Temperature Stability of Elastomeric Colloidal Quantum Dot Colour Converter

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Abstract— **The effect of temperature on the photoluminescent properties of an elastomeric colloidal quantum dot composite is presented. Results demonstrate that embedding CQDs in a composite increases the thermal stability and that thermal degradation is an issue above 100°C and this independently of other photo-induced or oxygen-related phenomena.**

I. INTRODUCTION

Knowing the optical performance of mechanically flexible colour converting materials under different conditions are needed to unlock novel applications in wearable displays, lighting and health technology. In this context, we study the heat resistance of the luminescence properties of light-emitting elastomeric materials made of polydimethylsiloxane (PDMS) and colloidal quantum dots (CQDs).

CQDs have become a popular material for optoelectronic applications in recent years due to their highly tuneable emission wavelength, colour purity and high luminescent efficiency [1]. They can be combined with efficient blue or UV emitting GaN-based light emitting diodes (LEDs) to obtain, through the process of colour conversion, narrow emission wavelengths in the visible. For example in this way, red and green CQD colour converters can be used in conjunction with a blue LED to produce a white LED with a warmer colour rendering index (i.e. a better light quality) than would be obtained with a yellow phosphor [1][2]. In turn, CQDs are found in, or explored for, different applications including displays [1], solid state lighting [3], and visible light communications [4].

CQDs are solution processable and can therefore be incorporated within so-called matrix materials to create composite materials with additional and/or improved properties. For example, polymethyl methacrylate and polyvinyl chloride can be used as matrix materials to protect CQDs from environmental factors [5]. However, these materials are rigid and inflexible limiting their usability in wearable applications. On the other hand, elastomeric materials such as PDMS and polyurethane can enable flexibility and even conformability, which in turn broadens the scope for colour converting composites, e.g. allowing their use in biomedical applications [5][6][7].

Despite their many desirable characteristics CQDs are susceptible to degradation when exposed to heat, water and oxygen [8]. Photo-oxidation is known to corrode CQDs, leading to a severe reduction in the luminescence efficiency and a blue shift of the emission wavelength. This process can be mitigated or even eliminated by preventing oxygen and water molecules to reach the CQDs. Therefore a composite format where the matrix material offers barrier properties to oxygen and/or water molecules certainly helps. Still, purely thermal degradation is also possible through direct effects on the CQDs or via the matrix material. In many applications CQD colour converting composites are to be placed in direct contact with a light source to produce the required colour conversion, and they have to remain stable under relatively high operating temperatures for the lifetime of the device. Understanding limitations and finding ways to circumvent them is therefore critical for CQD device applications.

In this work, we study the effect of heat, independently of the photooxidation process, on the luminescent properties of PDMS/CQD colour converting composites. For this, composite samples are annealed under vacuum at different temperatures and duration, and their photoluminescence characteristics are compared to non-annealed samples. Samples of neat CQDs are also measured to assess the effect of the PDMS matrix on the overall CQD stability.

II. COLOUR-CONVERTER FABRICATION

A. CQD/PDMS composites

The colour converters were fabricated using commercial CQD/ toluene solution from Cytodiagnostics (CdSeS/ZnS 575 nm intrinsic wavelength, 50 mg/ml concentration oleic acid ligands). The CQDs are added to a 10:1 PDMS (Sylgard 184) at weight ratios of 0.45 % and 0.25 %. The CQDs are then stirred in until there is a uniform dispersion within the PDMS. Once stirred the CQD/polymer mixture is poured into a petri dish and cured at 80 °C for 6 hours. Individual samples are cut from the same composite and have a thickness of 0.8 mm. There is a CQD concentration limit in the composite fabrication as there is a point where the PDMS can no longer cross-link and will not cure.

B. Neat samples

Neat samples consisting of a film of dense CQDs were made by spin coating CQD solution at a concentration of 22.5 mg/ml and 12.5 mg/ml onto an 18 x18 mm glass cover slip and spin coated at 500 rpm for 40 s to produce a thin film.

III. EXPERIMENTAL METHODS

A. Thermal treating

Different samples were heated in a vacuum oven (Memmert VO200) under a 50-mbar vacuum and a range of temperatures: 125°C, 150°C and 200°C. Each concentration of CQD/PDMS composite and neat film were temperature treated for a duration of 4 or 8 hours to determine the effect of prolonged heating on the luminescent output of the CQDs.
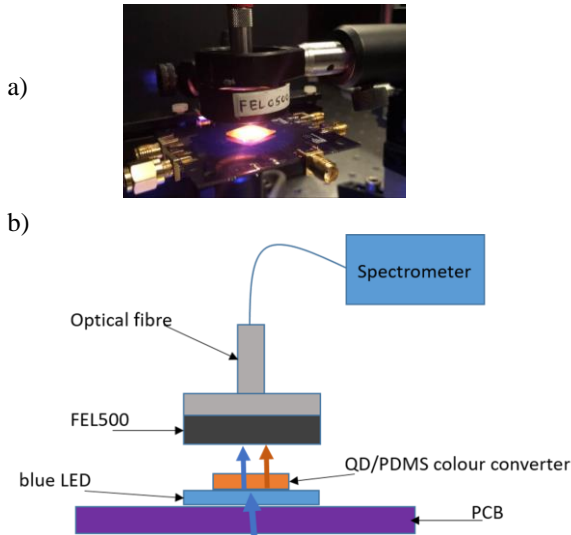
B. Characterisation of Samples

Fig. 1: a)µLED with 0.45 % QD/PDMS colour converter on top with optical fibre collecting photoluminescent spectrum b) schematic of optical set-up

The pump source used to characterize all the samples was a 45x45 µm² flip-chip GaN LED (emission through a sapphire substrate as in [9], which was driven at 50 mA producing an output power of 1 mW for an emission peak at 444 nm. The LED was wire bonded onto a PCB with SMA connectors as can be seen in Fig 1a. The samples were placed directly on the sapphire window of the LED in a "converter on top" configuration, shown in Fig. 1a. The pump light was filtered using a long pass filter (FEL500) from Thorlabs, and the spectral irradiance data was collected using a fibre-coupled CCD spectrometer (Ocean Optics, USB 4000). This set-up was calibrated using a tungsten halogen lamp (Ocean Optics HL-2000) to then directly aquire the spectral irradiance of the samples (CQD/PDMS composites and the neat thin films). Fig. 1b shows a schematic of the experimental set up, where the sample is placed directly onto the µLED.

IV.   RESULTS & DISCUSSION

A. Effect of CQD concentration

Fig 2. shows the spectral irradiance results for the non – annealed CQD/PDMS composites (the room temperature samples) and for the same types of composites but annealed at 200°C for 4 hours. The emission peak of the 0.45% room temperature sample is 589 nm, with a maximum spectral irradiance value of 1.09 µW/cm²/nm. It is 587 nm with a maximum spectral irradiance value of 0.78 µW/cm²/nm 0.25 wt% sample. The higher irradiance of the 0.45 wt% composite sample is simply because more of the LED pump light is colour converted due to the higher amount of CQDs, hence the higher optical density at the pump wavelength. Similarly, the higher optical density leads to a red-shifted emission by 2 nm due to the phenomenon of self-absorption [4]. To maximise the spectral output for a device at a constant composite thickness, a higher concentration of CQDs is beneficial. However, as noted in II.A, there is a limit of the concentration of CQDs that can be incorporated into the PDMS before cross-linking is disrupted [5].
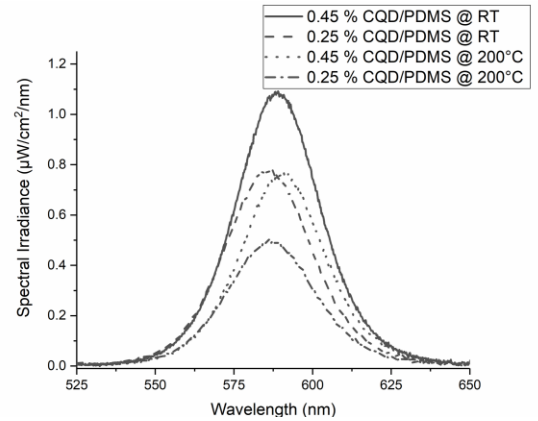
B. Effect of increasing temperature

Fig. 2 Spectral Irradiance as a function of wavelength for a comparison of the different weight ratios of the composites at two different temperatures temperature treated.
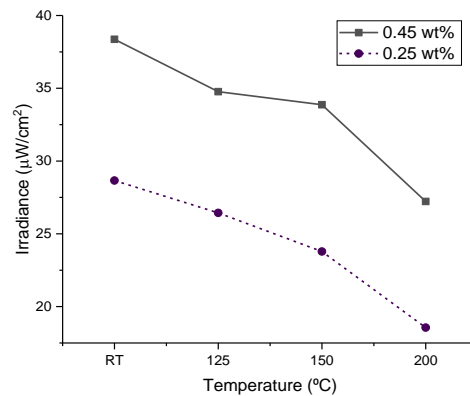

Fig. 3 Peak irradiance versus temperature of treatment (for 4 hours) for 2 concentrations of the CQD/PDMS composites.

The overall effect of increasing temperature on the samples is a reduction in the irradiance as can be seen in Fig.3 and is shown in more details in Fig 4. While the degradation
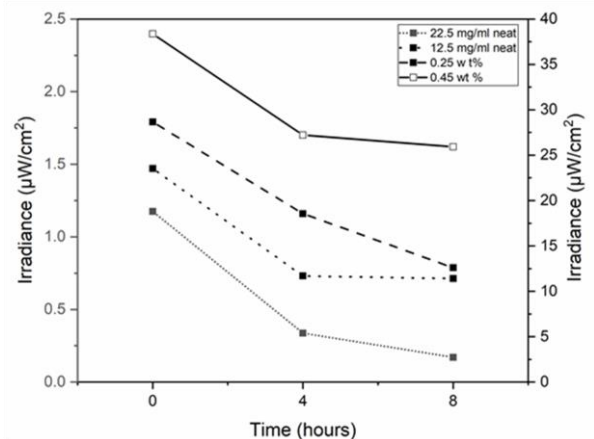

Fig. 4 Two different methods of preparing samples a) QD/PDMS composite b) neat thin films at two different concentrations temperature treated at 200°C show the effect of duration heated on the QD composites and films.

due to temperature leads to a decrease in the irradiance, hence a reduction in the conversion efficiency, the peak emission wavelength stays identical. This is unlike the oxidation process and therefore indicates that the irradiance decrease can be attributed solely to thermal degradation (although it should be noted that the study here is limited to 8 hours and

effect on wavelength may appear for longer treatment duration). As the temperature of the QDs increases, the heat, thermally quenches the core of the QD, reducing the luminescent properties of the sample. The decrease in irradiance is likely due to the increased thermal activation energy which would active the trap states and also increase non radiative Auger recombination [10]. The degradation increases with temperature, more dramatically at 200°C. While this is still under investigation, we expect no significant degradation for temperature at or below 100°C.

The effect of temperature on the CQD/PDMS composites was less dramatic than for the neat films. The largest reduction in irradiance was from the 22.5 mg/ml neat film which had been temperature treated at 200°C for 8 hours and had an 85 % decrease in irradiance when compared to its untreated counterpart. In comparison to this the 0.45 % composite only had a reduction in irradiance of 32 %. This indicates that the matrix is beneficial in helping to spread the heat load.

C. Effect of temperature with increasing time

To evaluate the effect of exposure duration on thermal stability, one temperature condition was assessed as shown in Fig. 4. As the time the QDs were heated increased, the irradiance decreased. When comparing the sample which had been in the oven for 4 hours compared to 8 hours, the percentage decrease in irradiance from the room temperature values was 29 % and 32 % respectively for the 0.45 % composite. When the weight ratio of QDs is lower the effect of prolonged heat exposure is increased from a 32% decrease at an 8-hour duration to a 56% decrease in irradiance for the 0.25% composite. When this is compared to the neat film samples the effect on irradiance degradation is larger at an 85% reduction from the room temperature value for the 0.45 % composite.

D. Effect of thermal stability on wavelength

It has been reported that as the temperature increases and thermal quenching of the QDs a blue shift of the wavelength can occur [10]. Fig. 5 shows the trend in wavelength shift as the duration of thermal treating increases. There is a small shift in the wavelength towards the blue end of the spectrum. It has been reported that a significant blue-shift in wavelength can occur when thermal quenching occurs due to photocorrosion of the QD core, however, due to the relatively short duration of thermal treating the effect does not appear significant within the scope of this report and further investigation would be required.
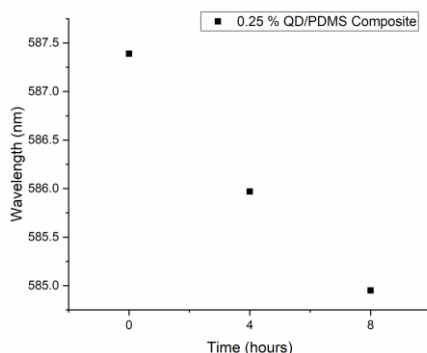

Fig. 5 Duration of the sample heated as a function of wavelength for the lower concentration of QD/PDMS composite, showing a blue shift in wavelength as heating duration increases.

V. CONCLUSION

In this paper we have studied the effect of heat on the stability of the photoluminescence properties of an elastomeric CQD composite. Results showed that embedding CQDs in a composite increases the thermal stability of CQDs when comparing them to a neat film. It also demonstrated that thermal degradation is an issue when the temperature is above 100°C, and independently of other photo-induced or oxygen-related phenomena such as photooxidation. The effect of the irreversible thermally induced degradation was compounded with the duration and magnitude of heating the QDs experienced. Overall, the results offer useful information for engineering and integrating mechanically flexible colour converters into practical device and systems.

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