

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

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## ABSTRACT

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.

**Keywords:** CdTe, nanoparticle, photoluminescence, temperature, light-emitting

## 1 INTRODUCTION

The development of synthetic techniques to produce nanoparticulate semiconductor materials has been an interesting and vibrant area of research for the past decade. Recent advances in the control of synthesis of nanoparticles (NPs) have produced CdSe NPs from routes as diverse as growth in olive oil [1], via aqueous routes [2] and using organometallic synthetic techniques [3]. The commonality between these techniques is that highly luminescent particles with a narrow size range can be produced. The narrow size range equates to a small distribution of emitted energies thus the light emitted from the particles is centred on a single wavelength with a distribution that can be measured in a few tens of nms [1-3]. This increase in the availability of the NPs has led to the possibility of producing devices from the NPs for applications such as light conversion [4], biolabeling [5] and light emitting devices (LEDs) [6,7].

The advantage of using NPs in LEDs comes from their high quantum efficiency which unlike organic materials is not limited by spin statistics and can reach 100% [8-10]. The ability to produce a device that emits light over a range of wavelengths without having to use

different emitting centres also makes the generation of light emitting devices using NPs very attractive.

An effective technique of producing thin films of NPs is the layer-by-layer (LBL) method pioneered by Decher [11]. A substrate is alternatively immersed into solutions of oppositely charged polyelectrolytes. Electrostatic forces between the particles allow the build up of bi-layers. Advantages of LBL are that it is simple, versatile and can be easily automated. LBL also offers a high degree of experimenter control and produces quality thin films [12] the technique has previously been used with CdS NPs [13].

If NPs are to be incorporated into hetero-structural devices it is important to consider the effects of the surrounding mediums. Changes to the properties of a NP or its surrounding medium are readily detected in its photoluminescence (PL) spectra. Research has been conducted into the effects of the thiol capping layer [14] the solvent molecules [15] and the temperature of the NPs.

Biju et al [16] investigated the effects of temperature within the range 298-353K on CdSe NP clusters. Here we expand their work to look at similar effects in CdTe NPs deposited as thin films. We then continue our investigation into the influences of post-preparative treatments by looking at the effects of UV irradiation and inter-particle distance.

## 2 RESULTS AND DISCUSSION

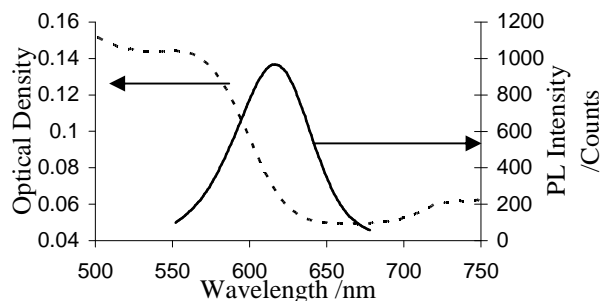


Figure 1: PL\_\_\_ and absorbance ... spectra of a typical CdTe NP suspension

Typical photoluminescence (PL) and absorption spectra of a NP suspension are shown in Figure 1. The absorbance spectra shows a featureless curve. The PL

spectra has a full width at half maximum (FWHM) of 53nm. Suggesting that the suspension consists of NPs of various sizes and is not truly monodisperse [17]. In Figure 1 the maximum of the PL peak is 616nm, this value changes with different suspensions and in all cases the shift for thin films is taken against the base PL spectra for that suspension.

## 2.1 Temperature

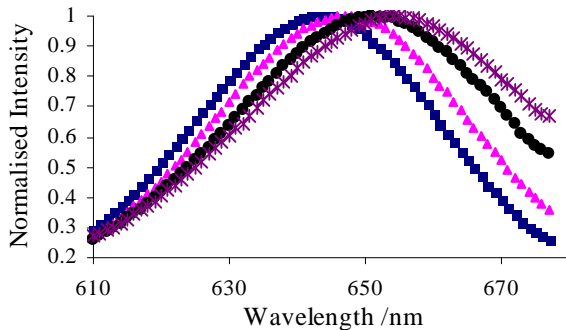


Figure 2: PL spectra of a thin film at various temperatures  
 ■ = 298K, ▲ = 314K, ● = 337K and x = 358K

Heating the thin films, from 293K to 358K (25°C to 80°C), produced a change in the wavelength and intensity of the PL spectra. The wavelength of the maximum moved from 644nm (at 293K) to 654nm (at 358K), was linear and can be seen in Figure 2. The intensity of the PL decreased with increasing temperature. At 358K the luminescence detected was only 29.5% of its original value. These trends reversed on cooling the sample. Figure 3 shows the effects of repeatedly heating and cooling a thin film. The peak maximum cycles between ~644nm at 293K and ~654nm at 358K showing a 10nm reversible shift

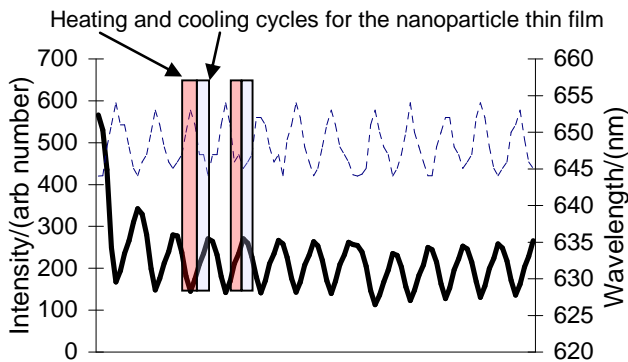


Figure 3: Wavelength ... and intensity \_\_\_ changes when a thin film is repeatedly heated and cooled

These results agree with those of Biju [16] who found a reversible 8nm shift for CdSe NPs when cycled between 298 and 353K. The reversible changes are consistent with emission from thermally activated trap states. Emission

from trap states produces lower energy luminescence and is accompanied by a loss of luminescence intensity due to non-radiative recombination [18].

To determine the cause of the reduced intensity of emission, SPM images of thin film samples were taken before and after heat treatment. Figure 4 shows an unheated sample and a sample heated for 1 hour at 333K. It is surprising to note that the temperature treatment has formed aggregates within the sample. PL and absorption spectra of the thin films were recorded both before and after heating the only significant difference between the spectra (not shown) was a loss of PL intensity to 44% of its original value. This suggests that a proportion of the NP population has been affected by the increase in temperature with consequent destructive effects of the particle emission properties. Figure 4 suggests that the NPs become incorporated into agglomerates. The increase in size means that they are no longer quantum confined and consequently do not emit at the wavelength of investigation. When deposited as thin film multilayers the CdTe NPs are in close proximity to one another and prolonged heating of the sample produces agglomeration. However, this is limited as once this initial stage of agglomeration has taken place no additional agglomeration can occur. The remaining NPs are now so distant that their inter-particle distances are fixed. Therefore, we would expect to see a large loss of luminescence in the first couple of heating cycles when the initial agglomeration takes place followed by a stability of luminescence intensity as no subsequent agglomeration can occur. This is found in Figure 3, a loss of luminescence occurs in the first two heating cycles followed by a stability of the low temperature luminescence. CdTe NPs in dilute suspensions have a much larger inter-particle distance than in thin films.

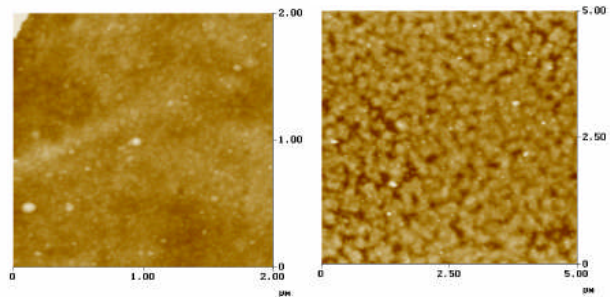


Figure 4: SPM images of the surface of a thin film. The left image, with a z-range of 25nm, is before heating and the right image, with a z-range of 75nm, after heating to 80°C.

## 2.2 Radiation

UV radiation is known to enhance the PL efficiency of NPs [14, 19]. Thin films were exposed to increasing periods of UV (365nm) light. Exposure for a short period of radiation resulted in an increase in luminescence intensity and a blue shift in the spectral peak. Figure 5 shows PL spectra of a thin film after different UV exposure

times. After 1 hour of exposure a 42% increase in intensity is seen and the peak maximum shifts 16nm to higher energy wavelengths. Exposure to longer periods of radiation however, drastically decreased the luminescence intensity and caused a red shift. Figure 5 shows a 51% loss and a red shift of 7nm after 4 hours of exposure. Small amounts of radiation serve to anneal or passivate surface traps on the NPs whereas further exposure to radiation creates trap states.

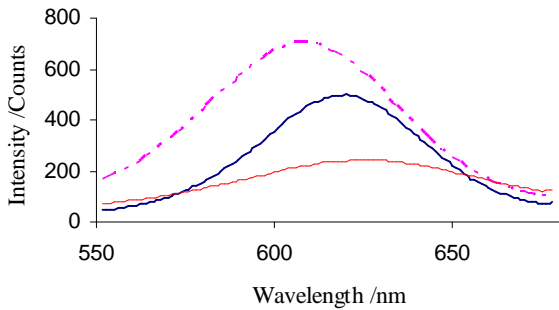


Figure 5: PL spectra of thin films after various UV exposure times \_\_\_ = start, \_ . \_ . = after 1 hour and \_ \_ \_ = after 4 hours

### 2.3 Inter-particle Distance

In 1994 Vossmeier et al [20] reported that the spectral position of the absorption band in CdS nanoclusters shifted to lower energy when a suspension was deposited as a thin film. In a thin film the inter-particle distance is in the order of a few Å. Vossmeier et al explain the shift in spectra as being due to inter-particle interaction. In previous work [21] we reported a 6nm red shift when a suspension of CdTe NPs was deposited as a thin film. Constraints in the substrate and binding polymer hold NPs closer together in the thin film than in suspension and facilitate energy transfer from small to large NPs resulting in an apparent red shift.

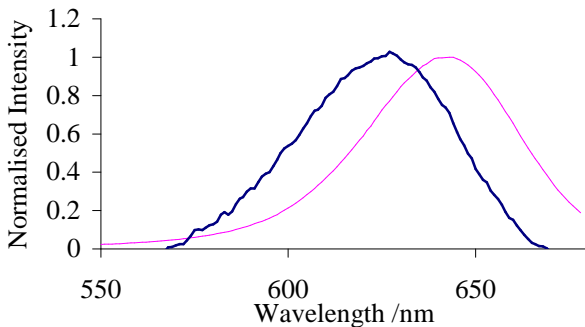


Figure 6: PL spectra of \_\_\_ single layer and \_ . \_ 10 layer thin films

Figure 6 shows an extension of the same effect. 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 NPs are within a few Angstrom of each other in two dimensions, in multilayer thin films NPs are within a few Angstrom of each other in three dimensions.

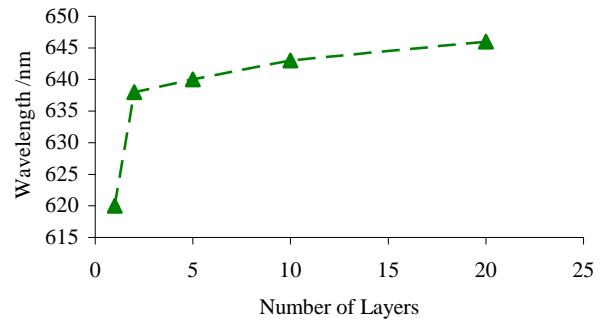


Figure 7: Wavelength of PL spectra peak maximum with thin films of various thicknesses

Figure 7 shows the change in wavelength of emission for thin films with different numbers of layers. The initial increase is due to a change from 2d to 3d interaction. The more gradual increase is due to space filling within the layers. The CdTe NPs used in this report have an average size of ~4nm but within the suspension there is size variation. PL spectra of the suspension typically have a full width at half maximum of ~50nm (as can be seen in Figure 1) a consequence of this size dispersion. Each layer deposited adds NPs of all sizes but subsequent depositions allow smaller NPs to penetrate 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 energy transfer range. Energy is transferred from smaller to larger NPs [22] resulting in lower energy luminescence. Figure 8 shows a proposed mechanism for the space filling deposition. Support for this mechanism comes from a study by Abu-Sharkh [23] 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.

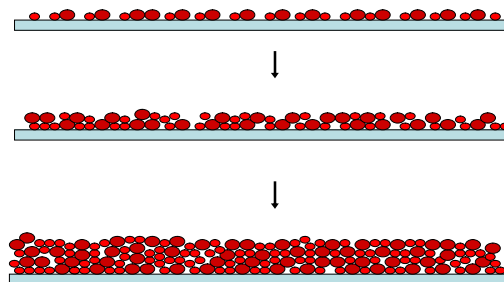


Figure 8: Proposed space filling mechanism, NPs of all sizes are deposited and as the number of layers increases smaller particles fill vacancies in the lower packing levels

### 3 CONCLUSION

Heating and cooling thin films of CdTe NPs within the range 293-358K produces a reversible PL wavelength shift and a reversible loss in PL intensity. These trends can be attributed to the presence on thermally activated low energy trap states. A non-reversible PL intensity loss is also observed and is due to the formation of non-radiative agglomerates.

Small amounts of UV irradiation increase the emission energy and intensity of a thin film of CdTe NPs by annealing out surface trap states. Larger amounts of radiation however, cause the formation of further trap states reducing the efficiency of the thin film.

A red shift in PL spectra has been found as a suspension is deposited as a thin film and again as the number of bi-layers in the thin film is increased. This shift to lower energy is caused by greater inter-particle interaction where energy is transferred from small to large particles and emission takes place at longer wavelengths. The increased inter-particle interaction is a result of a space-filling deposition mechanism where smaller NPs penetrate existing layers of the thin film.

### 4 EXPERIMENTAL

All the NPs 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 NPs were synthesized [14] in aqueous solution and were coated with a capping layer of thioglycolic acid (TGA). The stability of the NPs is high and the suspensions can be stored for months without degradation [14].

Thin films of CdTe NPs were deposited onto cleaned glass substrates using a LBL technique [11]. Since the CdTe NPs used are capped with (TGA) they have a negatively charged surface and require a cationic polymer. Substrates are dipped into a NP suspension for 20 minutes washed with deionised water for 2 minutes and then dipped into a polydiallyldimethylammonium chloride (PDDA) solution for a further 20 minutes. For the PDDA solution, PDDA 20w% in water (Mw 200,000 - 350,000) was obtained from Aldrich and was dissolved in a 0.2M NaCl buffer to a concentration of 5mg/ml before use. 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. The thin films used in this report all consist of 10 layers CdTe.

Absorbance and emission spectra were recorded using a Perkin Elmer lambda 7 UV/Vis spectrometer and a Varian Cary Eclipse spectrophotometer using an excitation beam with a wavelength of 365nm. SPM images were recorded on a Digital Instruments Dimension 3000 in tapping mode operation.

During the temperature experiments thin films were heated gradually from 293K to 358K and cooled in the

same manner. Heating was conducted whilst the sample was inside the spectrometer using a closed loop peltier stage. All temperature changes were maintained for at least 2 minutes before spectrometer measurement to allow the samples to adjust to the new conditions.

During the radiation experiments thin films were kept 25cm away from a UVP Blak-ray 100watt UV lamp emitting at 365nm for the required length of time.

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