular deposition technique used throughout this thesis is detailed in section 3.2

3 General Methodology

3.1 Nanoparticle Suspensions

All the CdTe nanoparticles used in this report were obtained from Dr N Gaponik of Technical University Dresden and were stored in the dark at 3-5°C before being used. The nanoparticles were synthesised(1) in aqueous solution and were coated with a capping layer of TGA. The stability of the nanoparticles was high and the suspensions could be stored for months without degradation(1). The structure of TGA is shown in Figure 3.1. The thiol group (marked yellow in the left-hand diagram) bonds to the surface of the nanoparticle with the carboxylic acid group (red in the diagram) forming a capping layer of negative charge around the particle.

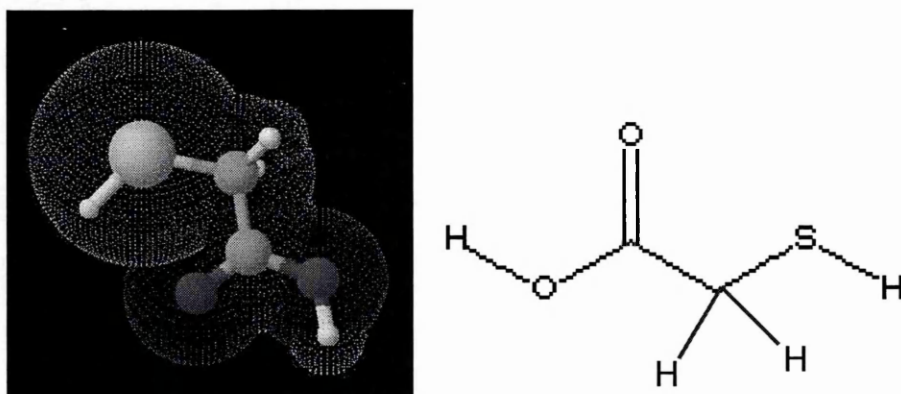


Figure 3.1: Structure of TGA

Before use the suspensions were usually (except for Chapter 4) diluted using high purity water obtained from Sigma Aldrich. Figure 3.2a shows a nanoparticle suspension irradiated by UV light at 365nm. Figure 3.2b is a schematic of the structure of a CdTe nanoparticle capped with TGA.

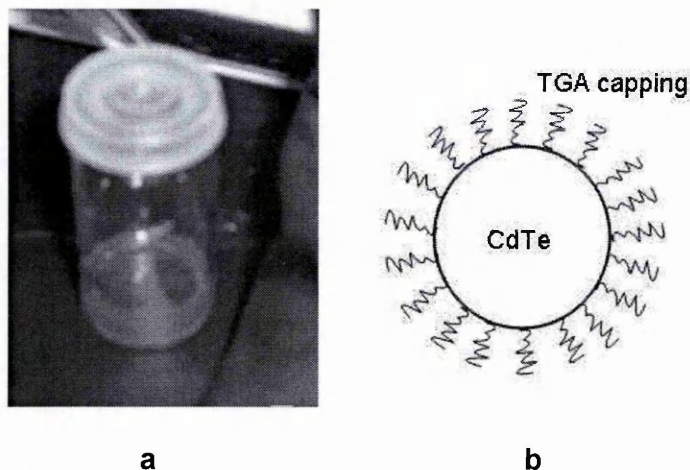


Figure 3.2: **a** CdTe nanoparticles under a UV light source and **b** a schematic of a TGA capped nanoparticle.

Throughout the experimental work several different CdTe suspensions have been used. Although all the suspensions are made using the same technique, slight differences occur between the different batches. Likewise, the conditions suspensions are kept in once they arrive and between experiments (e.g. kept in the dark in the fridge or kept in the laboratory) cause differences between the samples. These differences are most noticeable when measuring the photoluminescence spectra of the suspension, different batches and different conditions cause a difference in the photoluminescence spectra peak maximum. For the above reasons, comparisons are only drawn

between suspensions or thin films made from the same batch of CdTe and differences in wavelength from one part of this report to another are not further discussed.

3.2 Layer-by-layer Production of Thin Films

Thin films of CdTe nanoparticles were deposited onto cleaned glass substrates using a layer-by-layer (LBL) technique first reported by Decher(2) and previously used in our lab by Gallardo(3). Since the CdTe nanoparticles used were capped with TGA they had a negatively charged surface and required a cationic polymer for electrostatic interactions. Throughout this thesis (except where stated in Chapter 5) polydiallyldimethylammonium chloride (PDPA) was used as the polymer. The deposition technique is described below. Figure 3.3 shows a glass slide after being coated with 10 layers of polymer and nanoparticle using the LBL method.

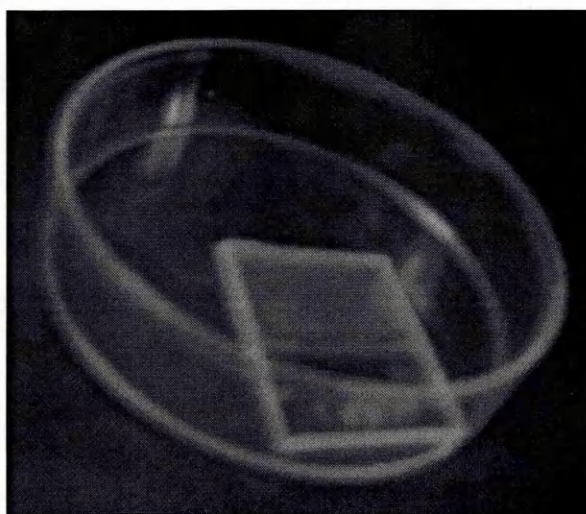


Figure 3.3: A glass slide after LBL coating

3.2.1 Substrate Preparation

Microscope glass slides were cut into $\sim 2.5\text{cm}^2$ substrates. The substrates were cleaned in a series of four ultrasonic baths using solutions of: detergent and water, distilled water, acetone, and finally isopropanol. The substrates were kept in each bath for a minimum of five minutes. The substrates were then left to dry in a dust free environment.

3.2.2 Polymer Solutions

PDDA solution was made up from 20w% PDDA in water (Mw 200,000 - 350,000) obtained from Aldrich dissolved in a 0.2M NaCl buffer to a concentration of 5mg/ml. The structure of PDDA is shown in Figure 2.14.

3.2.3 Layer-by-layer Deposition

Cleaned glass substrates were dipped into a PDDA solution for 20 minutes washed with deionised water for 2 minutes and then dipped into a CdTe suspension for a further 20 minutes. This cycle was repeated until the desired number of layers had been deposited. The samples are withdrawn from the solutions in incremental steps, this allows the meniscus to remove excess solution ensuring an even layer. No drying step is used. The process was automated (see Fig. 3.4); samples are moved using a robotic arm which removes all operator errors and ensures a repeatable procedure. The automated LBL apparatus was designed and programmed by Gallardo(3). Covers are fitted over each of the beakers to prevent dust contamination. An advantage of the LBL method is that it allows control, at the nm scale, of the

thickness of the film, its interfaces and its architecture. Unless otherwise stated the thin films used in this report all consist of 10 bi-layers of PDDA and CdTe.

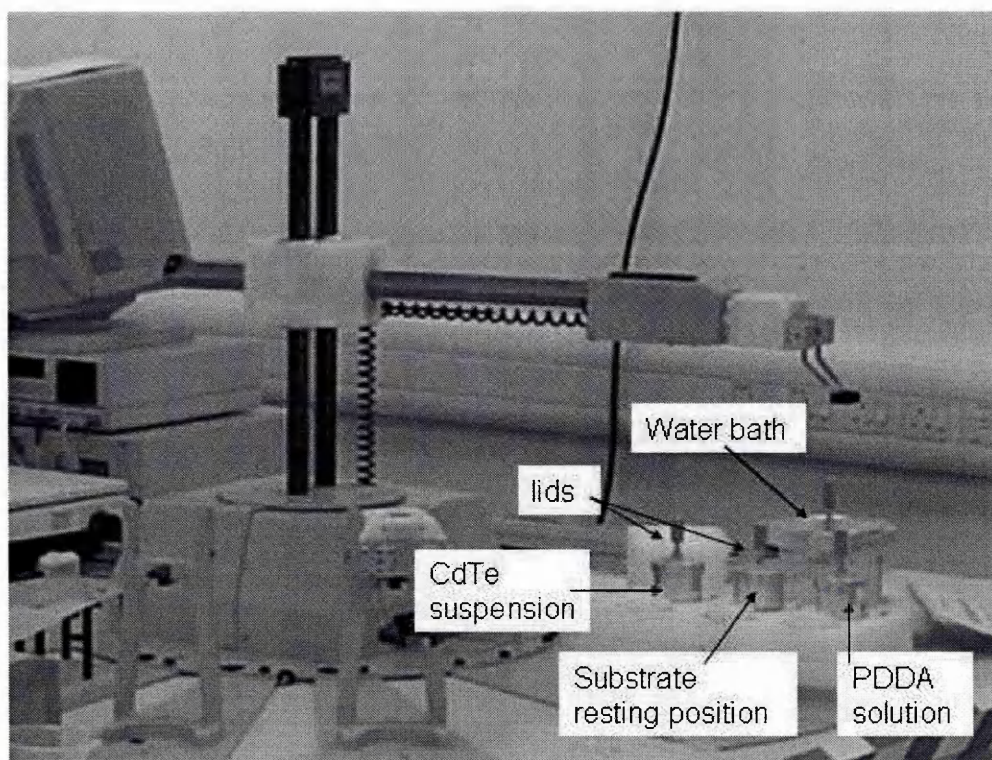


Figure 3.4: The automated LBL process

3.3 Spectroscopy

Absorbance and emission spectra were recorded using a Perkin Elmer lambda 7 Ultra Violet-Visual (UV-Vis) spectrometer and a Varian Cary Eclipse spectrophotometer using an excitation beam with a wavelength of 365nm. Raw data was extracted from the spectrometers and Microsoft excel was used to plot all graphs.

3.4 Microscopy

Atomic force microscopy (AFM) and scanning electron microscopy (SEM) images were recorded on a Digital Instruments Dimension 3000 in tapping mode and a Schottky Field Emission Gun Philips XL30 respectively.

4 Dilution and Deposition of Nanoparticles

4.1 Introduction

When nanoparticles are synthesized using wet chemical methods(1-3) the end product is often a concentrated suspension. Whatever the intended application, the suspension will need to be processed in some way. This Chapter looks at the simplest of processing techniques; namely the dilution of the suspension and the deposition of the nanoparticles to create a thin film.

Döllefeld *et al*(4) reported an interesting phenomenon when diluting a suspension of nanoparticles. Investigating the stability of CdS nanoparticles capped with various thiols they found that when the same nanoparticles were placed in suspensions of different concentrations the nanoparticles in more dilute suspensions appeared to have smaller sizes and decay of the particles occurred. The size of the nanoparticle was estimated using both analytical ultracentrifuge (AUC) measurements and absorbance spectra. A $150\mu\text{molL}^{-1}$ suspension of CdS particles had an average size of approximately 1.7nm measured by AUC whilst a $10\mu\text{molL}^{-1}$ suspension of the same particles showed an average particle size of 1.3nm when measured by the same technique. Döllefeld *et al* concluded that at lower concentrations the thiol capping layer desorbed from the nanoparticle. Removing the thiol shell decreases the size of the nanoparticle thus shifts the wavelength of absorbance to higher energy (see Section 2.3) (4,5). In Section 4.3.1 analogous experiments are conducted using CdTe nanoparticles capped with

TGA and similar results are found. We expand on the current research by looking at samples with two different solvents. Both water and chloroform based suspensions show a wavelength shift with dilution. An attempt is also made to re-concentrate the diluted samples.

The LBL technique, discussed more fully in Chapter 5, is a popular technique for producing thin films of nanoparticles by deposition from their suspension. Here, LBL is used to monitor how the photoluminescence of the nanoparticles change as they are deposited from a suspension to form a thin film.

Vossmeier *et al*(6) were the first to report a red-shift in absorbance spectra when a thin film is deposited from suspension. They found a low energy shift in the 1s-1s absorbance band of a spin-coated thin film. However, when the suspension was re-dissolved the spectra returned to its original position. Vossmeier *et al* attributed this observation to an increased electronic interaction between the nanoparticles. In Vossmeier's thin film he postulates that the nanoparticles are homogenous in size and the inter-particle distance is in the order of angstroms. In this scenario the nanoparticles can form collective excitation modes, similar to the energy bands of bulk semiconductors. Artemyev *et al*(7) compared isolated nanoparticles with close packed nanoparticles and explained the resulting red-shift by the formation of collective electronic states. However, in 2001 Döllefeld *et al*(8) conducted a numerical study of the interactions between semiconductor particles in close contact, they concluded that both electronic interactions and dipole-dipole coupling contribute to the shift seen by Vossmeier. In a later paper(9) the same researchers further investigated the

dipole-dipole interaction and concluded that it is the main cause of the red-shift.

Vossmeier, Döllefeld and Artemyev all used monodisperse nanoparticles but a similar effect has been seen in films of mixed size particles. Kagan *et al*(5) looked at close packed nanoparticle solids made from a mixture of 82% small (3.85nm) and 18% large (6.2nm) CdSe nanoparticles. They found a large increase in the ratio of emission from the large to small particles when converted from a suspension to a mixed solid and attribute this to long range resonant interactions.

Although Kagan's paper is an extreme example it is an important observation since the nanoparticles used in suspension throughout this report have a size distribution (see Section 2.6) and are not truly monodisperse. Both theories of collective electronic states and dipole-dipole interactions require the nanoparticles to be in close contact for a red-shift or broadening to occur. Thus we focus on inter-particle distance as we expand the above work to look at further photoluminescence changes as the LBL thin film develops. In this Chapter we observe a red-shift in photoluminescence as a thin film is deposited from suspension. A further red-shift is seen as the number of layers in the thin film is increased. To explain these observations and relate them to inter-particle distance a space filling deposition mechanism is proposed.

4.2 Experimental

To investigate the effects of diluting suspensions, photoluminescence spectra of unused and undiluted suspensions were recorded; small (5 μ l – 50 μ l) sequential volumes of solvent (water or chloroform) were added and spectra were re-recorded after each addition. The original (as received from Dresden) suspensions were given a nominal concentration of 1 and subsequent concentrations were calculated by allowing for the volume of solvent added to the volume of the original suspension i.e. if 0.5ml of a suspension (concentration 1) was used and a total of 5ml of solvent was added the end concentration would be $500/5500 = 0.09$ a.u..

One of the suspensions used in this Section is a chloroform based suspension of CdTe nanoparticles. The nanoparticles are capped with TOPO, the structure of which can be seen in Figure 4.1.

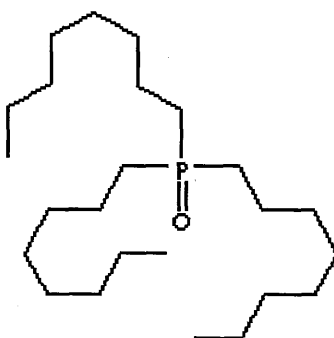


Figure 4.1 Structure of TOPO

UV-Vis absorbance spectra were recorded using a Perkin-Elmer lambda 7 UV-Vis spectrometer in absorbance mode.

4.3 Results and Discussion

4.3.1 Dilution of Suspensions

The addition of solvents to suspensions of CdTe nanoparticles caused changes in the photoluminescence spectra. Both water-based and chloroform-based suspensions have been diluted and attempts have been made to re-concentrate samples after dilution.

In the first example a suspension of TGA capped nanoparticles was used so the solvent required was water. As water was added to the suspension the wavelength of the photoluminescence peak maximum showed a shift to shorter wavelengths. Higher energy emission may indicate a smaller particle size(10). The shift was linear and can be seen in Figure 4.2. The wavelength of the peak maximum at concentration 1 is 557 nm but at concentration 0.17 has shifted to 550 nm. In several places in Figure 4.2 the wavelength of the peak maximum seems to show a spread or a plateau at a certain wavelength e.g. five spectra show a wavelength of 557nm. This is because the spectrometer detects emission intensity at 1.03nm increments thus only a finite number of readings are possible.

UV-Vis absorption measurements (not shown) were also taken before and after diluting a suspension. A shift to higher energy wavelengths occurred when the suspension was diluted mirroring the results of the photoluminescence spectra.

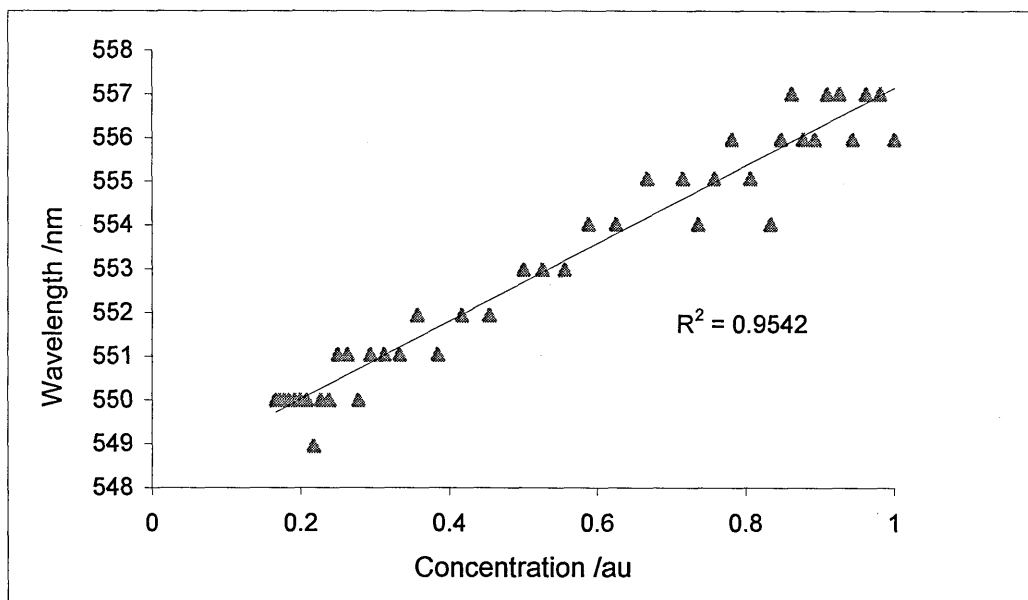


Figure 4.2 Change in the photoluminescence peak maximum as a suspension of TGA capped CdTe nanoparticles is diluted

The same result was seen in other suspensions of CdTe, Figure 4.3 shows two other water-based suspensions. Each of the suspensions showed a different gradient of transition but all had the same general trend. The wavelength shift is therefore not an anomaly of one particular suspension.

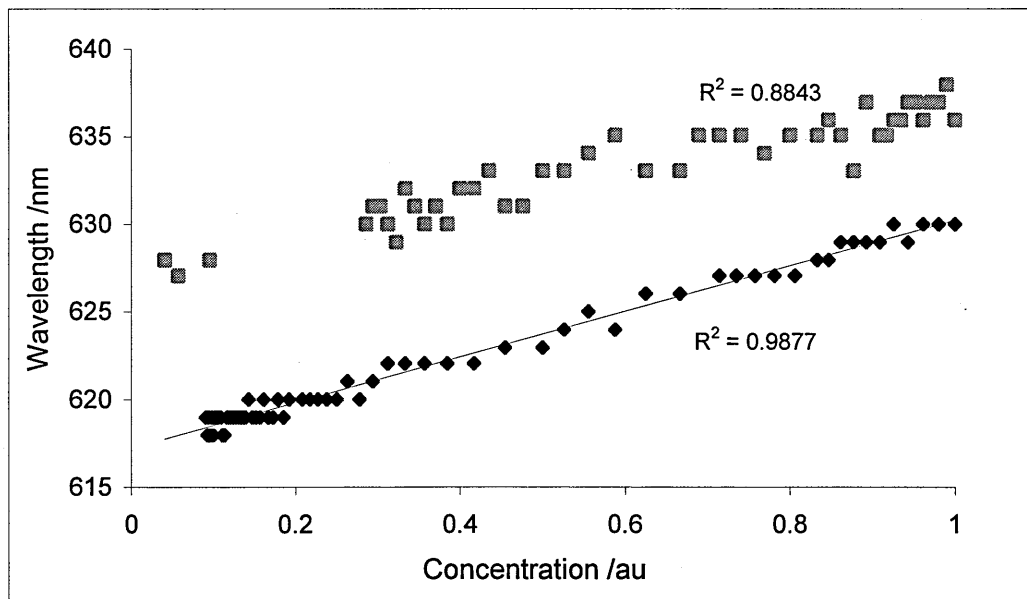


Figure 4.3 Change in the photoluminescence peak maximum as two further water based suspensions of CdTe nanoparticles are diluted.

A chloroform based suspension of CdTe nanoparticles was diluted and again showed a photoluminescence blue-shift with dilution. Figure 4.4 shows the results from the chloroform suspension. At concentration 1 the wavelength of the peak maximum is 591nm after dilution to concentration 0.07 this has changed to 585nm. The nanoparticles in the chloroform sample are capped with TOPO. The shifts seen are therefore also not an anomaly of the TGA/water based suspensions.

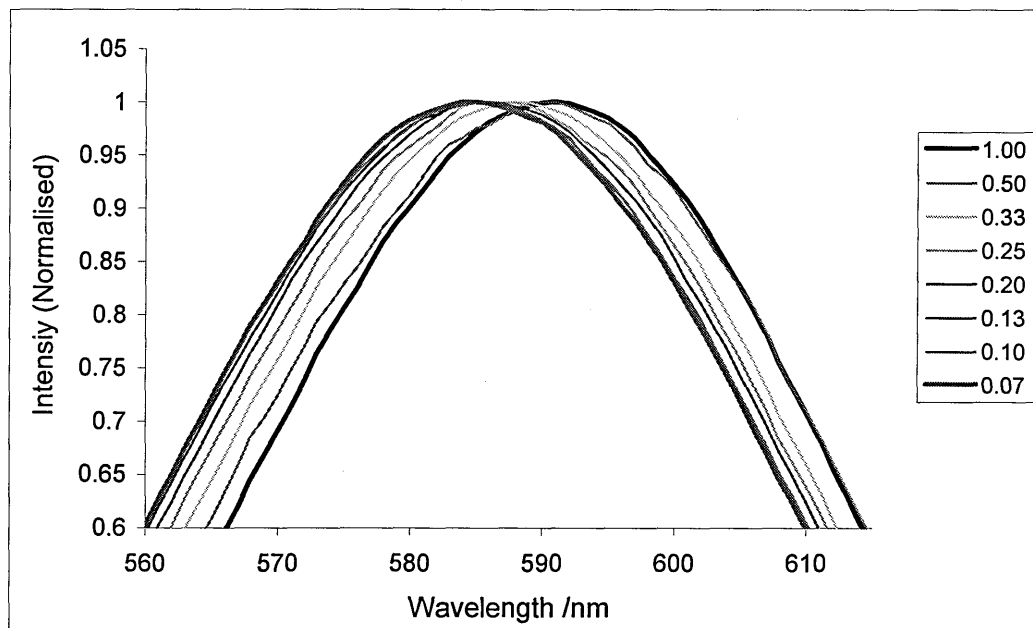


Figure 4.4 Spectral change when a chloroform based suspension of CdTe nanoparticles is diluted

A look at the actual photoluminescence spectra for diluted and undiluted suspensions shows a change in the peak shape. The spectrum of an undiluted suspension has a left-skewed distribution but this tends to a Gaussian distribution as the concentration is decreased (Fig. 4.5). The left shoulder (high-energy) of a photoluminescence spectrum represents the energy emitted from smaller nanoparticles. In Figure 4.5 the diluted spectrum displays a higher emission intensity at shorter wavelengths than concentration 1; this shows that the emission from smaller nanoparticles has increased. Stronger high-energy emission would occur if the number of smaller nanoparticles increased i.e. the nanoparticles in the sample are becoming smaller, or the energy transitions between the nanoparticles, i.e. dipole-dipole interactions, became weaker. The low-energy shoulder of the spectra

changes little from one concentration to another, indicating that the contribution from larger nanoparticles is less affected. In a numerical representation of this the FWHM increases from 56nm at concentration 1 to 60nm at concentration 0.04. An increase in FWHM reveals a broadening of the size dispersion of the suspension.

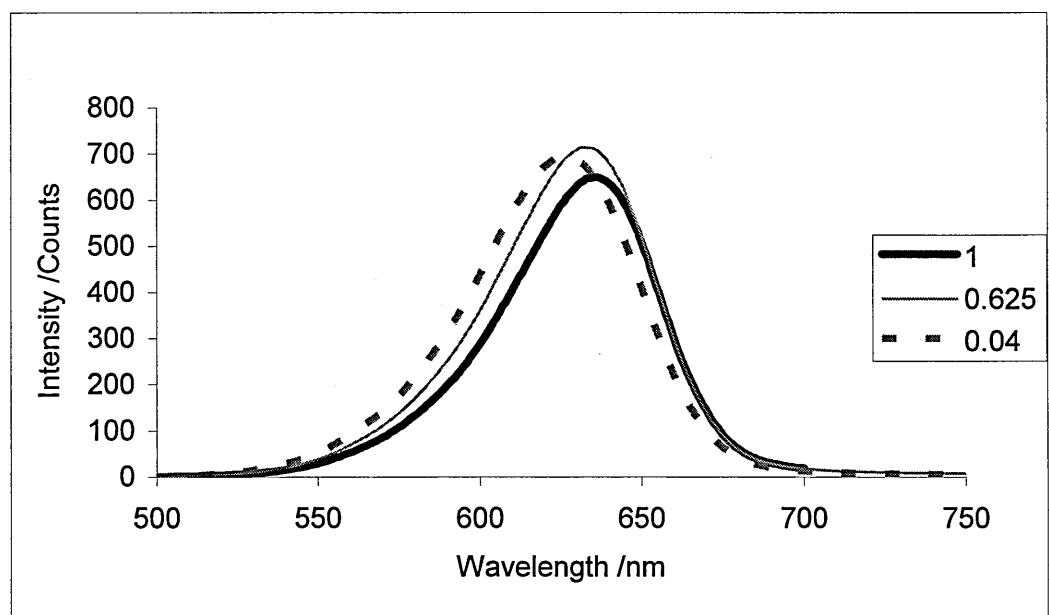


Figure 4.5 The photoluminescence spectra of the same suspension with three different concentrations

FWHM data for each of the suspensions discussed above are given in table 4.1. All suspensions show an increase in FWHM as the concentration is decreased.

Table 4.1 Summary of FWHM for various concentrations and suspensions

Suspension	Concentration	FWHM
Green Triangles (Fig. 4.2)	1	36 nm
	0.55	36 nm
	0.17	39 nm
Pink Squares (Fig. 4.3)	1	57 nm
	0.625	57 nm
	0.04	60 nm
Blue Diamonds (Fig. 4.3)	1	53 nm
	0.55	56 nm
	0.1	58 nm
Chloroform Sample (Fig. 4.4)	1	56nm
	0.5	58nm
	0.07	59nm

A blue-shift in the peak maximum as seen in Figures 4.2 to 4.4 suggests a decrease in particle size, since smaller particles will emit with higher energy luminescence(10). An increase in FWHM shows the detected emission is from a wider range of nanoparticle sizes. Again, this could be due to some of the nanoparticles decreasing in size.

Döllefeld *et al*(4) noticed a decrease in particle size when suspensions of thiol capped CdS nanoparticles were diluted. They attributed this decrease to the removal of the thiol capping layer from the nanoparticle surface. It is likely the same effect is being seen here. A desorbing capping layer could also explain the change in shape of the photoluminescence spectra. A bigger particle has a larger surface area, so if the thiol desorbs from all sites at the same rate it will take a longer period of time to desorb the same percentage of capping layer from a larger particle a tail would then appear on the high energy side of the spectrum. If the TGA capping layer is desorbing from the

nanoparticle surface we would also expect to see a loss in luminescence intensity as trap states formed on the surface of the nanoparticles. The nanoparticles would begin to agglomerate. Agglomeration was not observed in our samples because the diluted suspensions were not monitored over a prolonged period of time. However, in 2006 Boldt *et al*(11) investigated the stability of CdTe nanoparticles capped with TGA in various buffers, including water, and recorded an intensity deterioration over one week.

The TOPO capped nanoparticles (Fig. 4.4) showed the same trend as the TGA capped samples. TOPO binds to the nanoparticles through an oxygen lone pair forming a CdO bond this is a stronger bond than the CdS bond in the thiol capped sample(12). In ligand exchange reactions TOPO can not be completely removed from the surface of the nanoparticle. Kim *et al*(13) reported that 11% of TOPO remained after a ligand exchange reaction with pyridine involving refluxing at 60°C for up to 15 hours. It is therefore unlikely that by simply diluting the suspension we are removing the entire TOPO capping layer. The trend seen in Figure 4.3 does support the findings by Döllefeld *et al*(4) but also suggests that a secondary cause may be present.

As a suspension is diluted the ratio of solvent to particles increases. Although the position of the nanoparticles will be constantly changing (due to Brownian motion) if the particles remain dispersed the extra solvent will mean an increase in the average distance between particles. As we saw in Section 4.1 the distance between particles affects their energy interaction. Diluting the suspension and increasing the inter-particle distance would have the opposite effect to the deposition experiment observed by Vossmeier(6).

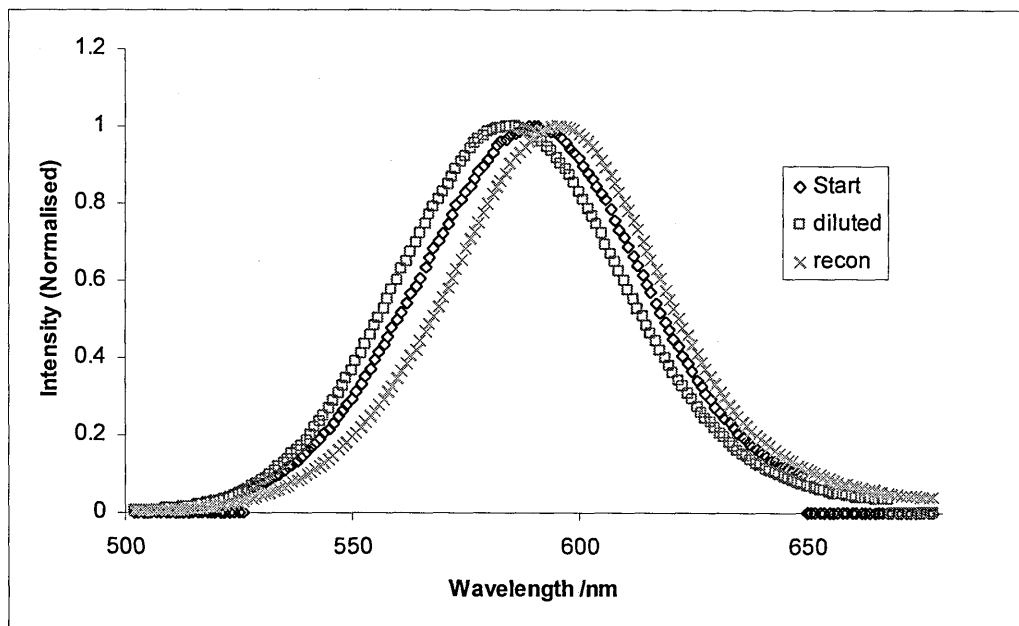


Figure 4.6: A diluted and re-concentrated suspension.

After dilution and measurement the chloroform based suspension was left to evaporate in a controlled environment. The photoluminescence spectrum was then re-measured and is shown in Figure 4.6. The wavelength of the peak maximum can be seen to shift from 591nm at the beginning of the experiment to 585nm when diluted and finally to 597nm when re-concentrated. If the shifts in wavelength seen in Figures 4.2 to 4.4 were solely due to a decrease in particle size as a result of the desorption of capping layer molecules, the shift seen on re-concentration would suggest an increase in particle size due to adsorption of the same molecules. Since the wavelength shifts to beyond that of the original, undiluted, sample it is difficult to see how adsorption could be the only cause. There is no more or less TOPO in the re-concentrated sample than in the original suspension. The

TOPO has also not formed a better arrangement of capping shell as if the original nanoparticles did not have a complete layer of TOPO capping they would not be stable. The inter-particle distance however, does change. Re-concentration removes the excess solvent between particles allowing stronger energy interactions. The effects of inter-particle distance are looked in more detail in the next Section.

4.3.2 Deposition of a Thin Film of Nanoparticles

Deposition of CdTe nanoparticles as thin films caused a change in their luminescence; on deposition of a single layer (Fig. 4.7) the photoluminescence peak maximum shifted from 639nm as a suspension to 644nm as a thin film. Again, there is little change in the low-energy tail of the spectra but a more pronounced change in the high-energy tail. Here, the emission from the smaller nanoparticles is reduced and the FWHM is also reduced from 56nm as a suspension to 47nm as a thin film. The effect is similar to that seen by Vossmeier(6) and other researchers(7,9) discussed in Section 4.1. The physical constraints inflicted by the substrate and binding polymer hold the nanoparticles closer together in a thin film than they have been in a suspension. Reduction of the inter-particle distance facilitates energy transfer from small to large nanoparticles resulting in enhanced luminescence from the larger dots and quenched luminescence from the smaller nanoparticles.

Zhang *et al* (14) observed a similar red-shift in wavelength and a reduction of the FWHM when conducting a low temperature study of CdSe/ZnSe nanoparticles. Using cathodoluminescence Zhang *et al* were

able to resolve the luminescence spectra and reported that there was a simultaneous increase in emission from larger particles and decrease in emission from smaller particles.

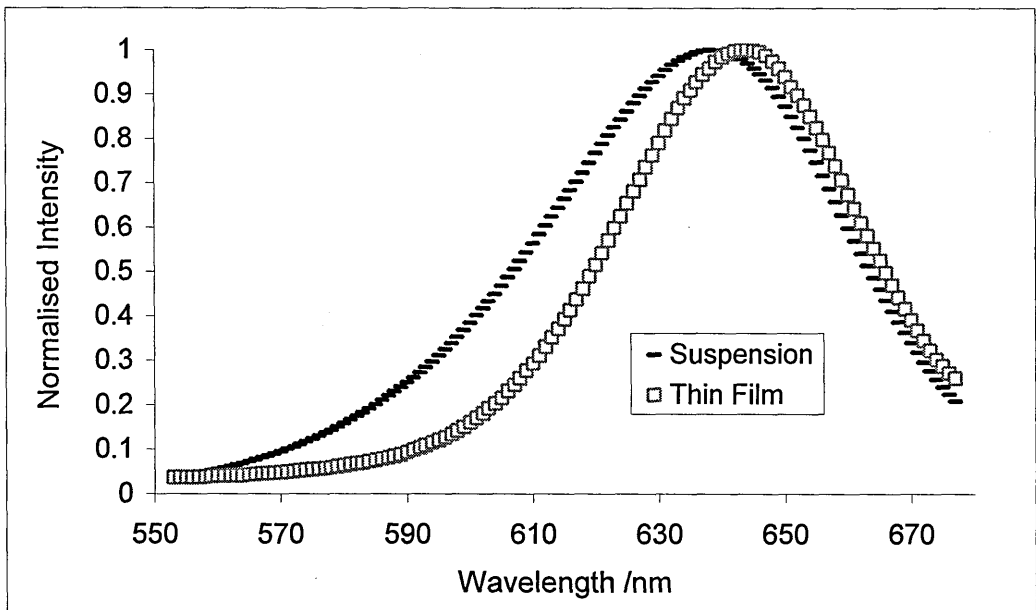


Figure 4.7 The change in photoluminescence as a suspension of nanoparticles is deposited by the LBL method

To expand on the previously published work characterisation was continued as multi-layers were produced allowing a per layer analysis. Figure 4.8 shows that the red-shift seen during the deposition of a single layer is enhanced when the number of layers is increased. Here, a single layer thin film shows a peak maximum of 628nm but a 10 layer thin film shows a peak maximum of 643nm. In a single layer thin film nanoparticles are within a few angstroms of each other in two dimensions, in multilayer thin films nanoparticles are within a few angstroms of each other in three dimensions.

The number of potential inter-particle interactions is therefore substantially increased and it is not surprising that a further red-shift is seen.

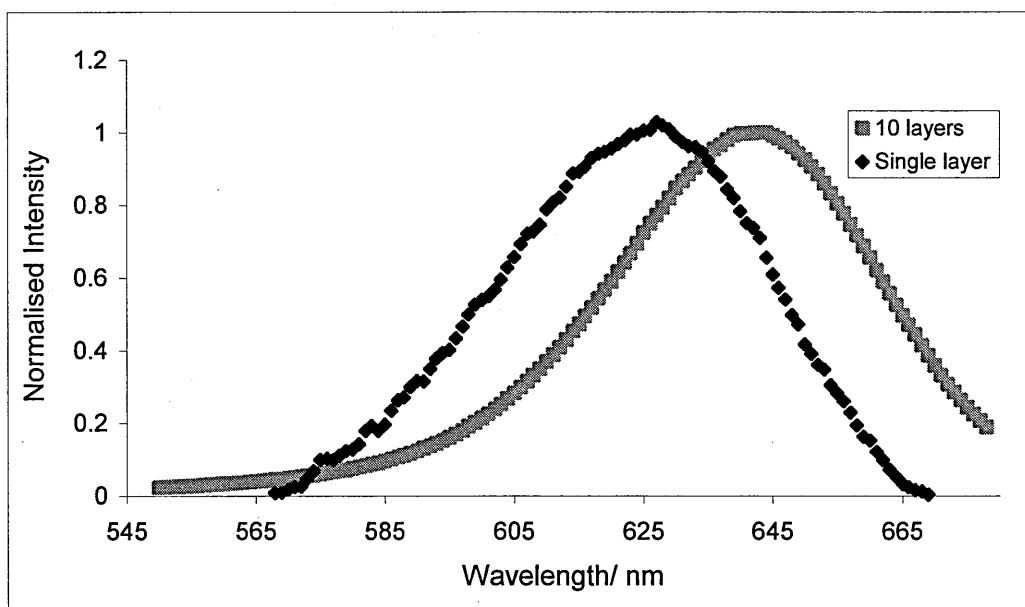


Figure 4.8 Photoluminescence spectra of a single layer and a 10 layer thin film

Three-dimensional interaction between nanoparticles can also be seen in a publication by Li *et al*(15) who embedded CdTe nanoparticles in a temperature sensitive smart polymer. Poly(N-isopropylacrylamide) (PNIPAM) is a thermoresponsive polymer thus will change shape as it is heated. At the low temperature state the nanoparticles embedded in the polymer show homogenous distribution. As the temperature is increased and conformational changes take place the distribution of the nanoparticles is disrupted leading to the formation of areas of high nanoparticle density. In these areas the nanoparticles are much closer together than in the low

temperature state. Li et al(15) observed a red-shift in photoluminescence on heating the sample.

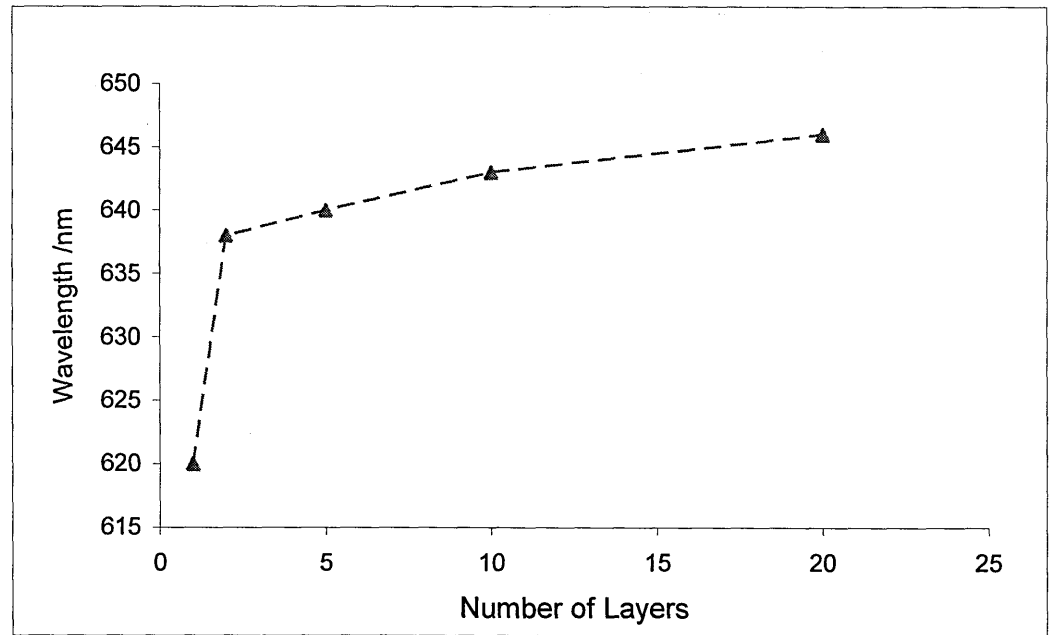


Figure 4.9: The peak maximum wavelength change in thin films of various thicknesses

Figure 4.9 shows the change in wavelength of emission for thin films with different numbers of layers. Two distinct shift patterns are seen. The spectra show a red-shift as the number of layers is increased. First, a large shift from 620nm to 638nm is seen; as the change from single layer to double layer is made. Then further layer depositions produce a more gradual change, reaching 646 nm after 20 layers have been deposited. I propose that the initial increase is due to a change from 2d to 3d interaction whilst the more gradual increase is due to space filling within the layers. Space filling can occur as follows. The CdTe nanoparticles used in this report have an average size of ~4nm but within the suspension there is size variation.

Photoluminescence spectra of the suspensions typically have a FWHM of ~50nm (as can be seen in Figure 4.7 and Section 2.6) this can be a representation of the size dispersion but can also indicate the presence of trap states. Each layer deposited adds nanoparticles of all sizes to the developing thin film. Repeated depositions allow smaller nanoparticles to “space-fill” in the layers below. As the number of bi-layers in a thin film increases the spaces within the layers become filled and more particles are within inter-particle interaction range. Energy is transferred from smaller to larger nanoparticles resulting in lower energy luminescence. Figure 4.10 shows a proposed mechanism for the space filling deposition. Support for this mechanism comes from a study by Abu-Sharkh(16) who conducted a molecular dynamic simulation into the formation of polyelectrolyte multilayers and found the structure of layers to be "fuzzy" with molecules experiencing a high degree of interpenetration.

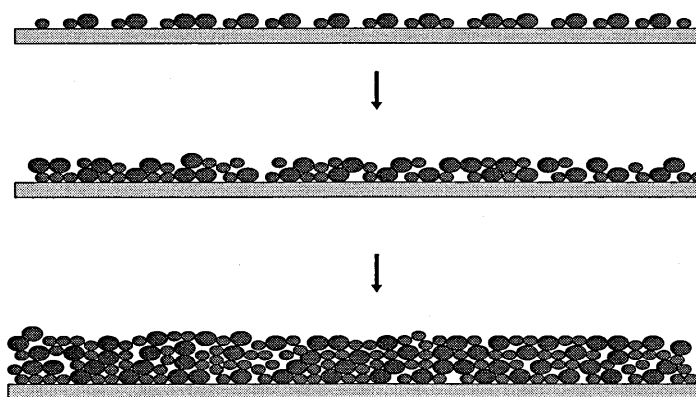


Figure 4.10: Proposed space filling mechanism, nanoparticles of all sizes are deposited and as the number of layers increases smaller particles fill vacancies in the lower packing levels

4.4 Conclusions

Dilution of suspensions of both TGA and TOPO capped CdTe nanoparticles showed a blue-shift in photoluminescence spectra as the suspension was diluted. This is in agreement with previous literature and is likely to be due to the thiol capping layer desorbing at lower concentrations creating a reduced effective particle size. However, re-concentration of the suspension showed a red-shift beyond the original position of the undiluted sample. This suggests that the distance between particles also plays a contributing role in determining the photoluminescent wavelength. Deposition of a suspension as a thin film shows a photoluminescence red-shift and a decrease in FWHM. Again this is in agreement with previous literature. Depositing the nanoparticles places them into a close packed environment reducing the inter-particle distance to within a few angstroms. This facilitates dipole-dipole interactions between the particles or allows the establishment of collective electronic states resulting in selective emission from the larger particles. As the thin film is further developed a further increase in emission wavelength is seen. The first 1-5 layers of the thin film show the greatest photoluminescence change. After this, the red-shift is reduced and presumably eventually stabilizes. These further changes in photoluminescence may again be due to nanoparticles being constrained to close-packed environments. As the number of layers in a thin film is increased the nanoparticles change from a 2d to a 3d environment. Each layer deposition adds nanoparticles through a space-filling technique increasing the number of nanoparticles within interaction distance of each other.

5 Layer-by-layer Deposition of CdTe Nanoparticles

5.1 Introduction

Applications such as NLEDs (see Section 2.5.2) require nanoparticles to be in a thin film form. For aqueous suspensions of cadmium chalcogenide nanoparticles a popular method of producing these thin films is by an electrostatic LBL deposition technique. The LBL method is popular because it is simple, can be easily automated and doesn't require expensive equipment or processing steps. The technique also allows a high degree of control over the thin film composition this is important as the quality of the thin film is likely to affect the performance of its application(1) and monolayer coverage is usually preferred to agglomerated thin films. For a general introduction to the LBL technique please see Section 2.7.4.

In this Chapter I will show CdTe nanoparticles being deposited using the LBL technique. Thin films of CdTe nanoparticles and three different polyelectrolytes are produced. Analysis of the different films shows that the chosen polyelectrolyte controls the thickness and roughness of the thin film produced. Finally, I look at the mechanics of the deposition process, how the thin film is formed, this leads to conclusions about how the LBL technique can be optimised for a particular nanoparticle-polyelectrolyte system.

A wide range of materials have been incorporated into LBL produced thin films, recent examples include: carbon nanotubes(2), gold nanoparticles(3), magnetic nanoparticles(4), DNA(5) and haemoglobin(6).

Applications of LBL produced thin films are also varied and include drug screening(7), thin film transistors(8) and gas sensors(9). Tang *et al*(10) provide an excellent review of the biomedical applications of the LBL technique.

Figure 5.1 is a schematic of the deposition process used most throughout this report. The cleaned glass substrate has a small negative charge as the surface contains SiOH molecules. PDDA is used as the first polyelectrolyte and CdTe nanoparticles are used in place of the second.

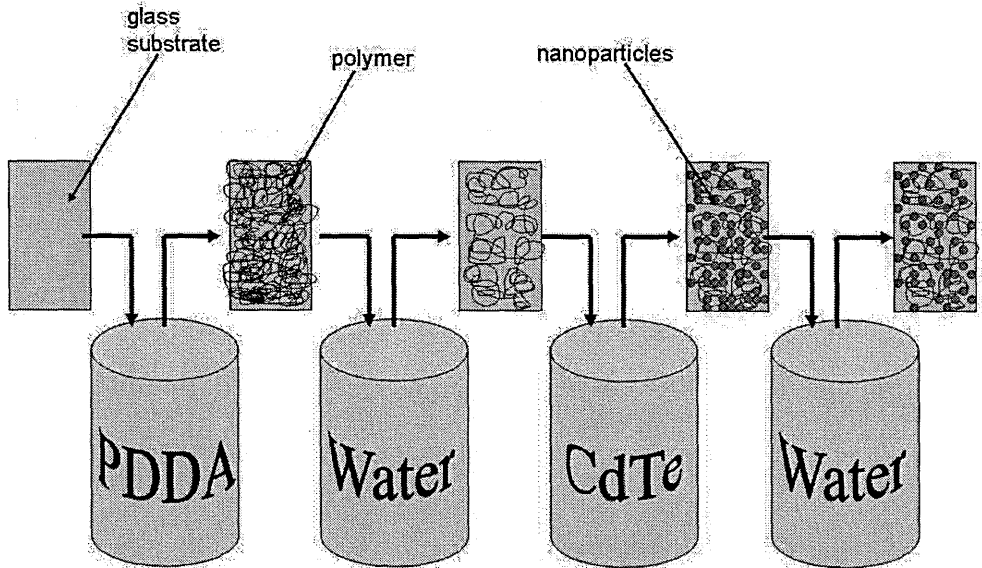


Figure 5.1: The layer-by-layer deposition process. PDPA is the most commonly used polyelectrolyte used throughout this thesis.

Kotov *et al*(11) were the first to report the use of the LBL technique with semiconductor nanoparticles and demonstrated the versatility of the technique by using a variety of nanoparticles and substrates. They found the

polyelectrolyte (PDDA) was able to form stable layers on quartz, glass, gold and platinum. Many applications of semiconductor nanoparticles require them to be in thin film form and the LBL technique provides a successful method of producing these thin films. Bertoni *et al*(1) investigated thin film electroluminescent devices and found the structure of the layering to be critically important to the emissive efficiency. Improved uniformity and homogeneity of the nanocrystal multilayer led to reduction of the current leakage through structural defects. Likewise, in photovoltaic research an important consideration is how to remove the generated charge carriers after absorption of a photon and before unwanted recombination can occur. Electrons need a clear, barrier-free, path to an electrode. Whilst nanoparticles will always have "grain boundaries" in the form of the edge of the nanoparticle the electron pathway would be better achieved if the film was in a close packed form. Breaks in the consistency of the film would increase the recombination sites, reducing the efficiency of the photovoltaic device(12).

Understanding how a thin film is formed is crucial to controlling the LBL process. Balancing the attractive forces, between the nanoparticles and polyelectrolyte, with the repulsive forces, between two nanoparticles, is an important step. If the nanoparticle-polyelectrolyte attraction is too strong clustering of the nanoparticles will occur because more than a single layer of particles will be deposited simultaneously. If the nanoparticle-nanoparticle repulsion is too strong a low particle density film will form(13). To produce good quality thin films it is also important to understand the arrangement within the thin film. Several studies discuss mixing of layers. When investigating CdSe and PPV thin films Gao *et al* used x-ray reflectivity studies

and found that the thin film did not have true bi-layers of polymer and nanoparticle. Instead, the film was more like a homogeneous mixture of polymer and CdSe(14,15). Castelnovo(16) and Abu-Sharkh(17) have made similar observations in theoretical studies of thin films made from just polymers.

However, these static measurements do not give enough insight into LBL, as self-assembly is a kinetic process. In this Chapter optical waveguide lightmode spectroscopy (OWLS) is used to monitor the thin film growth. Real-time measurements are used to record the entire deposition process. The OWLS technique allows in-situ monitoring with sub-nanometre resolution providing a clearer picture of both structure and kinetics than seen by any other technique. OWLS is a relatively new spectroscopy but is rapidly becoming more widely used. Kurrat(18) provides a good introduction. The technique was primarily used to measure biomolecule adsorption(19) but has recently been used to measure the deposition of polyelectrolyte multilayers(20).

To summarise, many applications of semiconductor nanoparticles require them to be in a thin film form. The LBL method allows cheap and easy production of these thin films. The quality of a thin film is vital to its function if efficiency of the device is required. To improve the quality of a thin film an understanding of the deposition process is needed. Static measurements can provide information on the structure of the completed thin film. However, OWLS can provide real-time in-situ data of the whole deposition process. In Section 5.3.1 thin films made with different polymers

are used to gain information on the layer thickness and functionality and in Section 5.3.2 OWLS is used to monitor an 8-layer deposition.

5.2 Experimental

All the nanoparticles used in this Section were capped in TGA which is negatively charged; therefore, to provide opposite charge for electrostatic interaction a cationic polymer was needed. Thin films were fabricated from three different polymers. PDDA 20w% in water with molecular weight 200,000 - 350,000 and Polyethylenimine (PEI) 50w% with average molecular weight 750,000 were obtained from Aldrich and were dissolved in a 0.2M NaCl buffer to a concentration of 5mg/ml before use. Poly-L-Lyseine (PLL) 0.01w% in water Mw 150,000 - 300,000 was obtained from Sigma and was used as provided.

Thickness measurements were made using a Taylor Hobson Talysurf Coherence Correlation Interferometer 6000 also known as a white light interferometer (WLI). To measure the total film thickness a scratch was made through the sample exposing bare substrate. The Taylor Hobson software allows an average step height measurement to be calculated between two areas. Thus by selecting an area within the scratch and an area of the top of the film an accurate step height measurement can be obtained (Fig. 5.2). Because two areas are used, rather than just two points or a surface profile line, the calculation is an average of all the height differences between the two areas. This means greater amounts of data have been used. Any anomalous data resulting from individual points of surface roughness will be lost in the

average and the measurement becomes more accurate. Figure 5.2a shows a 10 layer PDDA thin film being measured in this way and Figure 5.2b shows a 10 layer PEI film undergoing the same process. The blue areas marked **area 2** in each image are areas within the scratch, **area 1** is the top of the thin film surface.

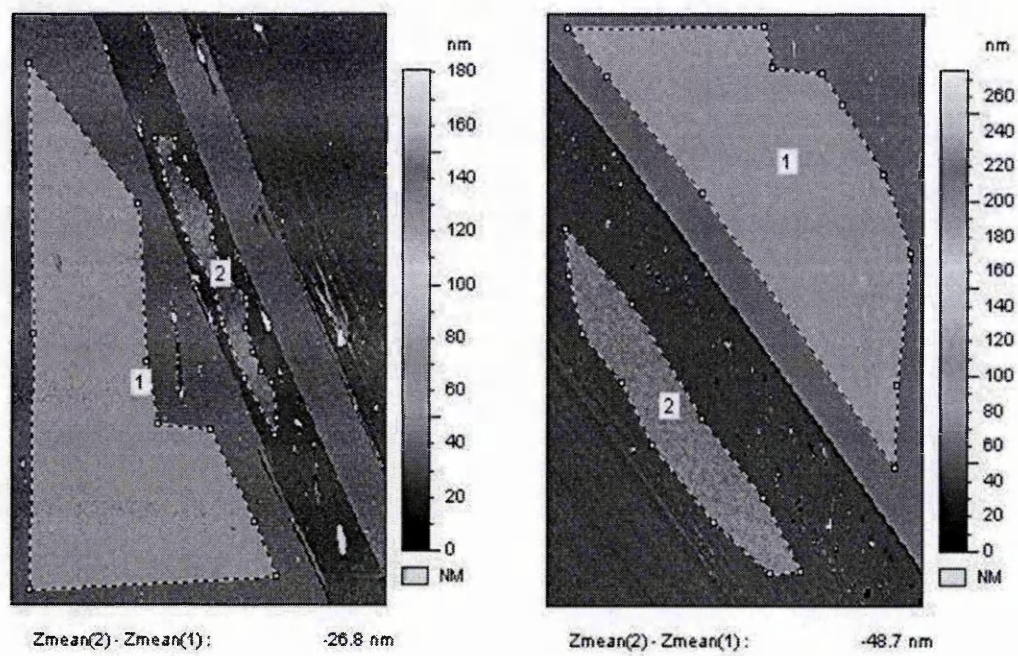


Figure 5.2: 10 layer thin films of a) CdTe and PDDA and b) CdTe and PEI undergoing a scratch test average step height measurement. Step heights are a) 26.8nm and b) 48.7nm.

An AFM was used to measure the roughness of the film surface. To ensure a representative sample was analysed a $2\mu\text{m}^2$ area of the thin film surface was scanned and a roughness average recorded. The root mean square has been calculated.

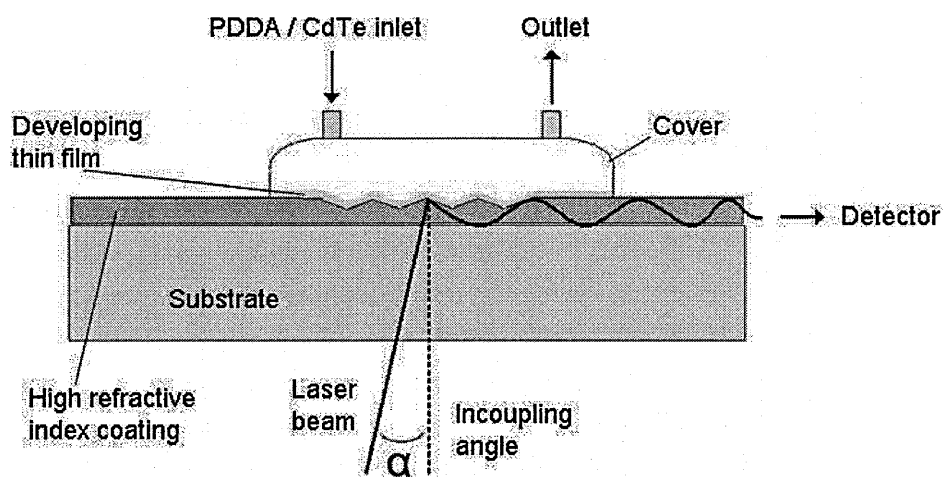


Figure:5.3 Schematic of how OWLS works. Adapted from Horvath *et al* (19).

To gain real-time in-situ data of the deposition process OWLS was used. Figure 5.3 shows a schematic of how OWLS works. A laser beam, usually He-Ne, is targeted at a waveguide before being collected by a detector. The waveguide consists of a thick substrate topped with a thin film of higher refractive index. A curvette on top of the waveguide allows the addition of the various solutions. Layers of PDDA and CdTe can then form on the surface of the waveguide. The incoming light beam undergoes total internal reflection, within the high refractive index coating at the interfaces with the substrate and developing thin film. The waveguide is very sensitive to changes in the adsorbed layer(21,22).

The OWLS experimental apparatus was built(23) and operated by Dr. Robert Horvath(24). Adsorption of monolayers could be measured in-situ and in real time. OWLS works by detecting a laser beam that is guided through a

developing thin film. Since the laser beam used had a wavelength of 633nm and nanoparticles used elsewhere in this report emit photoluminescence very close to this wavelength it was possible the nanoparticles would emit luminescence that would interfere with the measurement process by creating duplicate signals to the detector. To eliminate any potential problems and ensure our measurements were valid smaller nanoparticles, which emit at ~548nm, were used for these experiments. Absorbance and photoluminescence spectra of this batch of nanoparticles are shown in Figure 5.4. These nanoparticles do not show any luminescence at 630nm. The absorbance spectrum shows a baseline has been reached at ~575nm. The baseline has an absorbance intensity of 0.042 this is likely to be due scattering of light by the particles and is not truly absorption. This batch of nanoparticles were therefore suitable for use with the OWLS technique.

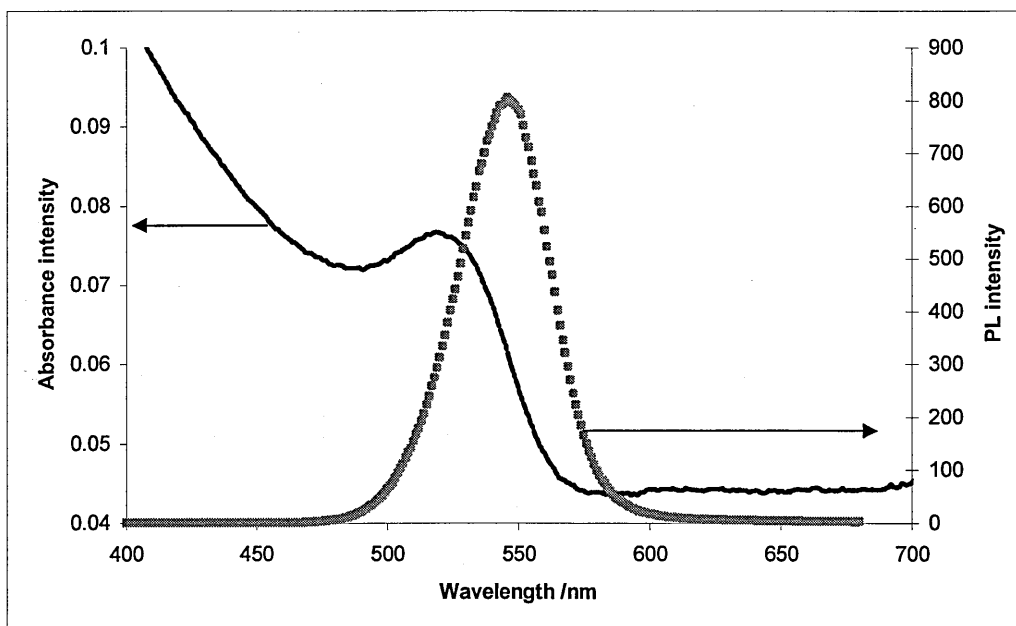


Figure 5.4: Absorbance and photoluminescence spectra of the suspension of nanoparticles used throughout Section 5.3.2.

As the aim of the OWLS experiments was to mimic as much as possible the current (Section 3.2) LBL process the length of time that the substrate was exposed to PDDA, CdTe and washing solutions was kept the same. In the laboratory LBL the PDDA and CdTe are contained in beakers and are stationary, only the washing step involves the solution flowing. However, in the OWLS experiment a flow rate is necessary as the solution must be passed over the waveguide and the volume of fluid above the thin film surface is smaller than in the beaker. A slow flow rate of 0.1ml/min was chosen as this represents a compromise between mimicking the laboratory process and ensuring there is not a depletion of polymer or nanoparticles.

First, deionised water was allowed to run through the system until a stable baseline was detected. PDDA was then passed through the waveguide at a flow rate of 0.1ml/min for 20 minutes. A short washing stage

of 2 minutes with deionised water was followed by 20 minutes of CdTe flow before a final washing step. The procedure was repeated to allow build-up of multiple bi-layers.

From the raw data (processed by Dr R. Horvath) optical mass (Q) could be calculated(25). Optical mass is proportional to the physical mass deposited per unit area. Using this value and the equation $Q = d_A (n_A - n_C)$ where n_A is the refractive index of the growing film and n_C is the refractive index of the solution covering the film the actual thickness of the layer (d_A) could also be calculated(25). Due to the anisotropy of the film d_A measurements for small numbers of bi-layers can be inaccurate(25) thus the only values used in this report are for thicker films.

5.3 Results and Discussion

5.3.1 Layer-by-layer with Different Polymers

Three different cationic polymers, PDDA, PLL and PEI were used for LBL production of thin films. Figure 5.5 shows the change in photoluminescence as the number of layers in each of these thin films is increased. All of the thin films show the same general trend seen in Section 4.3.2, the wavelength of the peak maximum shifts to the red as the number of layers is increased. The three different polymers have single layer thin films with very similar wavelengths 626nm or 627nm but as the number of layers increases differences between the films begin to show. The PEI thin films show higher energy luminescence than the other polymers, a 10 layer PEI thin film has a

wavelength of 636nm whereas the same film made with PDDA shows a photoluminescence peak maximum of 646nm. Thin films made with PEI show a lesser change in wavelength as the number of layers is increased. If the shifts in wavelength were due to greater inter-particle interaction (Section 4.3.2) this would suggest that the nanoparticles in the PEI film are less closely packed than in a PDDA thin film.

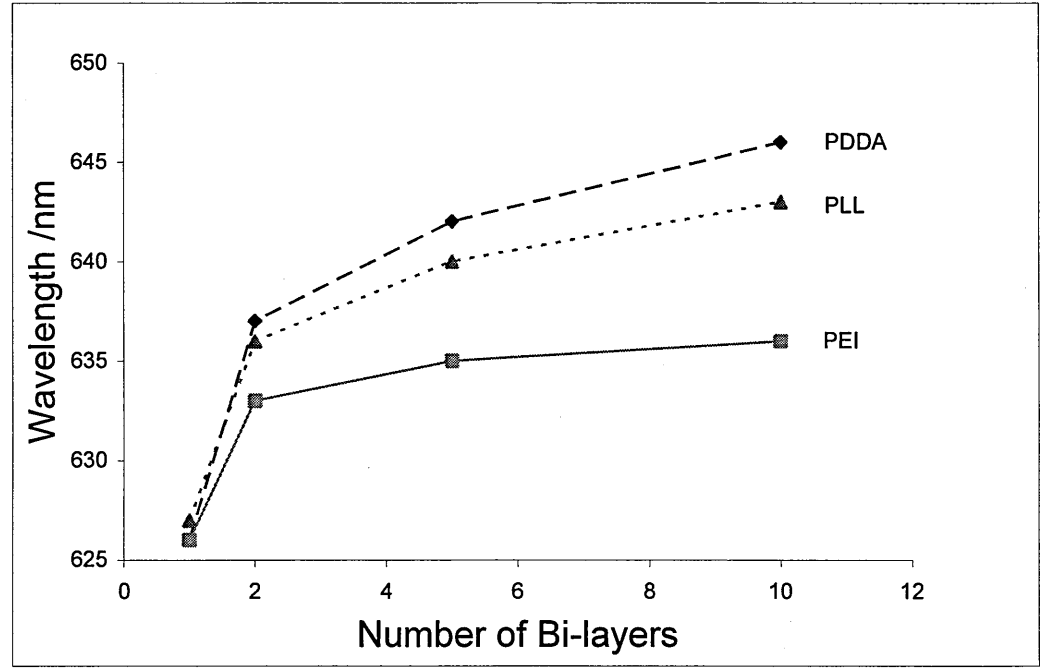


Figure 5.5: The change in peak maximum wavelength as the number of layers is increased for three thin films.

A WLI was used to measure the thickness of the two most different LBL produced thin films. An average step height was calculated between the bare substrate and the top of the nanoparticle-polyelectrolyte film. The thickness of various films can be seen in table 5.1. Thin films formed with PEI

showed a much larger thickness than PDDA thin films. A 10 layer PEI thin film had a thickness of 53.4nm more than double that of a PDDA film, 26.3nm, with the same number of layers. The polymer used therefore changes the thickness of the thin film. An increase in thickness could be caused by more nanoparticles being deposited or by less order within the layer.

Table 5.1: Average step-height measurements for various thin films, numbers in bold indicate an average of all the thin films measured.

Polymer	Number of Layers	Step Height /nm	Thickness per layer /nm
PEI	10	56.4	5.64
		53.8	5.38
		50.2	5.02
		53.4	5.34
PDDA	10	23.6	2.36
		28.6	2.86
		26.8	2.68
		26.3	2.63
PDDA	20	48.7	2.435
		49.4	2.47
		52.3	2.615
		50.1	2.5

If more particles were being deposited the inter-particle distance would be reduced and a red-shift in photoluminescence between the two polymer systems would be seen. However, as we saw in Figure 5.2, this is not the case - in fact the opposite occurs. PEI thin films have thicker layers but are blue-shifted with respect to the PDDA thin films. Less order within the layer would explain both the photoluminescence trend and the increased thickness. A disordered thin film would have a lower packing density so less opportunity of interactions between the nanoparticles. Schwartz *et al*(26) also compared thin films made from PDDA and PEI using surface plasmon resonance and found the films containing PEI were significantly thicker supporting the findings presented here. Tang *et al*(13) investigated the roughness of various thin films by measuring the rms of several samples (the rms is commonly used as a measure of roughness for surfaces measured by AFM as it allows for both positive and negative variance in the surface height). They found PEI films had a significantly higher rms than PDDA thin films. Tang explains this by a proposed clustering mechanism. PEI is a weaker polyelectrolyte than PDDA. This means the nanoparticles-PEI and PEI-substrate connections are more labile, once nanoparticles have been deposited PEI is able to rearrange on the substrate surface to accommodate more nanoparticles. This results in clusters of nanoparticles being deposited rather than a monolayer. This would explain the increased roughness and the increased thickness. Although a different substrate, different nanoparticles and a different measurement technique have been used here it is likely we are seeing a similar effect.

The WLI thickness measurements were performed on both 10 and 20 layer PDDA thin films (Table 5.1). Samples with a smaller number of layers proved too thin to be measured accurately by this technique. 10 layer thin films showed an average thickness of 26.3nm or 2.63nm per layer and 20 layer thin films showed an average of 50.1nm or 2.5nm per layer. This data suggests the per-layer thickness is stable throughout the thin film thus deposition is linear. Other researchers(11,27) have also found the LBL adsorption of polyelectrolyte and nanoparticles produces linear deposition. The results presented here therefore show good agreement with the literature.

The average nanoparticle diameter is 3-4nm(28) and the per-layer thickness is therefore in good correlation with this. The fact that the average per-layer thickness found here is slightly smaller than the nanoparticle diameter adds support to the space filling mechanism presented in Section 4.3.2. and is a similar finding to that of Lesser *et al*(29). Bertoni *et al*(1) reported that thin films produced in this way would have a packing density of 27% and Gao *et al*(14) produced similar data to find a packing density of 23%.

5.3.2 Real Time Measurements of Layer-by-layer Deposition

To gain an insight into the LBL process OWLS was used to monitor an 8 layer deposition process. Figure 5.6a shows changes in optical mass (see Section 5.2) during the whole of the deposition process and Figure 5.6b shows an enlargement of the deposition of the first layer. Initially a base-line of water was established to allow stabilisation of the system. PDDA was added at point a and optical mass showed an increase to 0.1nm over 4.5 minutes. This

showed the PDDA was being successfully adsorbed onto the surface of the waveguide. The PDDA flow was maintained for 20 minutes but optical mass remained constant at $\sim 0.1\text{nm}$. As a monolayer of PDDA had already been formed repulsive electrostatic charges prevented more polymer from being deposited. A two-minute washing solution of deionised water was introduced at point **b** and optical mass showed a small decrease. Excess PDDA was now being washed from the surface of the waveguide. At point **c** the CdTe nanoparticle suspension was introduced to the waveguide and optical mass showed an increase indicating nanoparticles were being deposited. A second washing stage took place at point **d** and resulted in a rapid drop in optical mass. Deposition of the second layer was started at point **e** by a switch back to the PDDA solution.

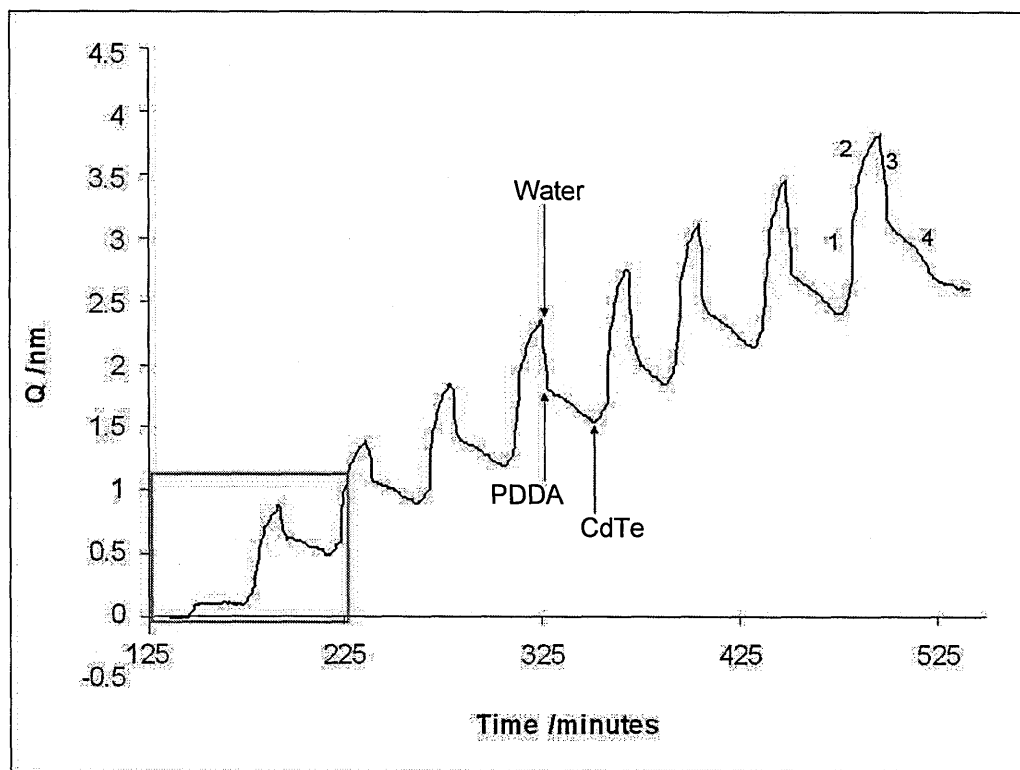


Figure 5.6a: A plot of optical mass versus time for the deposition of 8 layers of PDDA and CdTe. The numbers denote the various deposition stages as explained in the text.

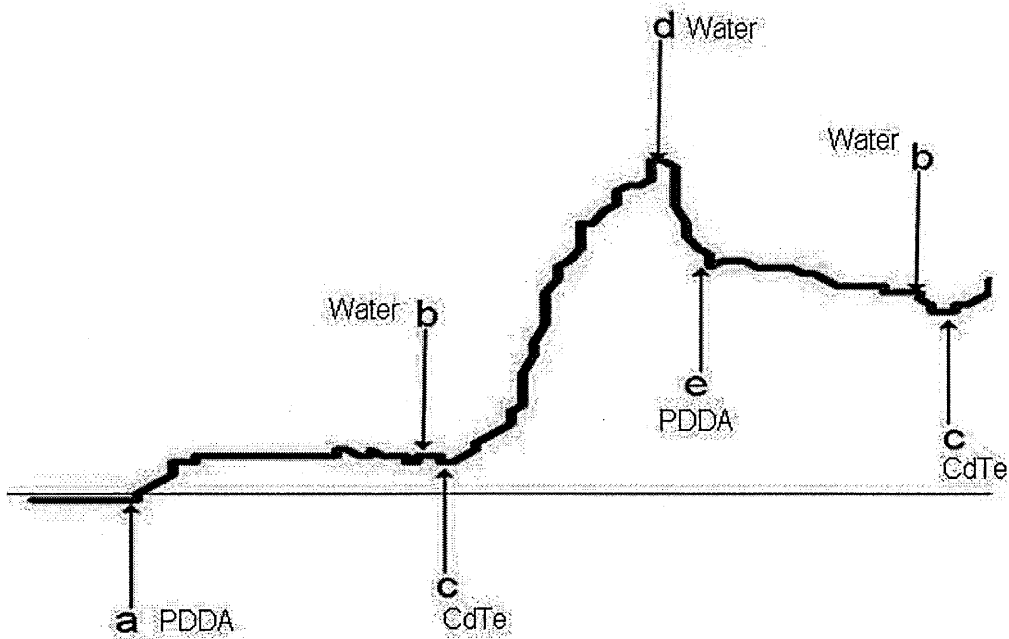


Figure 5.6b: An enlargement of the area inside the red box in Fig. 5.6a, starting points of various solutions are highlighted.

As can be seen in Figure 5.6a the change in optical mass for each future layer is almost identical. The observed deposition can be split into 4 stages. Stage 1 starts with the introduction of the nanoparticle suspension. As the suspension reaches the waveguide there is a rapid increase in optical mass. Nanoparticles are faced with a complete surface of charged polymer and are able to adsorb very quickly. After ~11 minutes this rapid increase gives way to a more gradual increase, highlighted as stage 2. Here the nanoparticles have already covered most of the surface and are now limited to few potential adsorption sites. Nanoparticles deposited in stage 1 are strongly bound to the thin film surface as they have multiple interactions with the polymer.

However, particles deposited in stage 2 are only loosely bound to the surface as the interaction is less. Figure 5.7 is a schematic of these interactions.

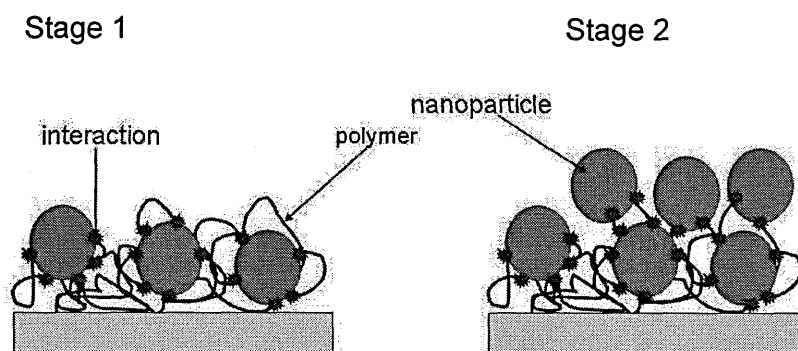


Figure 5.7: A schematic of strongly and loosely bound nanoparticles. The particles on the left have many interactions with the polymer thus are strongly bound. Whereas the additional particles on the right have fewer interactions so are only loosely bound.

Stage 3 is a washing stage. Here, the washing solution, in this case water, removes excess nanoparticles from the surface. The particles that are only loosely bound, from stage 2, are now removed, but strongly bound particles remain. PDDA addition marks the start of stage 4. The PDDA continues to have a washing effect as can be seen by the decreasing optical mass. For example at point e in Figure 5.6b optical mass decreases from 0.6nm to 0.5nm over a twenty minute time period. It appears excess nanoparticles are still being removed. It is also possible that rearrangement of the nanoparticles and polymer occurs at this stage(30). Although the optical mass decreases in stage 4 PDDA is still being deposited. If there was no

PDDA deposition during this period a second layer of nanoparticles would not be able to adsorb since the like electrostatic charges of the already deposited nanoparticles would repel further deposition. Figure 5.8 shows a schematic of the deposition process split into the different stages outlined above.

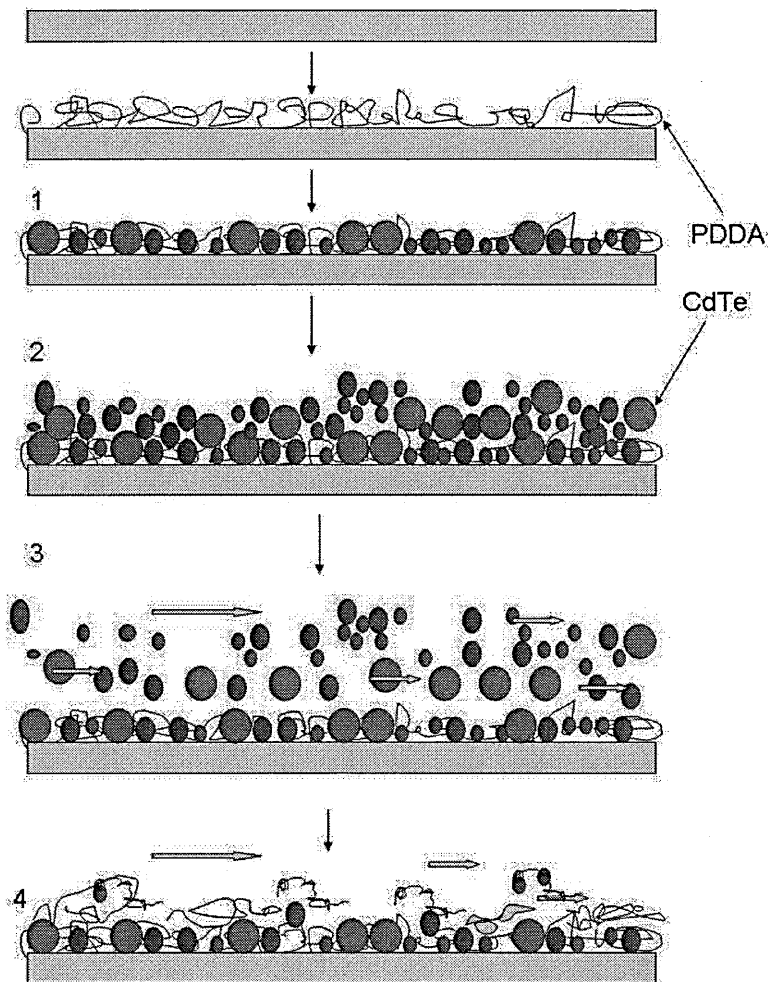


Figure 5.8: A schematic of the proposed mechanism for deposition of polymer and nanoparticles. The various stages outlined in the text are numbered.

Deposition of multiple layers resulted in a consistent pattern in the optical mass data. Each layer produced the same 4-stages outlined above. The repeatability shows the validity of the OWLS technique.

Figure 5.9 shows the cumulative optical mass values at the end of stage 3 for each of the layers deposited. A linear trend is seen which is consistent with both the body of literature(11,27) and the static WLI observations presented in Section 5.3.1. The actual thickness of the layer (d_A) as measured by OWLS is 21.04nm at the end of the seventh layer. This is a per-layer thickness of 3nm which is again consistent with the literature(1,14,29) and the WLI measurements. These consistencies further validate the OWLS data.

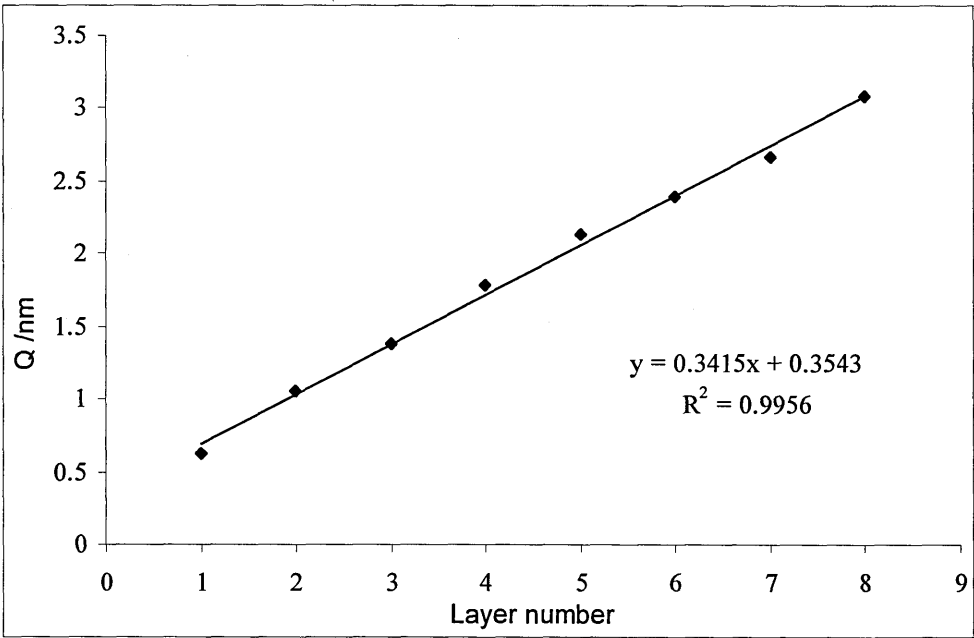


Figure 5.9: Cumulative optical mass after deposition of layers.

In Figure 5.6 during the first layer deposition a saturation of PDDA adsorption occurred after 5 minutes of PDDA flow. In stage 4, prolonged

PDDA flow causes nanoparticles to be removed from the film. Likewise in each layer a saturation of nanoparticles is being reached at around 20 minutes of deposition. It is important to be able to optimise the LBL process to ensure enough time for layers to form whilst avoiding making the process too time consuming. Kotov's original nanoparticle LBL procedure involved a 24 hour nanoparticle adsorption stage(11). The OWLS data suggests that in this case the process could be improved by shortening the PDDA deposition time. However, any reduction in the nanoparticles deposition time would reduce the quantity of nanoparticles adsorbed therefore reducing the quality of the thin film.

5.4 Conclusions

In this Chapter thin films have been produced with CdTe nanoparticles and three different polyelectrolytes, namely PDDA, PLL and PEI. All the thin films produced followed the deposition trends outlined in Section 4.3.2. i.e. emission was found to decrease in energy as the number of layers was increased. Spectroscopy and thickness analysis showed differences between the three polyelectrolyte systems. Thin films produced with PEI were thicker and showed blue-shifted emission. This indicates that PEI containing thin films are less ordered than their PLL and PDDA counterparts.

These static measurements also provide strong correlations with both the published literature and conclusions from the real-time data presented in Section 5.3.2. These consistencies add external validity to the OWLS data.

I have shown that OWLS can be used as a quick and convenient in-situ, real-time analysis technique for monitoring LBL deposition. All the OWLS experiments presented here have been conducted in a normal laboratory environment, not in an isolated environment. Despite this, information on the packing, thickness and layer structure of the thin films has been obtained. Using the OWLS technique in this way allows researchers to make changes to their LBL process and immediately monitor the results. Thus OWLS becomes a rapid optimisation procedure for improving individual set-ups without the need to produce fully functional LBL thin films. The popularity of the LBL technique and its many applications can only increase with a better understanding of the deposition process.

6 Heating and Cooling Suspensions and Thin Films

6.1 Introduction

In Chapters 4 and 5 nanoparticles have been studied as basic suspensions and thin films. For nanoparticles to be useful in any application it is important to understand how they may be affected by the environment they are faced with in that application. This Chapter looks at the effects of temperature changes on nanoparticles in both suspensions and thin films. A temperature increase from 293 to 358K results in a red-shift in the emission spectrum and a loss of photoluminescence intensity. Similar results are seen in both the thin film and suspension experiments.

Although colloidal nanoparticles are synthesized at temperatures between 523K and 673K and usually stored at 277K they often need to operate at ambient temperatures. It is therefore important to study their stability and optical properties at these temperatures. Temperature has been found to cause changes in the luminescence intensity and wavelength but this can be seen as either an advantage or a disadvantage depending on the application. Solar power has seen greatly increased usage in the last decade. The two countries with the highest number of solar cells are Germany and Japan. The highest average outside temperatures in these countries is 298K in Germany and 303K in Japan. However, the operating

temperature of a solar cell is often significantly higher than the air temperature since the solar cell is placed in direct sunlight and to function needs to absorb the sunlight. Cadmium chalcogenide nanoparticles can be used in two different ways in photovoltaics. Nozik(1) proposed that nanoparticles could be used as co-sensitizing agents or additional absorbers in a dye-sensitized solar cell and Gallagher *et al*(2) have shown how CdSe/ZnS nanoparticles can be used in a spectral converter (see Section 2.5.3). For either of these applications a small change in absorbance or photoluminescence wavelength would not be a concern but a loss of absorbance or photoluminescence intensity would affect the efficiency of the overall device. A large change in wavelength would also be detrimental to a spectral converter as it could shift the wavelength of the incident sunlight out of the optimum wavelength for the band gap of the attached solar cell. If the nanoparticles were unstable at temperatures within their operating range it would mean a decrease in the device lifetime, loss of efficiency or failure of the device.

However, Wang *et al*(3) present a novel concept where a change in luminescence due to temperature is not only an advantage but is the functioning property of the application. Wang *et al* propose that CdTe nanoparticles can be used to measure small temperature changes accurately, precisely and remotely. For example coating the surface of a turbine blade with the nanoparticles could allow temperature imaging whilst the blade was operating to aid in the detection of defects or weaknesses. An alternative application would be biomedical thermometry where the nanoparticles could be used as in-vivo temperature probes to monitor patients with hypothermia.

For applications where significant changes in luminescence would be a disadvantage developments could be made by looking at ways of preventing the nanoparticles from being affected by their operating temperature. Liu *et al*(4) investigated the effects of changing the temperature of CdSe/ZnS core shell nanoparticles within the range of 280 – 315K. They found that nanoparticles with thinner ZnS shells were more sensitive to the changing temperature. This would suggest that by increasing the shell thickness nanoparticles may be able to be masked from the temperature changes thus are more suited to applications such as photovoltaics. Another potential way of screening the nanoparticles from environmental changes could be to look at the capping ligand. Wuister *et al*(5) found the capping ligand played a part in temperature anti-quenching in CdSe nanoparticles. Several researchers have studied the effect of temperature changes on luminescence within a low temperature (2 – 230K) range. Within this range an increase in temperature is widely reported(5), (6)(7) to result in a decrease in quantum yield (temperature quenching) and an increase in lifetime-decay rate. However Wuister *et al*(5) found an anti-quenching of luminescence in CdSe nanoparticles around 250K. Interestingly, the onset temperature of this anti-quenching was determined by the alkyl chain length of the capping ligand.

Whatever the intended application a study into the effects of changing temperature is useful. The experimental work presented in this Chapter was conducted in 2005 to 2007 and first published in 2006(8). Around the same time period, literature reports of similar experiments started to appear; these are discussed within Section 6.3. The results from the two sources strongly agree.

6.2 Experimental

During the temperature experiments suspensions and thin films were heated gradually from 293K to 358K and cooled in the same manner. Suspensions of CdTe were heated using a series of standard water baths then rapidly transferred to the spectrometer. Thin films were heated whilst inside the spectrometer using a peltier stage purchased from RS Instruments. All temperature changes for both suspensions and thin films were maintained for two minutes before spectrometer measurement to allow the samples to adjust to the new conditions.

For prolonged heating times thin films were heated using a hotplate and suspensions were placed inside a temperature controlled environment.

6.3 Results and Discussion

6.3.1 Temperature Cycling of Suspensions

Suspensions of CdTe nanoparticles were heated gradually from 293K (20°C) to 358K (85°C) and photoluminescence spectra were recorded at regular intervals. Figure 6.1 shows the changes in photoluminescence wavelength as the different temperatures were reached. The spectra have been normalised with respect to intensity to improve the clarity of the wavelength shift. Heating the suspension caused the wavelength of the peak maximum to change from 616nm at 293K to 629nm at 358K, a 13nm shift to lower energy.

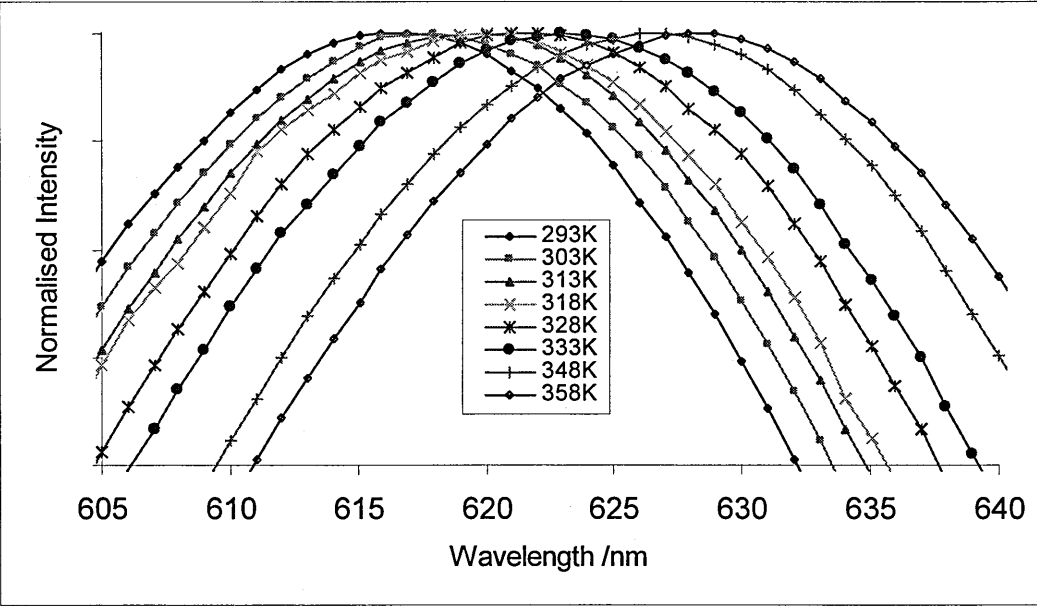


Figure 6.1: The change in photoluminescence wavelength when a suspension is heated.

A plot of the peak maximum against temperature (Fig. 6.2) shows that the shift in wavelength is linear.

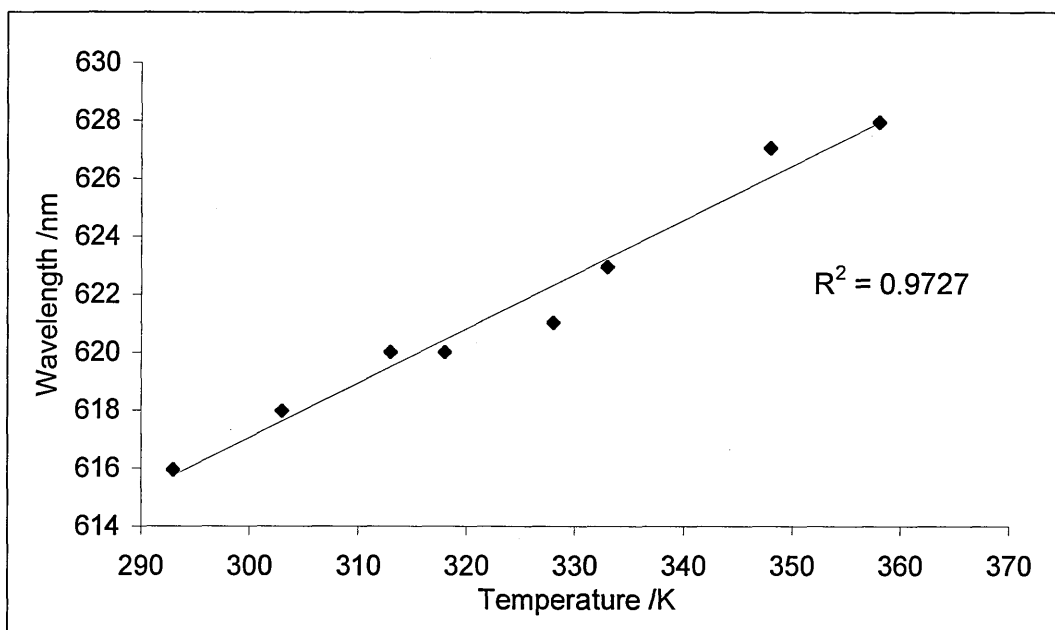


Figure 6.2: Wavelength of the peak maximum as a suspension of nanoparticles is heated.

This spectral shift to lower energy could be due to two things, an increase in the particle size of the nanoparticles or the presence of lower energy trap states. An increase in particle size would reduce the quantum confinement within the nanoparticle; change the band gap and result in lower energy emission (see Section 2.3). An increase in particle size would be seen if one of Ostwald ripening(9) or agglomeration were occurring. An attempt to measure the particle size of the nanoparticles at various temperatures was made using a Malvern zetasizer but the nanoparticles proved too small to measure using this particular machine.

If agglomeration was occurring the suspension would become unstable and precipitation would occur, this was not seen in the suspensions heated for short periods of time. Ostwald ripening(10), where smaller nanoparticles with

higher surface energy are broken up and the subsequent material is re-deposited onto larger nanoparticle, is also unlikely to occur here. It is normally only seen during the synthesis of nanoparticles or when the synthesis reaction mixture is first cooling at temperatures in the range of 373-573K. Kim *et al*(11) reported Ostwald ripening can occur at lower temperatures but over a timescale of days; this is not happening here as the nanoparticles are only maintained at each temperature for 2 minutes. Also, if the nanoparticles were undergoing Ostwald ripening the increase of particle size would be accompanied by a narrowing of the size distribution and hence a narrower FWHM; this is not seen here. Instead, the FWHM increases from 56nm at 293K to 58nm at 358K. Red-shifts in photoluminescence spectra with increasing temperature have been reported before accompanied by both broadening and narrowing of the FWHM(7,12).

If the cause of the red-shift is not due to increasing particle size we are left with the possibility of lower energy trap states. The presence of surface trap states would provide a lower energy pathway for recombination to occur resulting in both red-shifted emission and a loss of overall intensity, due to non-radiative emission. A loss of intensity with increasing temperature was observed in our experiments.

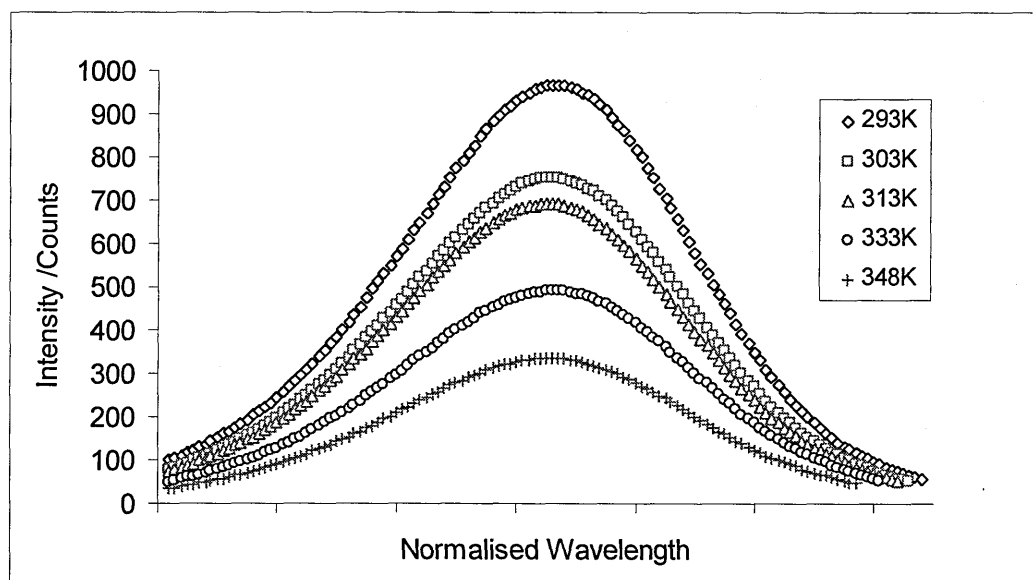


Figure 6.3: The change in photoluminescence intensity when a suspension is heated.

Figure 6.3 shows the change in photoluminescence intensity during the same heating sequence. Here the spectra have been normalised with respect to wavelength. As the suspension was heated a decrease in intensity was seen. At 348K the photoluminescence spectrum showed a 70% loss of the suspension's original intensity.

Both the red-shift and the loss of intensity seen with increasing temperature were reversed when the suspension was cooled. As the sample was cooled back to 293K the peak maximum shifted gradually back towards its starting position. The reversibility of the shift further rules out the causes of Ostwald ripening or agglomeration, as the particle size would now need to decrease by partial dissolution of larger particles to form less stable smaller particles.

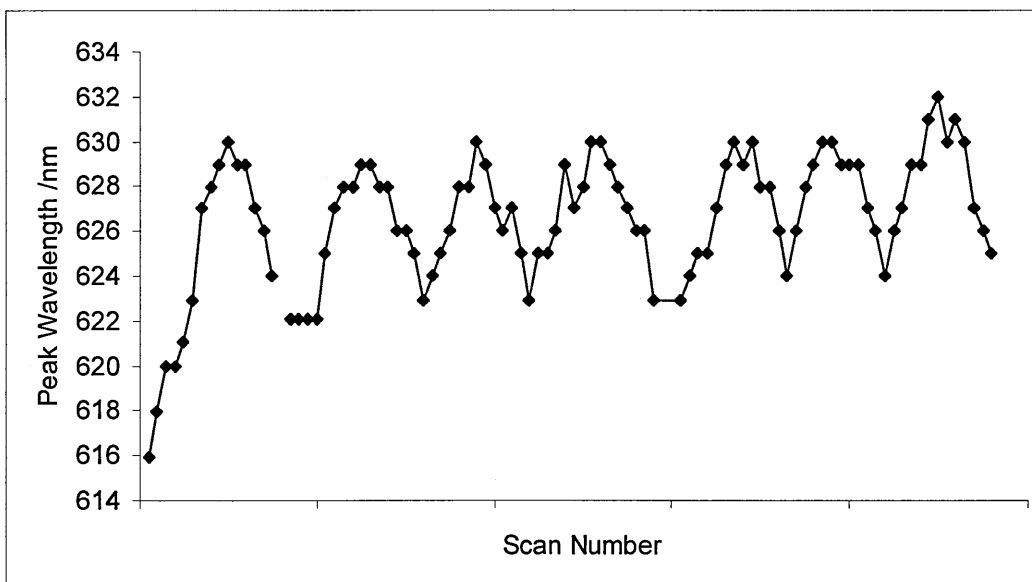


Figure 6.4: The change in wavelength as a suspension is repeatedly heated and cooled.

Figure 6.4 shows the change in wavelength as the suspension is repeatedly heated and cooled. The first heating cycle shows a one-time non-reversible shift of 6nm from 616nm to 622nm. The wavelength of the peak maximum is subsequently cycled between ~622nm at 293K and ~630nm at 358K showing an 8nm reversible shift. The difference in the first heating cycle is further highlighted in Figure 6.5 where the wavelength of the peak maxima at various temperatures is plotted for the first and then subsequent heating cycles. Multiple readings at the same temperature are taken during different heating cycles. The spread in wavelength e.g. 622-625nm when measured at 293K is likely to be due to the inaccuracy of the manual heating method employed.

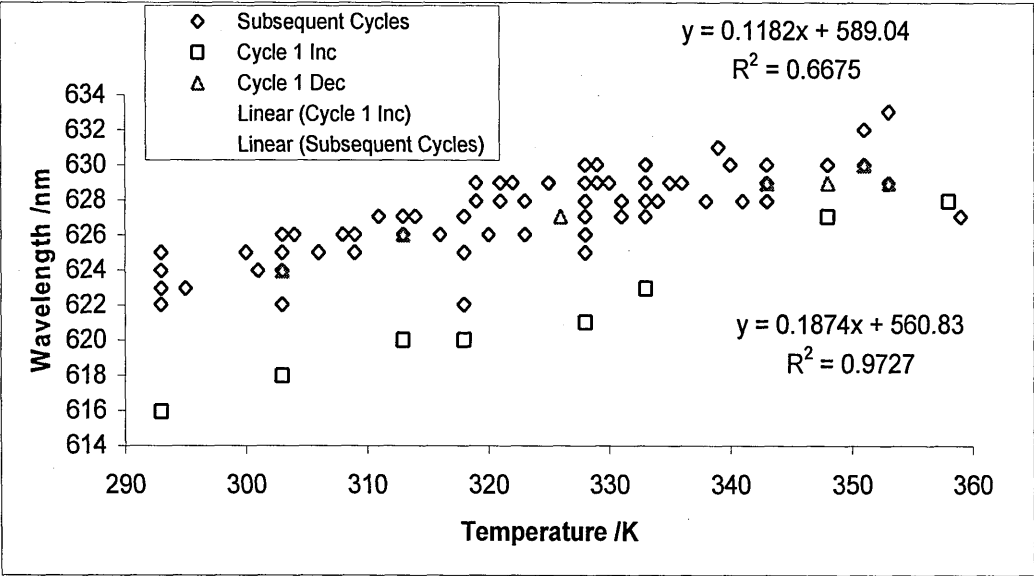


Figure 6.5: The position of the peak maxima at various temperatures.

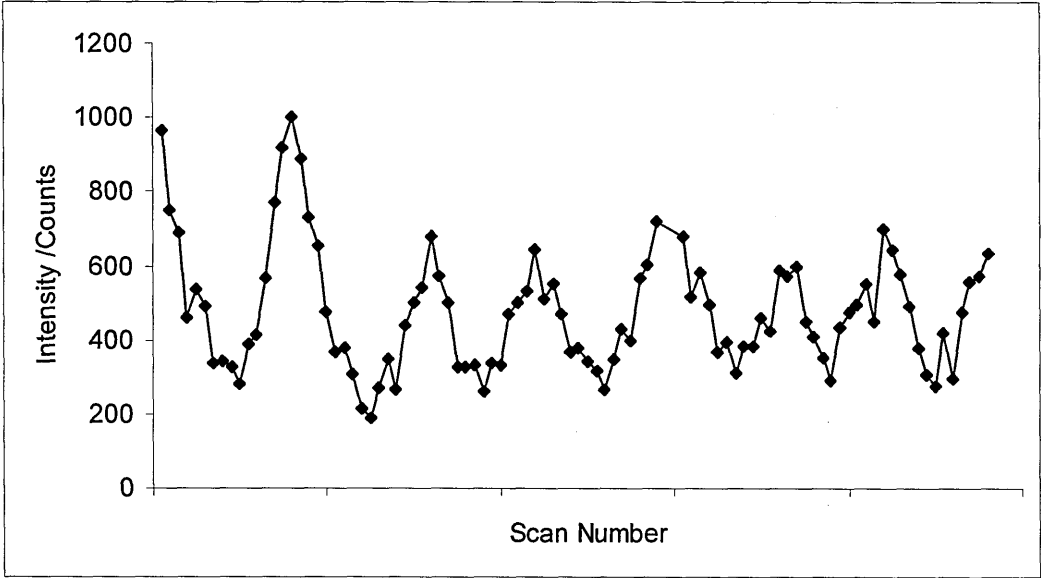


Figure 6.6: The change in intensity as a suspension is repeatedly heated and cooled.

Figure 6.6 shows the change in intensity as the suspension is repeatedly heated and cooled. Again the first heating cycle produces a different result from the general trend; a small intensity gain is observed followed by a permanent loss in photoluminescence.

Wang *et al*(3), aiming to demonstrate their application of biomedical thermometry, observed nanoparticles at various temperatures. They also found a decrease in intensity on heating the sample and in CdTe nanoparticles they found this change was reversible. They did not look at wavelength changes nor did they report any temperature cycling results. In 2005 Biju *et al* published a report of similar results(13). In their experiments, CdSe clusters suspended in butanol were heated and cooled repeatedly. Biju found a residual shift of 9nm over the first four heating cycles similar to the shift seen in the first heating cycle in our results. Biju suggests that this could be due to the thermal removal of grain boundaries establishing better connectivity between the nanoparticles.

If the nanoparticles used in this thesis were also (at least partially) part of clusters then the 6nm non-reversible shift seen in Figure 6.4 could also be due to the establishing of energy transfer pathways. Figure 2.9 shows that the absorbance spectrum of the CdTe suspension is featureless suggesting the presence of clusters. Biju's residual shift was followed by an 8nm reversible spectral shift(13) mirroring the reversible 8nm shift reported in our results. Biju attributes the reversible shifts to changes in the inter-dot dipole-dipole interactions in the excited state within the individual clusters and suggests it is possible that the short inter-particle distance in clusters facilitates the dissociation of excitons in neighbouring particles or at the inter-

particle interfaces(13). The spectral shifts seen in our results could therefore be due to increased efficiency of exciton transfer between neighbouring nanoparticles within a cluster at higher temperatures but could also be due to increased emission from lower energy thermally activated deep traps.

Biju's results showed an increase in intensity during the first four heating cycles and they suggest this is due to thermal or irradiative surface passivation. During each of our photoluminescence measurements the sample was exposed to 30 seconds of UV at 365nm; cumulatively, over one cycle, the sample was exposed to ~7.5 minutes of UV. Several researchers have reported enhancement of photoluminescence due to UV irradiation and have used the effect to increase the quantum yield of the nanoparticles at the synthesis stage(14,15). The small increase in intensity in our results could therefore be due to passivation by irradiation.

6.3.2 Temperature Cycling of Thin Films

Heating and cooling a thin film produces very similar results to those seen in the suspension experiments. The thin films used in this experiment were 10 layers thick. Here the spectral peak shifts reversibly between 644nm at 293K and 654nm at 358K (Figure 6.7). Interestingly, in thin film form the initial non-reversible shift was not seen. Again, this observation is supported by the literature. Walker *et al*(7) investigated CdSe/ZnS nanoparticles fixed in a poly(lauryl methacrylate) matrix. They cycled the temperature of the nanoparticles and found that before, during and after the heating, measurements taken at the same temperature showed an almost exactly superimposed spectral peak. It is likely that the irreversible shift seen in the

suspension data and also the wavelength drift seen in later temperature cycles of the suspension (Fig. 6.4) was due to the establishing of energy transfer pathways between the nanoparticles similar to the process occurring when the nanoparticles were deposited as thin films (Fig. 4.7) – both result in a 6nm shift. Once deposited in thin film form the nanoparticles are embedded in a polymer matrix, consequently, the temperature cycling cannot change the inter-particle distances or any inter-particle interactions that are related to distance thus, the 6nm non-reversible shift with temperature was only seen in the suspensions. The reversible red-shift observed for CdTe thin films would therefore be entirely due to thermally activated traps.

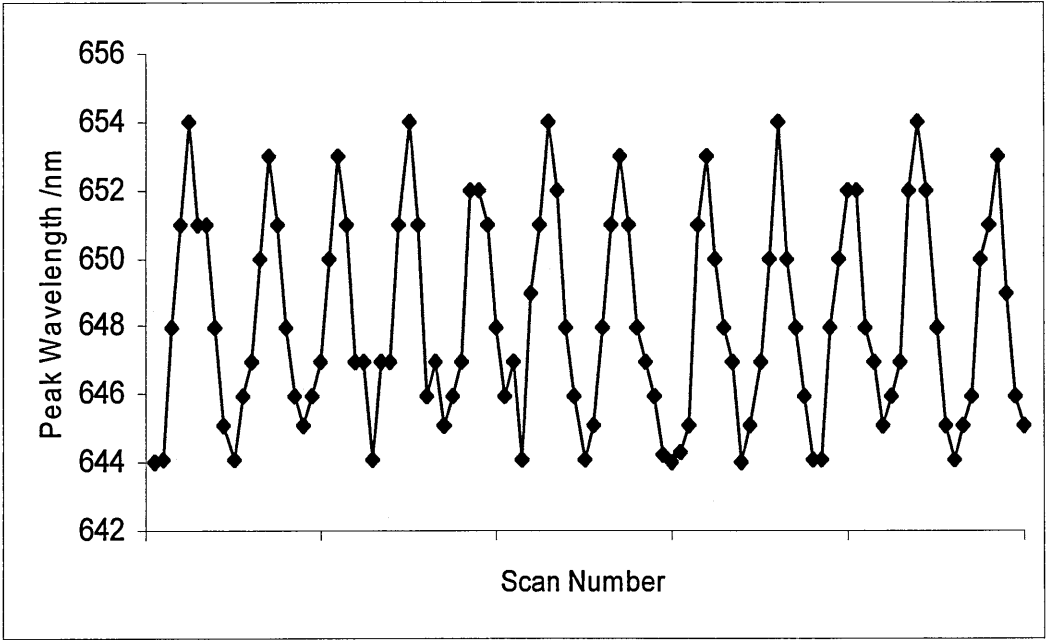


Figure 6.7: The change in wavelength as a thin film is temperature cycled.

As can be seen in Figure 6.8 the intensity of the photoluminescence in a CdTe thin film device is also dependent on temperature. An initial loss of

photoluminescence is seen during the first two heating cycles followed by a reversible loss of luminescence with increasing temperature and restoration of intensity with cooling. There is no increase in intensity after the first heating cycle as was seen in the nanoparticle suspension. This would suggest that the irradiative surface passivation does not occur when the particles are embedded in thin film form.

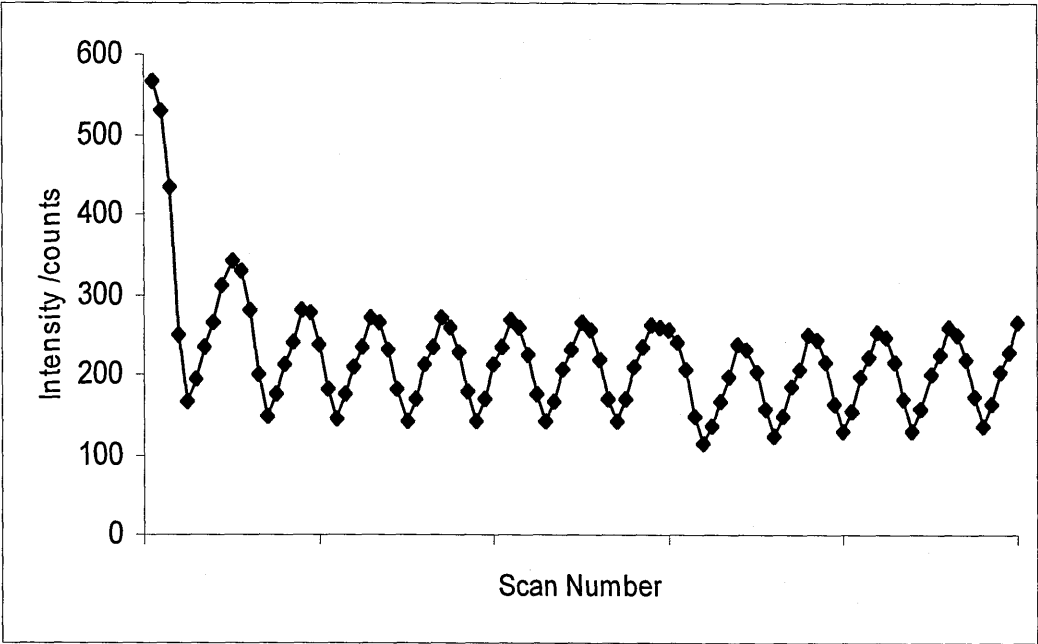


Figure 6.8: The change in intensity as a thin film is temperature cycled.

The permanent loss in photoluminescence intensity seen in Figure 6.8 and also to a lesser extent in Figure 6.6 can be attributed to the formation of permanent non-radiative trap states at the connecting point of nanoparticles within clusters.

6.3.3 Prolonged Heating of Suspensions and Thin Films

Suspensions and thin films were also heated for prolonged periods of time. Figure 6.9 shows photoluminescence and absorbance spectra of a thin film before and after it was heated at 333K for 1 hour. The only significant difference between the spectra is a loss in photoluminescence intensity. There is no difference in the photoluminescence maximum thus there has been no change in the size of the nanoparticles.

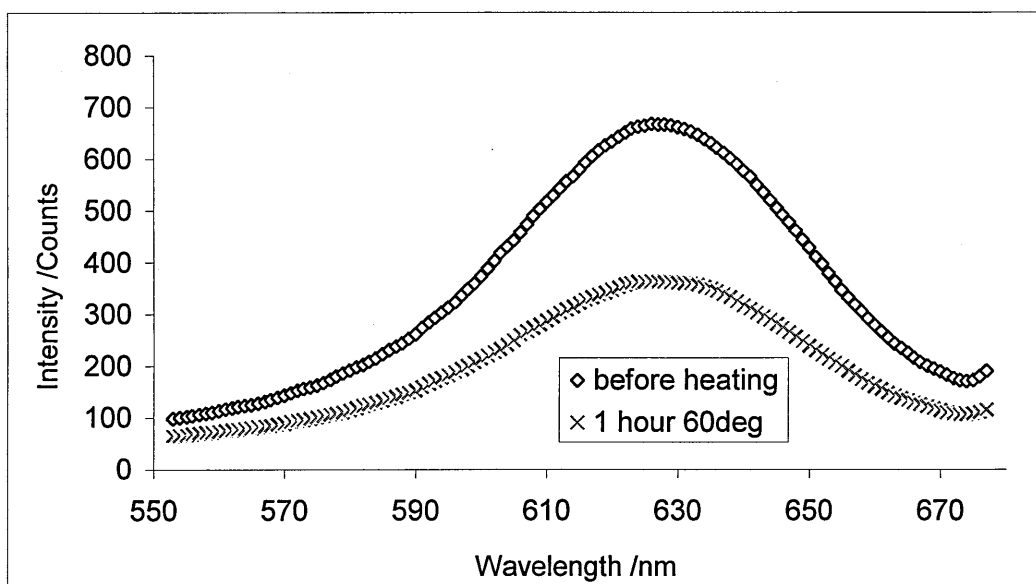


Figure 6.9: Photoluminescence spectra of a thin film before and after heating for 1 hour.

AFM images of the thin films were taken before and after heating. Figure 6.10a shows an unheated sample and Figure 6.10b shows a sample after being heated for 1 hour at 333K. The temperature treatment seems to induce the formation of aggregates.

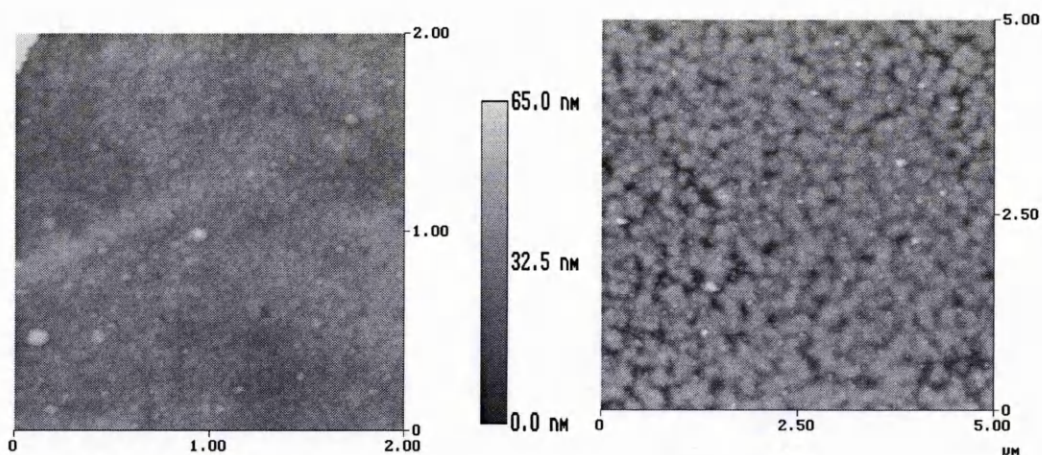


Figure 6.10a: An AFM image of the unheated thin film

Figure 6.10b: An AFM image of the same thin film after heating for 1 hour.

Since the size of the nanoparticles has not changed the aggregates seen in Figure 6.10b must be constructed of nanoparticles and nanoparticle clusters. The permanent loss in intensity seen in Figure 6.9 is again due to non-radiative areas of nanoparticles at the connecting points of nanoparticle clusters. During the suspension cycling (Fig 6.6) we saw a 35% permanent photoluminescence intensity loss after 7 heat cycles whereas in the cycling of thin films (Fig 6.8) we saw a 51% intensity loss after only 2 heat cycles. In thin film form neighbouring clusters merge to form larger aggregates when heated, increasing the areas of connectivity between the nanoparticles and reducing the luminescence.

6.4 Conclusions

This Chapter has shown that a change in temperature produces both reversible and irreversible changes in the luminescence from CdTe

nanoparticles. In general, increasing the temperature within the range 293-358 K of both nanoparticle suspensions and thin films results in a reversible spectral shift to longer wavelengths and a reversible loss of intensity. The shift in wavelength is linear and is consistent with other published literature.

The main cause of both the shift and the intensity loss is the presence of thermally activated trap states within the nanoparticles. As temperature is increased the trap states become accessible this leads the particles to emit at lower energy (wavelength shift) and creates non-radiative recombination pathways (loss of intensity). These changes are reversible as once the temperature is lowered the trap states are no longer accessible.

The changes are not only reversible but also highly repeatable. A cycled thin film returned to within 1nm of its wavelength each time the maximum temperature was reached. With careful temperature control and measurement it is likely that this accuracy could be improved on. Wang *et al*(3) have projected that that temperature induced intensity changes can be used in a biomedical thermometry application. The findings of this Chapter show this is also true for the wavelength of emission.

Through comparison between experiments in suspension and thin film form the irreversible lower energy wavelength shift found in suspensions is attributed to an increase in the efficiency of energy transfer between particles. This proposal is further supported by the data in Chapter 4. There a 6nm shift was seen as a suspension was deposited to form a thin film. The irreversible shift seen in the current Chapter is also 6nm. In both cases the change is due to the establishment of energy transfer pathways.

We report a temperature induced aggregation of nanoparticles. AFM analysis of thin film samples shows agglomerates are formed after the sample is heated for an extended time period. Photoluminescence spectra of the thin films show no permanent change in wavelength but a permanent loss in intensity. The formation of agglomerates explains the irreversible loss of luminescence seen in the cycled thin films and to a lesser extent also in the cycled suspensions.

This permanent loss in intensity would be detrimental to applications such as Gallagher's proposed spectral concentrator(16). The lifetime of solar cells is usually expected to be around 25 years. Whilst the lifetime of a concentrator may not need to match that of the cell nanoparticle stability under prolonged heating conditions will be essential. Future work in this area will therefore need to focus on shielding the nanoparticles from their temperature environment.

7 Final Conclusions

The many applications of semiconductor nanoparticles or quantum dots are rapidly growing areas of research. In cancer research nanoparticles have been used to confirm the presence of cancer cells, image cancer cells, monitor the development and spread of cancers by cell tracking and even to provide therapeutic treatment. In optoelectronic technologies nanoparticles are being developed as materials for nanostructured light emitting devices or in combination with organic polymers as hybrid OLEDs. OLEDs are already being used in large area displays; in December 2007 Sony released a 27" OLED television. The addition of semiconductor nanoparticles to these technologies is likely to increase their commercial potential against rival liquid crystal displays. In photovoltaic devices nanoparticles are set to increase the efficiency of solar cells either as retrofitted spectral converters or as an integral part of the absorption layer. Adding nanoparticles to Grätzel cells is expected to greatly increase the energy harvesting efficiency of the cell whilst maintaining low material costs. This would decrease the cost per watt of the energy produced and make Grätzel cells viable contenders in the growing solar energy market.

Biomedical, optoelectronic and photovoltaic technologies are only three examples of the applications of nanoparticles. There are many more applications undergoing research and probably many more as yet undiscovered. The growing potential of nanoparticles means that research into understanding their properties is important. Perhaps the most promising method of producing nanoparticles is via wet chemical synthesis. Chemical

production allows a high degree of choice and control over the composition and size of the nanoparticles and is a cost-efficient method. When fabricated in this way the nanoparticle end product is usually a concentrated suspension or a powder. Before use in any application the nanoparticles therefore need to be processed into dilute suspensions or deposited as thin films.

Results throughout this work have shown that energy transfer from small to large nanoparticles occurred whenever the particles were within close enough range and produced a red-shift in the wavelength of the photoluminescence peak maximum. The effects of this energy transfer were readily seen in the photoluminescence spectra. Since the nanoparticles needed to be in close range for this energy transfer to occur the inter-particle distance played a big role in many of the observed photoluminescent phenomenon.

When nanoparticles were deposited from a suspension to a thin film the inter-particle distance decreased and a red-shift in photoluminescence occurred. When the thin film was then built-up into a multilayer film nanoparticles could interact on a 3d rather than a 2d scale. A further red-shift was seen. When the polymer used to deposit the thin film was changed from PDDA to PEI the red shift on the development of multilayers was less pronounced. Analysis of the PEI thin film found it to be less ordered than its PDDA counterpart. The nanoparticles in the PEI thin film would therefore have longer average inter-particle distances.

Dilution of a suspension of nanoparticles showed the reverse of this effect. As the suspension was diluted the average inter-particle distance

increased. The resulting blue-shift occurred because less energy transfer could take place. Re-concentration of the suspension produced a red-shift.

The blue-shift seen on diluted a suspension may not be entirely due to the change in inter-particle distance. The thiol capping layer of the nanoparticles is known to desorb at lower concentrations. Removing the capping layer would decrease the size of the overall nanoparticle thus a blue-shift would be expected. The results from the re-concentration experiment however showed that the blue shift cannot be entirely due to the loss of thiol.

For nanoparticles to be useful in any application it is important to understand how they may be affected by the environment they are faced with within that application. One of the most important considerations is to look at the affects of the operating temperature of the application. The photoluminescence of nanoparticles has previously been reported to be temperature sensitive at low temperatures. The final experimental chapter of this report looked at the effects of changing temperature within an ambient range.

It was found that when heated the nanoparticle suspensions and thin films showed reversible and repeatable wavelength and intensity changes. The repeatability of these results demonstrates that the CdTe nanoparticles would be suitable for a temperature sensing application. Irreversible photoluminescent changes due to temperature were also found. Prolonged heating of a thin film sample produced an irreversible loss of luminescence intensity. AFM analysis showed that this loss was due to agglomeration of the nanoparticles into clusters of nanoparticles. This finding limits the usefulness of these CdTe nanoparticles within the fields of optoelectronic and

photovoltaic technologies. Future suggested work would therefore be to investigate methods of shielding these nanoparticles from any high temperatures in their operating environment.

The reversible changes in wavelength and intensity seen in both the suspensions and thin films was found to be due to the presence of thermally activated trap states. At low temperatures these trap states are not accessible. However, as the temperature increases lower energy luminescent and non-radiative recombination pathways become available. The changes are reversible because once the temperature has decreased the trap states are again inaccessible.

Finally, OWLS was used as an in-situ, real-time analysis technique for monitoring LBL deposition. OWLS was found to be a quick and convenient method for this analysis. Using the OWLS technique in this way would allow researchers to make changes to their LBL process and immediately monitor the results. Thus OWLS would become a rapid optimisation procedure for the improvement of individual experimental set-ups without producing fully functional LBL thin films.

For the particular deposition method used within this report we were able to identify different stages of deposition. At first, the nanoparticles deposit very rapidly onto the surface of the waveguide. At this stage the nanoparticles are faced with a complete surface of charged polymer and are able to adsorb quickly. After a short time this rapid deposition gives way to a more gentle increase of nanoparticles. Now the incoming nanoparticles must compete for space at the remaining adsorption sites. The nanoparticles deposited in the rapid deposition stage become strongly bound to the polymer

surface but the nanoparticles deposited later may be only weakly attached and can be washed off during the rinsing stages.

This thesis has looked at various post-preparative treatments of CdTe nanoparticles. The aim of the thesis was to further the scientific understanding of CdTe nanoparticles and their interaction within their surrounding environment. By looking at the effects of temperature changes on CdTe nanoparticles we have looked at one of the key environmental factors a nanoparticle experiences. An insight has been gained into how a nanoparticle will react in such an environment and areas for future work have been highlighted. The findings of this work are likely to be useful to researchers considering the use of CdTe nanoparticles within a particular application.

8 Future work

8.1 Effects of Strain

The original aim of this PhD was to design, construct and evaluate a strain tuneable luminescent device where the luminescence is modified by piezoelectric actuation. A basic design for such a device is shown in Figure 8.1.

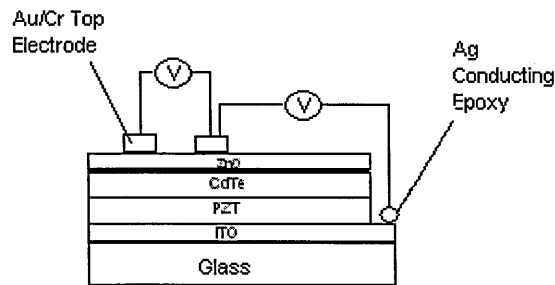


Figure 8.1 Schematic of a strain tuneable luminescent device

The device consisted of a glass substrate with thin films of ITO, lead zirconium titanate (PZT), CdTe nanoparticles and zinc oxide topped with chromium/gold electrodes. Applying a field between the two top (Cr/Au) electrodes was designed to create a d_{33} strain in the ferroelectric PZT layer and applying a field between one top electrode and the ITO bottom electrode created a d_{31} strain. A d_{33} strain is the strain measured in the same direction as the applied voltage whereas a d_{31} strain is measured perpendicular to the applied voltage. These strains would then produce a change in the surface of

the PZT layer and thus also the CdTe layer. The ZnO layer is also ferroelectric so applying a voltage to the top two electrodes would be more likely to produce a strain in the ZnO layer rather than the PZT layer. Due to the sandwich nature of the device this may still produce the desired effect in the CdTe. Changing the strain applied to the CdTe layer would change the size, shape or proximity of the nanoparticle and thus change their wavelength of emission.

An ITO coated glass substrate was used as a transparent bottom electrode to provide a hole injecting layer to the ferroelectric and to allow UV absorption and light emission through the bottom of the sample. The PZT layer was created using a sol-gel technique by spin coating from a sol made by Qi Zhang(1). The CdTe layer was fabricated using the LBL deposition method described earlier in this report (Section 3.2.3) but using manual deposition rather than the automated deposition used elsewhere in this report. The manual method has since been disregarded as it produces thicker inhomogeneous layers. The ZnO layer provides a protective barrier between the CdTe and the air, preventing oxidation and consequently degradation of the nanoparticles. ZnO was chosen as in this thickness (layer is 70nm thick) it is transparent.

The first year of my research concentrated on establishing an understanding of the various components of the device and fabricating and testing preliminary devices. On applying voltages between the two top electrodes of a device the photoluminescence spectra showed interesting results. As the voltage was increased from 0v to 20v, <5v showed no significant change, 7.5-15v showed small shifts to longer wavelengths and

17.5 and 20v showed larger shifts in the same direction. The voltage was then decreased and the peak maximums were seen to shift back towards the blue direction. However, the peaks did not return to their original positions. The peak maximum start position was ~610nm, this shifted to ~660nm and returned to ~625nm. This can be seen in Figure 8.2, the top spectra are due to increasing voltage and the bottom spectra are due to decreasing the voltage again.

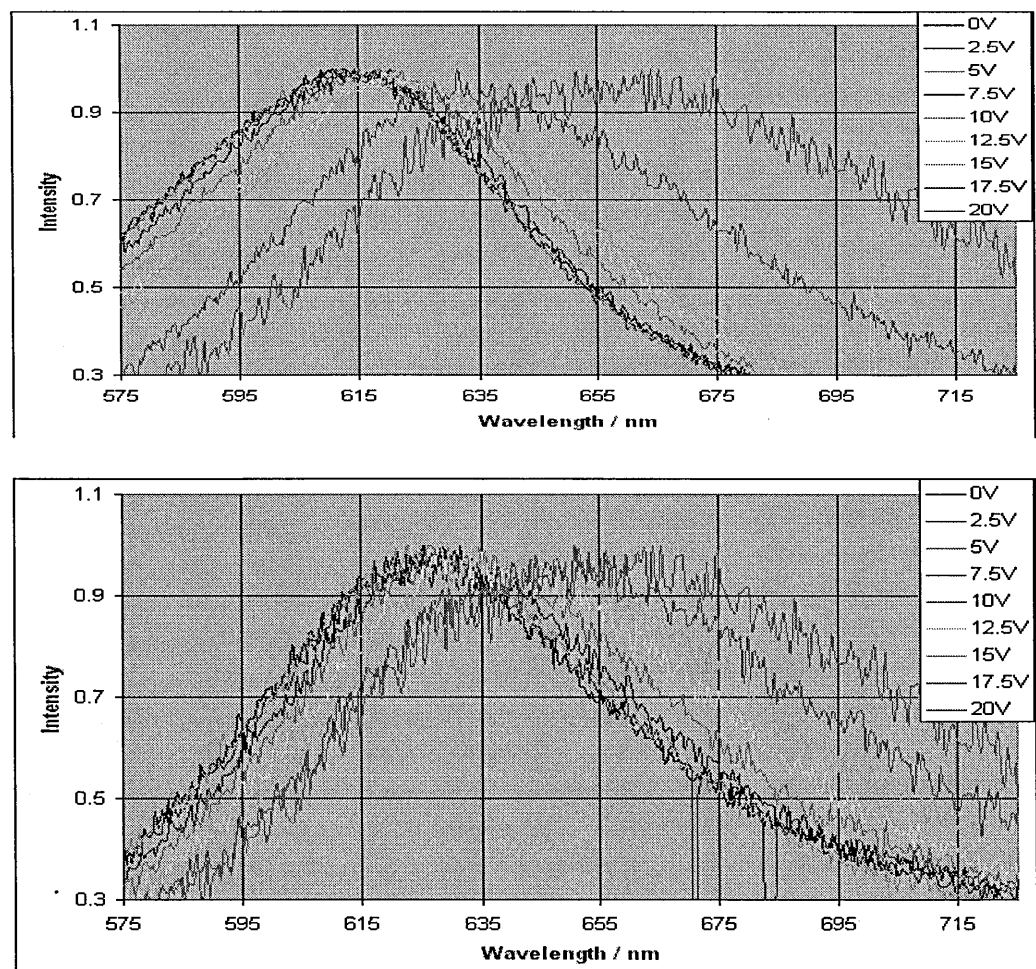


Figure 8.2: Photoluminescent spectra observed whilst increasing (Top) and decreasing (Bottom) the voltage applied between the two top electrodes of a ferroelectric strain device.

However, further investigation showed the wavelength changes were at least partially due to effects other than any strain induced in the PZT layer. High currents produced heating of the device. A control experiment was conducted whereby a sample was heated using an external heat source, the change in temperature was found to produce similar wavelength shifts to those seen in Figure 8.2. Furthermore, a calculation of the change in wavelength likely to be induced by a strain in the PZT layer was found to be very small. A change in wavelength of $< 1\text{nm}$ could be expected.

To continue to look into the effects of strain without the inherent heating of the PZT device a simpler method was devised. CdTe thin films were deposited onto flexible polymethylmethacrylate (PMMA) substrates. The substrates were then placed into a bending jig, supplied by the National Physics Laboratory, capable of measuring deflection changes of 0.1 microns. Photoluminescence spectra were recorded whilst the deflection of the substrate was changed.

Figure 8.3 shows the change in photoluminescence spectra as a convex strain was applied. The strain values have been calculated with respect to the radius of curvature and the thickness of the sample. An increasing strain results in a shift to the blue.

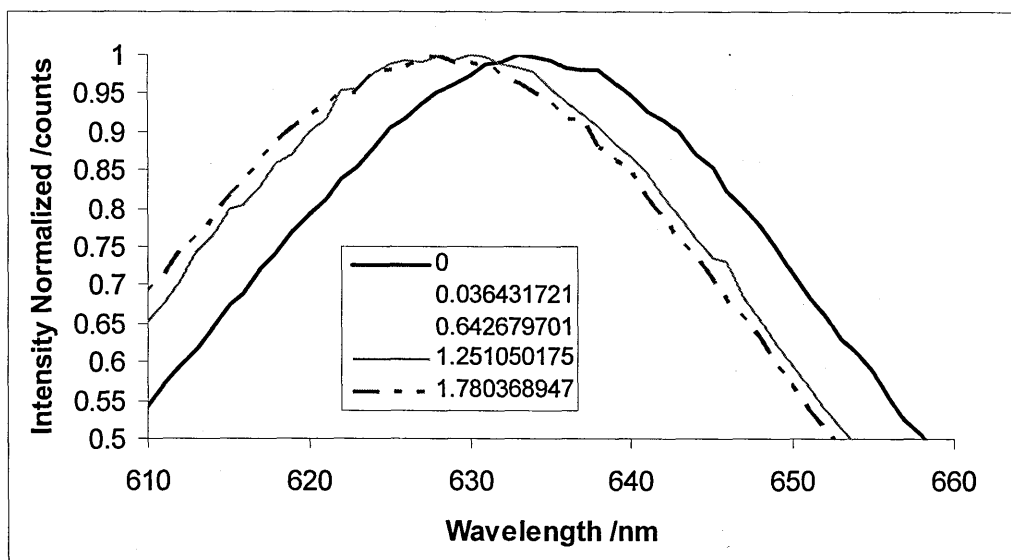


Figure 8.3: The change in photoluminescence when the substrate is deformed

Figure 8.4 shows a schematic of how changing the shape of the substrate may affect the nanoparticles. When the substrate is flat the nanoparticles are a set distance apart, if their positions are fixed then as the substrate is curved convexly the inter-particle distance will increase. Similarly, as the substrate is curved concavely the inter-particle distance will decrease.

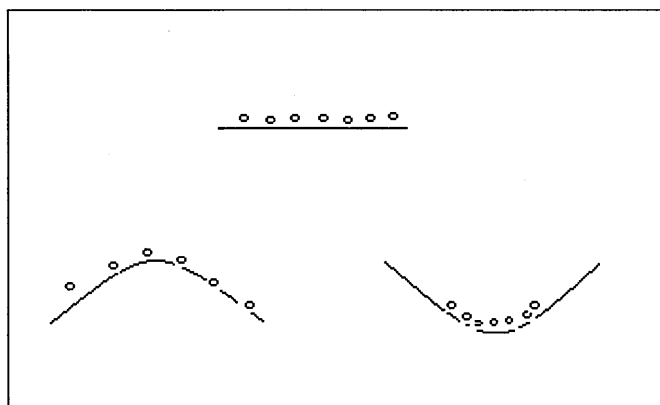


Figure 8.4: Schematic of how bending the substrate will affect the nanoparticles.

As a convex strain is applied the particles move further apart thus less inter-particle energy interactions can occur and we see a shift to the blue. These results fall in line with the results seen in Chapter 4 when the changing of the inter-particle distance during dilution and deposition of nanoparticles produced similar wavelength shifts.

However, a look back at the results from the PZT device shows that the changes in photoluminescent spectra here are of a different order of magnitude to those seen in the PMMA device. Table 8.1 lists the wavelengths of the spectral peak maxima recorded at different applied voltages and Figure 8.5 shows a plot of the wavelength versus the voltage.

Table 8.1: Peak positions for various voltages applied

Voltage Applied	Peak Position /nm
0	612.765
2.5	614.251
5	611.773
7.5	620.195
10	618.215
12.5	619.205
15	620.69
17.5	631.569
20	670.949
20	664.078
17.5	650.802
15	634.039
12.5	628.11
10	626.132
7.5	625.638
5	622.67
2.5	625.638
0	622.67

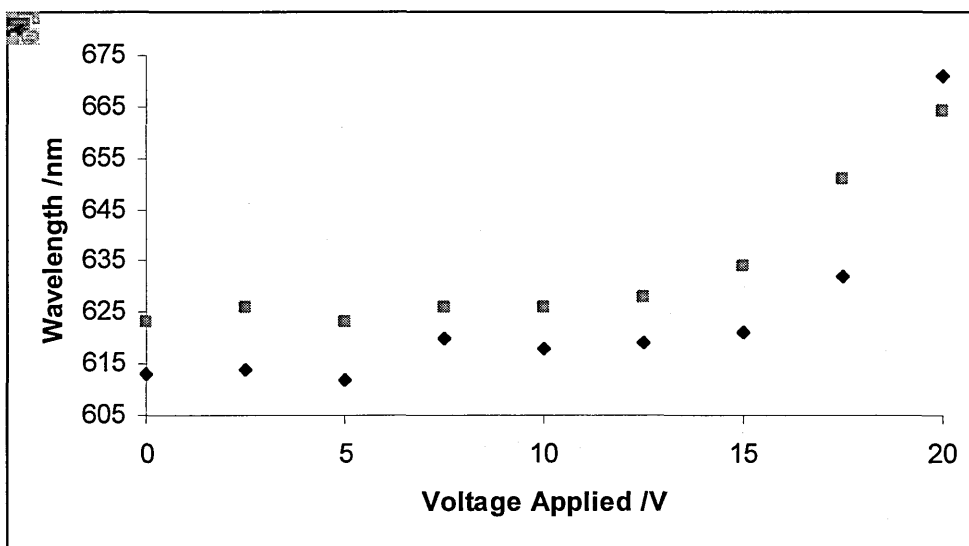


Figure 8.5: A plot of the wavelength of the photoluminescence peak maximum versus voltage; blue diamonds are when the voltage is being increased and pink squares are when the voltage is being decreased.

An applied voltage of 0 to 15 volts produces small shifts in the wavelength of the luminescence similar to those seen in the PMMA device. But increasing the voltage from 15 to 20 volts produces a much larger change in wavelength. The temperature of the device after application of 20 volts was estimated at ~358K. From Chapter 6 we see that this change in temperature can also not explain such a large wavelength shift.

Unfortunately, after a short period of measurement the devices no longer displayed photoluminescence thus repeat experiments could not be conducted. Future work into this area would therefore be to fabricate similar PZT/CdTe devices to see if the results reported here could be replicated and explained.

References

Chapter 1

- (1) Feynman R. "There's plenty of room at the bottom" transcript available at: <http://www.its.caltech.edu/~feynman/plenty.html>.
- (2) Nanotechnology at Leeds. Available at: <http://www.nanotech.leeds.ac.uk/coursecontent.html>.
- (3) Nanotechnology at QMUL. Available at: http://www.qmul.ac.uk/courses/courses.php?course_id=381&course_level=1&dept_id=20.
- (4) Nanotechnology. Available at: www.iop.org/EJ/journal/0957-4484.
- (5) Nature Nanotechnology. Available at: www.nature.com/nnano/index.html.
- (6) Evident quantum dots. Available at: www.evidenttech.com.
- (7) Nanocar. Available at: http://en.wikipedia.org/wiki/Tata_Nano.
- (8) Grey goo. Available at: http://en.wikipedia.org/wiki/Grey_goo.
- (9) Madou MJ. Fundamentals of microfabrication: the science of miniaturisation. US: CRC; 2002.
- (10) Poole CP, Owens FJ. Introduction to Nanotechnology. US: Wiley Interscience; 2003.
- (11) Foster LE. Nanotechnology: Science, innovation and opportunity. US: Prentice Hall; 2005.

Chapter 2

- (1) Nature. Available at: www.nature.com/nature/index.html.
- (2) Science. Available at: www.scienceonline.org.
- (3) Nano Letters. Available at: <http://pubs.acs.org/journals/nlalefd/index.html>.
- (4) Nanotechnology. Available at: www.iop.org/EJ/journal/0957-4484.
- (5) Nature Nanotechnology. Available at: www.nature.com/nnano/index.html.
- (6) Small. Available at: www.interscience.wiley.com/journal/107640323/home.

- (7) Parry V. Food fight on a tiny scale. The Times 2006; Life and Style(Oct 21).
- (8) Sample I. Cheap nano know how cleans arsenic from water. The Guardian 2006; National(Friday 10th November):8.
- (9) Williams L, Adams W. Nanotechnology demystified. US: McGraw-Hill Professional; 2006.
- (10) Ratner RA, Ratner D. Nanotechnology: A gentle introduction to the next big idea. US: Prentice Hall; 2002.
- (11) Turton R, The quantum dot: A journey into the future of microelectronics. W.H. Freeman 1995.
- (12) Booker RD, Boysen E. Nanotechnology for dummies. US: For Dummies; 2005.
- (13) Crichton M. Prey: Avon; 2003.
- (14) Stephenson N. The diamond age: Or a young lady's illustrated primer: Spectra; 2000.
- (15) Bell AT. The impact of nanoscience on heterogeneous catalysis. Science 2003;299:1688.
- (16) Gu H, Xu B, Rao J, Zheng XX, Fung KK, Wong CYC. Chemical synthesis of narrowly dispersed SmCo_5 nanoparticles. J.Appl.Phys. 2003;93:7589.
- (17) Donbrow M. Microcapsules and nanoparticles in medicine and pharmacy. : CRC Press; 1991.
- (18) Bauer G, Hassmann J, Walter H, Haglmüller J, Mayer C, Schalkhammer T. Resonant nanocluster technology - from optical coding and high quality security features to biochips. Nanotechnology 2003;14:1289.
- (19) Walter P, Welcomme E, Hallegot P, Zuluzec NJ, Deeb C, Castaing J, Veyssiere P, Breniaux R, Leveque J, Tsoucarist G. Early use of PbS nanotechnology for an ancient hair dying formula. Nano Letters 2006;6:2215.
- (20) Reibold M, Paufler P, Levin AA, Kochmann W, Patzke N, Meyer DC. Materials: Carbon nanotubes in an ancient Damascus sabre. Nature 2006;444:286.
- (21) Skaff H, Emrick T. Semiconductor nanoparticles: synthesis, properties and integration into polymers for the generation of novel composite materials. In: Rotello R, editor. Nanoparticles building blocks for nanotechnology USA: Springer; 2004. p. 29-52.

- (22) Trindade T, O'Brien P, Pickett NL. Nanocrystalline semiconductors: Synthesis, properties, and perspectives. *Chemistry of Materials* 2001 NOV;13(11):3843-3858.
- (23) Murray CB, Kagan CR, Bawendi MG. Synthesis and Characterisation of Monodisperse Nanocrystals and Close-Packed Nanocrystal Assemblies. *Annual Review of Materials Science* 2000;30:545-610.
- (24) Available at: www.research.phillips.com/newscentre/pictures/lm-nanotech.html.
- (25) Efros AL, Efros AL. Interband absorption of light in a semiconductor sphere. *Sov.Phys.Semicond.* 1982;16(7):772-775.
- (26) Ekimov AI, Onushchenko AA. Quantum size effect in the optical spectra of semiconductor microcrystals. *Sov.Phys.Semicond.* 1982;16:775-778.
- (27) Gaponenko SV. Electron states in an ideal nanocrystal. *Optical Properties of Semiconductor Nanocrystals* Cambridge: Cambridge University Press; 1998. p. 27.
- (28) Gaponenko SV. Electron states in crystal. *Optical Properties of Semiconductor Nanocrystals* Cambridge: Cambridge University Press; 1998. p. 1.
- (29) Murray CB, Shouheng S, Gaschler W, Doyle H, Betley TA, Kagan CR. Colloidal synthesis of nanocrystals and nanocrystal superlattices. *IBM Journal of Research and Development* 2001;45(1):10.1147.
- (30) Wuister SF, van Driel F, Meijerink A. Luminescence of CdTe Nanocrystals. *J Lumin* 2003;102-103:327-332.
- (31) Hines MA, Guyot-Sionnest P. Synthesis and characterisation of strongly luminescing ZnS-capped CdSe nanocrystals. *J.Phys.Chem.* 1996;100:468-471.
- (32) Bao H, Gong Y, Gao M. Enhancement effect of illumination on the photoluminescence of water-soluble CdTe nanocrystals: Toward highly fluorescent CdTe/CdS core-shell structure. *Chemical Materials* 2004;16:3853-3859.
- (33) LaMer VK, Dinegar RH. Theory, production and mechanism of formation of monodisperse hydrosols. *J.Am.Chem.Soc.* 1950;72(11):4847-4854.
- (34) Ostwald W. *Lehrbuch der Allgemeinen Chemie*. Leipzig, Germany; 1986.

- (35) Rogach AL, Eychmüller A, Hickey SG, Kershaw SV. Infrared-emitting colloidal nanocrystals: Synthesis, assembly, spectroscopy, and applications. *Small* 2007 APR;3(4):536-557.
- (36) Bawendi MG, Carroll PJ, Wilson WL, Brus LE. Luminescence properties of CdSe quantum crystallites - Resonance between interior and surface localized states. *J.Chem.Phys.* 1992;96(2):946-954.
- (37) Spanhel L, Haase M, Weller H, Henglein A. Photochemistry of colloidal semiconductors. 20. Surface modification and stability of strong luminescing CdS particles. *J.Am.Chem.Soc.* 1987;109:5649-5655.
- (38) Chan WCW, Maxwell DJ, Gao XH, Bailey RE, Han MY, Nie SM. Luminescent quantum dots for multiplexed biological detection and imaging. *Curr.Opin.Biotechnol.* 2002;13(1):40-46.
- (39) Murray CB, Norris DJ, Bawendi MG. Synthesis and characterisation of nearly monodisperse CdE (E = S, Se, Te) semiconductor nanocrystallites. *J.Am.Chem.Soc.* 1993;115:8706-8715.
- (40) Bowen Katari, JE, Colvin VL, Alivisatos AP. X-ray photoelectron spectroscopy of CdSe nanocrystals with applications to studies of the nanocrystal surface. *J. Phys. Chem.* 1994;98:4109-4117.
- (41) Talapin DV, Haubold S, Rogach AL, Kornowoski A, Haase M, Weller H. A Novel organometallic synthesis of highly luminescent CdTe nanocrystals. *J. Phys. Chem. B* 2001;105:2260-2263.
- (42) Sapra S, Rogach AL, Feldmann J. Phosphine-free synthesis of monodisperse CdSe nanocrystals in olive oil. *Journal of Materials Chemistry* 2006;16(33):3391-3395.
- (43) Gaponik N, Talapin DV, Rogach AL, Hoppe K, Shevchenko EV, Kornowoski A, Eychmüller A, Weller H. Thiol-capping of CdTe nanocrystals: An alternative to organometallic synthetic routes. *J. Phys. Chem. B* 2002;106:7177-7185.
- (44) Alivisatos AP. Semiconductor clusters, nanocrystals, and quantum dots. *Science* 1996;271:933-937.
- (45) Rosenthal SJ, McBride J, Pennycook SJ, Feldman LC. Synthesis, surface studies, composition and structural characterization of CdSe, core. *Surface Science Reports* 2007 APR 30;62(4):111-157.

- (46) Peng X, Schlamp MC, Kadavanich AV, Alivisatos AP. Epitaxial growth of highly luminescent CdSe/CdS core/shell nanocrystals with photostability and electronic accessibility. *Journal of Chemical Society* 1997;119:7019-7029.
- (47) Alivisatos P. The use of nanocrystals in biological detection. *Nat.Biotechnol.* 2004;22(1):47-52.
- (48) Michalet X, Pinaud FF, Bentolila LA, Tsay JM, Doose S, Li JJ, Sundarasan G, Wu AM, Gambier SS, Weiss S. Quantum dots for live cells, in vivo imaging, and diagnostics. *Science* 2005;307(5709):538-544.
- (49) Medintz IL, Uyeda HT, Goldman ER, Mattoussi H. Quantum dot bioconjugates for imaging, labelling and sensing. *Nature Materials* 2005;4(6):435-446.
- (50) Michalet X, Pinaud F, Lacoste TD, Dahan M, Bruchez MP, Alivisatos AP, Weiss S. Properties of fluorescent semiconductor nanocrystals and their application to biological labelling. *Single Molecules* 2001;2(4):261-276.
- (51) Costa-Fernandez JM, Pereiro R, Sanz-Medel A. The use of luminescent quantum dots for optical sensing. *Trac-Trends in Analytical Chemistry* 2006 MAR;25(3):207-218.
- (52) Yezhelyev MV, Al-Hajj A, Morris C, Marcus AI, Liu T, Lewis M, Cohen C, Zrazhevskiy P, Simons JW, Rogatko A, Nie S, Gao X, O'Reagan RM. In situ molecular profiling of breast cancer biomarkers with multicolor quantum dots. *Adv. Mater.* 2007 OCT 19;19(20):3146.
- (53) Portney NG, Ozkan M. Nano-oncology: drug delivery, imaging, and sensing. *Analytical and Bioanalytical Chemistry* 2006 FEB;384(3):620-630.
- (54) Gao XH, Cui YY, Levenson RM, Chung LWK, Nie SM. In vivo cancer targeting and imaging with semiconductor quantum dots. *Nat.Biotechnol.* 2004 AUG;22(8):969-976.
- (55) Pellegrino T, Parak WJ, Boudreau R, Le Gros MA, Gerion D, Alivisatos AP, Larabell CA. Quantum dot-based cell motility assay. *Differentiation* 2003 DEC;71(9-10):542-548.
- (56) Loo C, Lin A, Hirsch L, Lee MH, Barton J, Halas N, West J, Drezek R. Nanoshell-enabled photonics-based imaging and therapy of cancer. *Technology in Cancer Research & Treatment* 2004 FEB;3(1):33-40.
- (57) Choi MR, Stanton-Maxey KJ, Stanley JK, Levin CS, Bardhan R, Akin D, Badve S, Sturgis J, Robinson JP, Bashir R, Halas N, Clare SE. A cellular

Trojan horse for delivery of therapeutic nanoparticles into tumors. *Nano Letters* 2007;7:3759-3765.

(58) Bertoni C, Gallardo D, Dunn S, Gaponik N, Eychmüller A. Fabrication and characterization of red-emitting electroluminescent devices based on thiol-stabilized semiconductor nanocrystals. *Appl.Phys.Lett.* 2007 JAN 15;90(3):034107.

(59) Geffroy B, le Roy P, Prat C. Organic light-emitting diode (OLED) technology: materials, devices and display technologies. *Polym.Int.* 2006;55:572-582.

(60) Colvin VL, Schlamp MC, Alivisatos AP. Light-emitting diodes made from cadmium selenide nanocrystals and a semi-conducting polymer. *Nature* 1994;370:354-357.

(61) Schlamp MC, Peng X, Alivisatos AP. Improved efficiencies in light emitting diodes made with CdSe(CdS) core/shell type nanocrystals and a semiconducting polymer. *J.Appl.Phys.* 1997;82(11):5837-5842.

(62) Gaponik NP, Talapin DV, Rogach AL. A light-emitting device based on a CdTe nanocrystal/polyaniline composite. *Physical Chemistry Chemical Physics* 1999;1:1787-1789.

(63) Gao M, Lesser C, Kirstein S, Mohwald H, Rogach AL, Weller H. Electroluminescence of different colors from polycation/CdTe nanocrystal self-assembled films. *J.Appl.Phys.* 2000;87(5):2297-2302.

(64) Dorn JG. Solar cell production jumps 50 percent in 2007. 2007; Available at: <http://www.earth-policy.org/Indicators/Solar/2007.htm>. Accessed 15/1, 2008.

(65) Bermel P, Luo C, Zeng L, Kimerling LC, Joannopoulos JD. Improving thin-film crystalline silicon solar cell efficiencies with photonic crystals. *Optics Express* 2007 DEC 10;15(25):16986-17000.

(66) Green MA, Wenham SR. Novel parallel multijunction solar cell. *Appl.Phys.Lett.* 1994;65:2907.

(67) Huynh WU, Dittmer JJ, Alivisatos AP. Hybrid nanorod-polymer solar cells. *Science* 2002 MAR 29;295(5564):2425-2427.

(68) Ho M. Quantum dots and ultra-efficient solar cells? ISI Press Release 2006 19/01/2006:01/02/2008.

- (69) Nozik AJ. Exciton multiplication and relaxation dynamics in quantum dots: Applications to ultrahigh-efficiency solar photon conversion. *Inorg.Chem.* 2005 OCT 3;44(20):6893-6899.
- (70) Shabaev A, Efros AL, Nozik AJ. Multiexciton generation by a single photon in nanocrystals. *Nano Letters* 2006 DEC 13;6(12):2856-2863.
- (71) Gur I, Fromer NA, Geier ML, Alivisatos AP. Air-stable all-inorganic nanocrystal solar cells processed from solution. *Science* 2005 OCT 21;310(5747):462-465.
- (72) Li B, Wang L, Li J, Qiu Y. Improved performance of solid state Grätzel cell by cosensitization of quantum dot and dye. *Chin. Phys. Lett.* 2004;21(7):1391.
- (73) Han LL, Qin DH, Jiang X, Liu YS, Wang L, Chen JW, Cao Y. Synthesis of high quality zinc-blende CdSe nanocrystals and their application in hybrid solar cells. *Nanotechnology* 2006 SEP 28;17(18):4736-4742.
- (74) Gallagher SJ, Norton B, Eames PC. Quantum dot solar concentrators: Electrical conversion efficiencies and comparative concentrating factors of fabricated devices. *Solar Energy*, 2007 6;81(6):813-821.
- (75) Gallagher SJ, Rowan BC, Doran J, Norton B. Quantum dot solar concentrator: Device optimisation using spectroscopic techniques. *Solar Energy*, 2007 4;81(4):540-547.
- (76) Biju V, Makita Y, Sonoda A, Yokoyama H, Baba Y, Ishikawa M. Temperature-sensitive photoluminescence of CdSe quantum dot clusters. *J Phys. Chem. B* 2005;109:13899-13905.
- (77) Sonotek. Available at: www.sono-tek.com.
- (78) Langmuir I. The constitution and fundamental properties of solids and liquids. II Liquids. *J.Am.Chem.Soc.* 1917;39(9):1848.
- (79) Blodgett KB. Films built by depositing successive monomolecular on a solid surface. *J.Am.Chem.Soc.* 1935;57(1007).
- (80) Petty M. Langmuir-Blodgett films an introduction. Cambridge, UK: Cambridge University Press; 1996.
- (81) Kolliopoulou S, Tsoukalas D, Dimitrakis P, Normand P, Paul S, Pearson C, Molloy A, Petty MC. Field effect devices with metal nanoparticles integrated by Langmuir-Blodgett technique for non-volatile memory applications. *Journal of Physics: Conference Series* 2005;10:57.

- (82) Decher G, Hong JD, Schmitt J. Buildup of ultrathin multilayer films by a self-assembly process .3. Consecutively alternating adsorption of Anionic and cationic polyelectrolytes on charged surfaces. *Thin Solid Films* 1992 APR 30;210(1-2):831-835.
- (83) Decher G. Fuzzy Nanoassemblies: Toward layered polymeric multicomposites. *Science* 1997;277:1232.
- (84) Dobrynin AV, Rubinstein M. Theory of polyelectrolytes in solutions and at surfaces. *Progress in Polymer Science* 2005;30:1049-1118.
- (85) Liang Z, Dzienis L, Xu J, Wang Q. Covalent layer-by-layer assembly of conjugated polymers and CdSe nanoparticles: multilayer structure and photovoltaic properties. *Advanced functional materials* 2006;16:542-548.
- (86) Szekeres M, Szechenyi A, Stepan K, Haraszti T, Dekany I. Layer-by-layer self-assembly preparation of layered double hydroxide/polyelectrolyte nanofilms monitored by surface plasmon resonance spectroscopy. *Colloid Polym. Sci.* 2005;283:937.
- (87) Takita R, Okamura Y, Endo Y, Anzai J. Redox properties of ferricyanide ion on layer-by-layer thin film-coated gold electrodes; effects of type of polycation component in the film. *Electroanalysis* 2006;18(16):1627.
- (88) Castelnovo M, Joanny J. Formation of polyelectrolyte multilayers. *Langmuir* 2000;16:7524-7532.

Chapter 3

- (1) Gaponik N, Talapin DV, Rogach AL, Hoppe K, Shevchenko EV, Kornowoski A, Eychmüller A, Weller H. Thiol-capping of CdTe nanocrystals: An alternative to organometallic synthetic routes. *J. Phys. Chem. B* 2002;106:7177-7185.
- (2) Decher G. Fuzzy Nanoassemblies: Toward layered polymeric multicomposites. *Science* 1997;277:1232.
- (3) Gallardo DE, Bertoni C, Dunn S. Light emitting devices based on nanostructured semiconductors. *Proceedings of SPIE Photonics: Materials Devices and Applications*. 2006 07;5840:516-522.

Chapter 4

- (1) Gao M, Kirstein S, Mohwald H, Rogach AL, Kornowoski A, Eychmüller A, Weller H. Strongly photoluminescent CdTe nanocrystals by proper surface modification. *J. Phys. Chem. B* 1998;102:8360-8363.
- (2) Talapin DV, Rogach AL, Kornowoski A, Haase M, Weller H. Highly luminescent monodisperse CdSe and CdSe/ZnS nanocrystals synthesized in a hexadecylamine-trioctylphosphine oxide-triethylphosphine mixture. *Nano Letters* 2001;1(4):207-211.
- (3) Sapra S, Rogach AL, Feldmann J. Phosphine-free synthesis of monodisperse CdSe nanocrystals in olive oil. *Journal of Materials Chemistry* 2006;16(33):3391-3395.
- (4) Dollefeld H, Hoppe K, Kolny J, Schilling K, Weller H, Eychmüller A. Investigations on the stability of thiol stabilized semiconductor nanoparticles. *Physical Chemistry Chemical Physics* 2002;4:4747-4753.
- (5) Kagan CR, Murray CB, Nirmal M, Bawendi MG. Electronic energy transfer in CdSe quantum dots. *Phys.Rev.Lett.* 1996;76:1517-1520.
- (6) Vossmeier T, Katsikas L, Giersig M, Popovic IG, Diesner K, Chemseddine A, Eychmüller A, Weller H. CdS nanoclusters: synthesis, characterisation, size dependent oscillator strength, temperature shift of the excitonic transition energy, and reversible absorbance shift. *J.Phys.Chem.* 1994;98:7665-7673.
- (7) Artemeyv MV, Woggon U, Jaschinski H, Gurinovich LI, Gaponenko SV. Spectroscopic study of electronic states in an ensemble of close-packed CdSe nanocrystals. *J. Phys. Chem. B* 2000;104:11617-11624.
- (8) Dollefeld H, Weller H, Eychmüller A. Particle-particle interactions in semiconductor nanocrystal assemblies. *Nano Letters* 2001;1(5):267-269.
- (9) Dollefeld H, Weller H, Eychmüller A. Semiconductor nanocrystal assemblies: Experimental pitfalls and a simple model of particle-particle interaction. *J Phys Chem B* 2002;106:5604-5608.
- (10) Murray CB, Kagan CR, Bawendi MG. Synthesis and characterisation of monodisperse nanocrystals and close-packed nanocrystal assemblies. *Annual Review of Materials Science* 2000;30:545-610.

- (11) Boldt K, Bruns OT, Gaponik N, Eychmüller A. Comparative examination of the stability of semiconductor quantum dots in various biochemical buffers. *J. Phys. Chem. B* 2006 9;110(5):1959-1963.
- (12) Esquivias L, Litran R, Rodriguez-Ortega J, Blanco E, Ramirez-del-Solar M, de la Rosa-Fox N. Structure of CdS/SiO₂ nanocomposites: Influence of the precursor and Cd concentration. *J. Sol-gel Sci. Technol.* 1998;11:217.
- (13) Kim BS, Avila L, Brus LE, Herman IP. Organic ligand and solvent kinetics during the assembly of CdSe nanocrystal arrays using infrared attenuated total reflection. *Appl.Phys.Lett.* 2000;76(25):3715.
- (14) Zhang XB, Ha KL, Hark SK. Evidence of thermally activated transfer of excited carriers between CdSe/ZnSe quantum dots. *J Electron Mater* 2001;30:1332-1337.
- (15) Li J, Hong X, Liu Y, Li D, Wang Y, Li J, Bai Y, Li T. Highly photoluminescent CdTe/Poly(N-isopropylacrylamide) temperature-sensitive gels. *Adv Mater* 2005;17(2):163-166.
- (16) Abu-Sharkh B. Structure and mechanism of formation of polyelectrolyte multilayers. *Polymer* 2006;47:3674-3680.

Chapter 5

- (1) Bertoni C, Gallardo D, Dunn S, Gaponik N, Eychmüller A. Fabrication and characterization of red-emitting electroluminescent devices based on thiol-stabilized semiconductor nanocrystals. *Appl.Phys.Lett.* 2007 15;90(3):034107.
- (2) Zhang MN, Yan YM, Gong KP, Mao LQ, Guo ZX, Chen Y. Electrostatic layer-by-layer assembled carbon nanotube multilayer film and its electrocatalytic activity for O₂ reduction. *Langmuir* 2004 28;20(20):8781-8785.
- (3) Malikova N, Pastoriza-Santos I, Schierhorn M, Kotov NA, Liz-Marzan LM. Layer-by-layer assembled mixed spherical and planar gold nanoparticles: Control of interparticle interactions. *Langmuir* 2002 30;18(9):3694-3697.
- (4) Mamedov AA, Kotov NA. Free-standing layer-by-layer assembled films of magnetic nanoparticles. *Langmuir* 2000 27;16(13):5530-5533.

- (5) Lang J, Lin MH. Layer-by-layer assembly of DNA films and their interactions with dyes. *J. Phys. Chem. B* 1999 23;103(51):11393-11397.
- (6) Shi GY, Sun ZY, Liu MC, Zhang L, Liu Y, Qu YH, Jin LT. Electrochemistry and electrocatalytic properties of haemoglobin in layer-by-layer films of SiO₂ with vapour-surface sol-gel deposition. *Anal.Chem.* 2007 15;79(10):3581-3588.
- (7) Kohli N, Worden RM, Lee I. Direct transfer of preformed patterned bio-nanocomposite films on polyelectrolyte multilayer templates. *Macromolecular Bioscience* 2007 7;7(6):789-797.
- (8) Stricker JT, Gudmundsdottir AD, Smith AP, Taylor BE, Durstock MF. Fabrication of organic thin-film transistors using layer-by-layer assembly. *J. Phys. Chem. B* 2007 14;111(23):6322-6326.
- (9) Du N, Zhang H, Chen BD, Ma XY, Liu ZH, Wu JB, Yang DR. Porous indium oxide nanotubes: Layer-by-layer assembly on carbon-nanotube templates and application for room-temperature NH₃ gas sensors. *Adv. Mater.* 2007 18;19(12):1641.
- (10) Tang ZY, Wang Y, Podsiadlo P, Kotov NA. Biomedical applications of layer-by-layer assembly: From biomimetics to tissue engineering. *Adv. Mater.* 2006 18;18(24):3203-3224.
- (11) Kotov NA, Dekany I, Fendler JH. Layer-by-Layer self-assembly of polyelectrolyte-semiconductor nanoparticle composite films. *J.Phys.Chem.* 1995;99:13065-13069.
- (12) Li B, Wang LD, Li JW, Qiu Y. Improved performance of solid-state Grätzel solar cell by co-sensitization of quantum dot and dye. *Chinese Physics Letters* 2004;21(7):1391-1393.
- (13) Tang Z, Wang Y, Kotov N. Semiconductor nanoparticles on solid substrates: Film structure, intermolecular interactions and polyelectrolyte effects. *Langmuir* 2002;18:7035-7040.
- (14) Gao MY, Richter B, Kirstein S, Mohwald H. Electroluminescence studies on self-assembled films of PPV and CdSe nanoparticles. *J. Phys. Chem. B* 1998 21;102(21):4096-4103.
- (15) Gao M, Lesser C, Kirstein S, Mohwald H, Rogach AL, Weller H. Electroluminescence of different colors from polycation/CdTe nanocrystal self-assembled films. *J.Appl.Phys.* 2000;87(5):2297-2302.

- (16) Castelnovo M, Joanny J. Formation of polyelectrolyte multilayers. *Langmuir* 2000;16:7524-7532.
- (17) Abu-Sharkh B. Structure and mechanism of formation of polyelectrolyte multilayers. *Polymer* 2006;47:3674-3680.
- (18) Kurrat R, Textor M, Ramsden JJ, Boni P, Spencer ND. Instrumental improvements in optical waveguide light mode spectroscopy for the study of biomolecule adsorption. *Rev.Sci.Instrum.* 1997 ;68(5):2172-2176.
- (19) Horvath R, Skivensen N, Larsen NB, Pederson HC. Reverse symmetry waveguide for optical biosensing. 2005.
- (20) Horvath R, Pederson HC, Cuisiner FJG. Guided wave sensing of polyelectrolyte multilayers. *Appl.Phys.Lett.* 2006;88:111102.
- (21) Ramsden JJ. Optical Biosensors. *J Mol. Recogn.* 1997;10:109.
- (22) Picart C, Gergely C, Arntz Y, Voegel JC, Schaaf P, Cuisinier FJG, Senger B. Measurement of film thickness up to several hundreds of nanometers using optical waveguide lightmode spectroscopy. *Biosens.Bioelectron.* 2004 15;20(3):553-561.
- (23) Gardner HC, Horvath R, Ramsden JJ, Dunn S. In-situ kinetic analysis of self-assembled nanoparticle-polyelectrolyte thin films. Up Coming Paper .
- (24) Available at: www.cranfield.ac.uk/sas/staff/horvathr.htm.
- (25) Horvath R, Ramsden JJ. Quasi-isotropic analysis of anisotropic thin films on optical waveguides. *Langmuir* 2007;23:9330-9334.
- (26) Schwartz S, Nagel J, Jaeger W. Comparison of polyelectrolyte multilayers built up with polydiallyldimethylammonium chloride and poly(ethylenimine) from salt-free solutions by in-situ surface plasmon resonance measurements. *Macromolecular Symposium* 2004;211:201-216.
- (27) Liang Z, Dzienis L, Xu J, Wang Q. Covalent layer-by-layer assembly of conjugated polymers and CdSe nanoparticles: multilayer structure and photovoltaic properties. *Advanced functional materials* 2006;16:542-548.
- (28) Yu WW, Qu L, Guo W, Peng X. Experimental determination of the extinction coefficient of CdTe, CdSe and CdS nanocrystals. *Chem. Mater.* 2003;15:2854.
- (29) Lesser C, Gao M, Kirstein S. Highly luminescent thin films from alternating deposition of CdTe nanoparticles and polycations. *Materials*

Science & Engineering C-Biomimetic and Supramolecular Systems 1999 1;8-9:159-162.

(30) Chen J, Luo G, Cao W. The study of layer-by-layer ultrathin films by the dynamic contact angle method. *J. Colloid Interface Sci.* 2001;238:62-62.

Chapter 6

(1) Nozik AJ. Quantum dot solar cells. NREL CP-590-31-11; 14-17th October 2001.

(2) Gallagher SJ, Rowan BC, Doran J, Norton B. Quantum dot solar concentrator: Device optimisation using spectroscopic techniques. *Solar Energy*, 2007 4;81(4):540-547.

(3) Wang S, Westcott S, Chen W. Nanoparticle luminescence thermometry. *J. Phys. Chem. B* 2002;106:11203-11209.

(4) Liu TC, Huang ZL, Wang HQ, Wang JH, Li XQ, Zhao YD, Luo QM. Temperature-dependent photoluminescence of water-soluble quantum dots for a bioprobe. *Anal. Chim. Acta* 2006;559:120.

(5) Wuister SF, van Houselt A, de Mello Donega, C, Vanmaekelbergh D, Meijerink A. Temperature anti-quenching of the luminescence from Capped CdSe quantum dots. *Angewandte Chemie International Ed* 2004;43:3029-3033.

(6) Labeau O, Tamarat P, Lounis B. Temperature dependence of the luminescence lifetime of single CdSe/ZnS quantum dots. *Phys. Rev. Lett.* 2003;90(25):Art #257404.

(7) Walker GW, Sundar VC, Rudzinski CM, Wun AW, Bawendi MG, Nocera DG. Quantum-dot optical temperature probes. *Appl. Phys. Lett.* 2003;83(17):3555-3557.

(8) Gardner HC, Gallardo DE, Bertoni C, Dunn S. Temperature shifted photoluminescence in CdTe nanocrystals. *Proceedings of SPIE: Nanophotonics* 2006;6195:10.1117/12.661233.

(9) Ostwald W. *Lehrbuch der Allgemeinen Chemie*. Leipzig, Germany; 1986.

- (10) Murray CB, Kagan CR, Bawendi MG. Synthesis and characterisation of monodisperse nanocrystals and close-packed nanocrystal assemblies. *Annual Review of Materials Science* 2000;30:545-610.
- (11) Kim JC, Rho H, Smith LM, Jackson HE, Lee S, Dobrowolska M, Merz JL, Furdyna JK. Spectroscopic characterization of the evolution of self-assembled CdSe quantum dots. *Appl.Phys.Lett.* 1998;73(23):3399.
- (12) Zhang XB, Ha KL, Hark SK. Evidence of thermally activated transfer of excited carriers between CdSe/ZnSe quantum dots. *J. Electron. Mater.* 2001;30:1332-1337.
- (13) Biju V, Makita Y, Sonoda A, Yokoyama H, Baba Y, Ishikawa M. Temperature-sensitive photoluminescence of CdSe quantum dot clusters. *J Phys Chem B* 2005;109:13899-13905.
- (14) Bao H, Gong Y, Gao M. Enhancement effect of illumination on the photoluminescence of water-soluble CdTe nanocrystals: Towards highly fluorescent CdTe/CdS core-shell structures. *Chemical Materials* 2004;16:3853-3859.
- (15) Bakalova R, Zhelev Z, Jose R, Nagase T, Ohba H, Ishikawa M, Baba Y. Role of free cadmium and selenium ions in the potential mechanism for the enhancement of photoluminescence of CdSe quantum dots under ultraviolet irradiation. *Journal of Nanoscience and Nanotechnology* 2005;5:887-894.
- (16) Gallagher SJ, Norton B, Eames PC. Quantum dot solar concentrators: Electrical conversion efficiencies and comparative concentrating factors of fabricated devices. *Solar Energy*, 2007 6;81(6):813-821.

Chapter 8

- (1) Huang Z, Zhang Q, Whatmore RW. Low temperature crystallization of lead zirconate titanate thin films by a sol-gel method. *J.Appl.Phys.* 1999;85(10):7355-7361.

Appendix

A Photoluminescence Study of Film Structure in CdTe Nanoparticle Thin Films

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Journal of Nanoscience and Nanotechnology, 2008, **8**, 2578-2581.

The layer-by-layer deposition of thin films of CdTe nanoparticles and three different polyelectrolytes has been investigated. Photoluminescence spectra were used to monitor the energy transfer properties within the films. As the number of bi-layers in a thin film was increased a decrease in the energy of the light emitted was observed. The wavelength change is a two-stage process. Deposition of the first one to two bi-layers of a thin film produced a sharp energy change (626nm to 637nm with the addition of a single bi-layer) whereas deposition of subsequent bi-layers produced a more gradual energy change (642nm - 646nm with the addition of 5 bi-layers). A space-filling mechanism is suggested to account for these changes; smaller nanoparticles penetrate the earlier levels of a thin film and increase the inter-particle energy transfer opportunities within the layers.

Red shift for CdTe nanoparticle thin films and suspensions during heating

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Journal of Nanoscience and Nanotechnology, 2008, 8, 2544-2548.

The work that we have conducted shows that temperature affects the wavelength of light emitted from CdTe nanoparticle clusters that are in a suspension or deposited into thin films via a layer-by-layer process. Compared with the stock suspension, the films show an initial photoluminescent shift, of *circa* 6-8nm to the red, when the particles are deposited. A shift of *circa* 6-8nm is also seen when the suspensions are first heated to 85°C from room temperature (20°C) having been stored in a fridge at 5°C. This shift is non-recoverable. With continual cycling from room temperature to 85°C the suspensions show a slight tendency for the emission to move increasingly to the red; whereas the films show no such tendency. In both cases, the range in emission is *ca* 10nm from the room temperature state to 80°C. The intensity of the emission from the film drops abruptly (*ca* 50% reduction) after one cycle of heating; in the suspension there is an initial increase (*ca* 3-5% increase) in intensity before it decays. We see that the shift towards the red has been attributed to energy transfer or a rearrangement of the packing of the particles in the thin films. After conducting analysis of the films using scanning probe microscopy we have determined that a change in the morphology is responsible for the permanent shift in emission wavelength

associated with prolonged heating. The influence of traps has not been ruled out, but the morphological change in the samples is very large and is likely to be the dominating mechanism affecting change for the red shift at room temperature.

Degradation of Photoluminescence in CdTe Nanoparticles Due to Cl₂ Contamination

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Advanced Materials Research, 2008, 31, 150-152.

Nanostructured CdTe is proving a popular material for a variety of modern applications. Here, we report photoluminescent deterioration of CdTe due to Cl₂ contamination. Cl₂ gas was bubbled through a 2ml suspension of thioglycolic acid capped CdTe nanoparticles whilst photoluminescence was monitored. With the addition of only 0.02ml of Cl₂ a loss of luminescence intensity was observed. Addition of 0.4ml of Cl₂ resulted in a 70% loss of luminescence intensity, a 21nm shift in wavelength, and a large narrowing of the full-width-at-half-maximum. Cl₂ attacks the Cd-S bond in the thiol capping layer of the nanoparticle, disrupting the passivation of the nanocrystal, and allowing the formation of non-radiative trap states. Smaller nanocrystals with a larger surface area to volume ratio are more heavily affected as is shown in the selective reduction of intensity from the smaller particles resulting in a narrower full-width-at-half-maximum and an apparent photoluminescence

shift. A decrease in overall intensity is seen due to the lower number of emitting particles.

Temperature shifted photoluminescence in CdTe nanocrystals

Hannah C. Gardner, Diego E. Gallardo, Cristina Bertoni, Steve Dunn

Proceedings of SPIE, Nanophotonics, 2006, 6195, 10.1117/12.661233.

If semiconductor quantum dots are to be incorporated into hetero-structural devices such as light emitting diodes it is important to understand the influences of the surrounding medium on the properties and particularly the photoluminescence of the nanocrystals. Here we investigate the temperature dependence of emission from CdTe quantum dots in aqueous solution with capping layers of thioglycolic acid. Results from quantum dots both held in suspension and deposited as thin films are shown. In both suspensions and thin film multilayers a reversible spectral shift to lower energy is seen with increasing temperature. This red shift of photoluminescence is thought to be the result of increased exciton carrier transfer between the quantum dots at higher temperatures and the thermal activation of emission from lower energy trap states. Both suspension and thin film devices also show a recoverable loss in photoluminescence intensity when the sample is heated. These changes are explained by the thermal activation of non-radiative surface traps. Finally, an irreversible loss in photoluminescence is reported in the CdTe thin film devices and to a lesser extent also in the quantum dot

suspensions. This observation is explained by the heat induced formation of agglomerates imaged by AFM analysis.

Influences of the Surrounding Materials on CdTe Nanoparticles within Self-Assembled Thin Films

H.C. Gardner, C. Bertoni, D.E. Gallardo, S. Dunn, M.G. Cain

Technical Proceedings of the 2007 NSTI Nanotechnology Conference and Trade Show, 2007, 1, 395.

We report the effects of temperature, radiation and inter-particle distance on thin films of CdTe nanoparticles. Temperature cycling thin films between 293K and 358K resulted in a shift of 10nm in photoluminescence wavelength and a loss in emission intensity. Thermally activated trap states cause the nanoparticles to emit at different wavelengths at different temperatures. Small amounts (1 hour) of UV irradiation enhance emission from the thin films leading to higher energy wavelengths and increased intensity. Longer (4 hour) exposure to UV radiation reverses these effects and causes deterioration of the luminescence. Increasing the number of layers in a thin film results in a red-shift in the photoluminescence spectra. The inter-particle distance is decreased increasing the opportunity for inter-particle energy transfer.