White Light Emission Characteristics of Polymer-encapsulated CdSe Nanocrystal Films

Jonathan D. Gosnell, Sandra J. Rosenthal, and Sharon M. Weiss

Abstract—A white, cadmium selenide (CdSe) nanocrystal-based phosphor light-emitting diode (LED) was fabricated in this work using a commercial ultraviolet (UV) LED topped with a thin film of nanocrystals encapsulated in a polymer. A range of film thicknesses were fabricated and different wavelength LEDs were employed to analyze their influences on the emission properties of the phosphor LEDs. The absorbance and emission intensity of light passing through the films were optimized without compromising the excellent inherent color quality of the white-light nanocrystals. These results indicate a potential to improve the color quality and lower the scattering losses found in current white LEDs based on much larger, micron-sized phosphors.

Index Terms—Nanotechnology, Light-emitting diodes, Thin film devices, Optics, Photoluminescence, Optical films.

I. INTRODUCTION

Research into solid state lighting devices has become a priority in recent years due to the capability of light emitting diodes (LEDs) to achieve higher efficiency and longer lifetimes than current lighting technologies. While monochromatic LEDs have become commonplace in traffic signals, signage, and indicator lights, commercial white LEDs struggle with a tradeoff between high efficiency, excellent color balance, and high brightness [1]. This issue, among other problems, has hindered the transition to solid state lighting devices as envisioned by the U.S. Department of Energy [2].

An alternative to the YAG:Ce³⁺ phosphor [3] was recently found in ultra-small cadmium selenide (CdSe) nanocrystals with an approximate diameter of 1.5 nm [4]. These nanocrystals absorb blue and ultraviolet (UV) light and emit a well-balanced, broadband white light with International Commission on Illumination (CIE) chromaticity coordinates of (0.324, 0.322) and a color rendering index (CRI) of 93 [5]. Advantages of using the single-size CdSe nanocrystals for white LEDs compared to using multiple sizes of nanocrystals that each emit a different color in the visible spectrum [6] include a lower self-absorption due to a large Stokes shift of ~45 nm and simpler, more cost-effective device fabrication that does not require active color balancing techniques. Compared to white LEDs that employ multiple phosphors [7], the use of white-light CdSe nanocrystals enables significantly reduced scattering losses due to a scattering cross-section that is nine orders of magnitude smaller than the phosphors used in white LEDs [8].

In this study, the emission characteristics of polymer encapsulated white-light CdSe nanocrystal films are investigated in a configuration mimicking a typical phosphor LED. Previous work has shown that the thickness of a film with encapsulated nanocrystals or phosphors can have a significant effect on emission intensity [9-11] and color quality [11-13]. Hence, this work experimentally analyzes the influence of film thickness on the absorbance, emission intensity, and color qualities (CRI, CIE coordinates) of the white CdSe phosphor LED. These findings indicate that the absorbance and emission intensity can be optimized without compromising the excellent color of the CdSe nanocrystals.

II. EXPERIMENT

A. Sample Preparation

The CdSe nanocrystals used in this work were synthesized and purified according to previously reported methods [14], and solvated in toluene. The white-light emitting nanocrystals were mixed with a clear biphenylperfluorocyclobutyl polymer (BP-PFCB) in solution, dropcast onto glass slides, and cured at 100°C until hardened. Based on prior nanocrystal loading experiments in BP-PFCB [5], a 10% w/w loading was chosen for this work. A large range of film thicknesses from approximately 5 - 1200 µm was produced by using different volumes of dropcast solution on the glass slides.

B. Thickness, Absorbance, and Emission Measurements

Film thickness measurements were performed using a Veeco DekTak 150 profilometer and a digital micrometer. Absorbance measurements were carried out on a Varian Cary 5000 UV-VIS spectrophotometer. Photoluminescence of the films was excited via UV LEDs or the UV lines (350-355 nm) of a Coherent Innova 70C Spectrum Ar-Kr laser, and was measured with a Labsphere SLMS-0400 integrating sphere and an ISS PC1 photon counting spectrofluorimeter.

III. RESULTS

A. Absorbance

Fig. 1 shows the wavelength-dependent absorbance of several CdSe nanocrystal films. As expected, the absorbance increases as the film thickness increases. Moreover, for wavelengths below 400 nm, the absorbance is nearly constant for a given film thickness. The fraction of light absorbed at the
band-edge absorption wavelength is plotted in the inset of Fig. 1 as a function of film thickness. In accordance with the Beer-Lambert Law, the absorbance increases linearly with film thickness until it reaches ~100%, which occurs for thicknesses above 150 µm. Hence, it is expected that for CdSe phosphor LEDs, the thickness need not be more than ~150 µm.

regions of the spectrum can become significant. For example, the ~400 µm film absorbed 5% of the incident light at 550 nm while the ~1200 µm film absorbed nearly 50%.

![Fig. 1. The absorbance of nanocrystal-polymer films as a function of wavelength at a few film thicknesses, with the arrow pointing in the direction of increasing film thickness (21 µm, 43 µm, 68 µm, 143 µm, 220 µm, and 418 µm). The inset shows the absorption (in percent) at the band-edge absorption wavelength (approximately 415 nm) as a function of film thickness.](image1)

**B. Photoluminescence**

The nanocrystal films were first excited using UV laser lines (350-355 nm) to analyze their intrinsic light emission properties without confounding excitation light. As seen in Fig. 2, the thinnest films had a mostly balanced but weaker emission spectrum overall than the thicker samples. As the thickness is increased, more blue light gets re-absorbed by the film until, with the thickest film, the emission becomes somewhat yellow. Additionally, the emission intensity begins to decrease with the very thick films, which is also attributed to re-absorption by the nanocrystals in the film.

![Fig. 2. The photoluminescence spectra of nanocrystal-polymer films excited by a UV laser at a few different film thicknesses (21 µm - solid, 61 µm - dotted, 143 µm - dashed, 220 µm - solid/bold/red, 418 µm - dotted/bold/red, and 1212 µm - dashed/bold/red). The two spikes near 700 nm are the second-order peaks from the two main laser lines.](image2)

This effect is more clear in Fig. 3, which shows the normalized luminous flux as a function of thickness. The data indicates that the largest emission intensity was achieved with films in the 150-200 µm range. Thus, for films below this thickness, the emission intensity and absorbance both increase linearly with thickness. However, due to self-absorption, the emission intensity decreases above 200 µm. Though self-absorption for this material is lower than for the larger, single color nanocrystals, when they are used at high concentrations and in very thick films the absorption in the yellow and red

![Fig. 3. The normalized luminous flux of nanocrystal-polymer films excited by a UV laser as a function of film thickness.](image3)

Since these films are designed to be used as the phosphor layer of a white LED, any excitation light that leaks through the film must be considered in the overall device emission properties. Thus, the photoluminescence of the same films was then measured using UV LEDs to determine which LED resulted in the optimal emission properties. Fig. 4 displays the emission intensity as a function of wavelength for a few film thicknesses using a 365 nm LED for excitation, as well as a photograph of a CdSe nanocrystal-polymer film excited with a UV LED.

![Fig. 4. The photoluminescence spectra of nanocrystal-polymer films excited by a 365 nm LED at a few different film thicknesses (21 µm - solid, 61 µm - dotted, 143 µm - dashed, 220 µm - solid/bold/red, 418 µm - dotted/bold/red, and 1212 µm - dashed/bold/red). The emission near 400 nm is a result of LED excitation light that has either reflected off of or leaked out the side of the glass slide. The inset is a photograph of a UV LED exciting a CdSe nanocrystal-polymer film.](image4)

The luminous flux of the films, excited by different wavelength LEDs and normalized to the output power of the LED alone, can be seen in Table I. The films were placed on top of the LEDs to simulate a typical device configuration. As was seen with the laser excitation, the emission intensity increases linearly with thickness and then drops off for larger thicknesses. When compared with the emission data using laser excitation, the peak intensity appears to shift to slightly thinner films when using 365 nm and 385 nm LEDs. This is likely due to LED excitation light that is not absorbed by the film and thus does not get converted by the nanocrystals which leads to a higher luminous flux than the films that absorb all of the excitation light. The effect is even more apparent using a 405 nm LED for excitation, as the highest emission intensity occurs for films < 50 µm thick.
The luminous flux (in lumens) of nano crystal phosphor LEDs. Table I also shows the CIE coordinates and CRI for the range of film thicknesses when excited with the various UV LEDs. As expected, as the wavelength of the LED is increased for the same thickness, the emission becomes more blue as the excitation light passing through the films is at longer wavelengths. Also, as the film thickness is increased for the same wavelength LED, the emission changes from blue-white to pure white and then yellowish-white due to self-absorption.

The best device characteristics resulted from films in the 60-140 µm range when excited with a 365 nm or 385 nm LED. While the luminous efficacy of these devices is near 1 lm/W, increases in the nanocrystal quantum yield and UV LED efficiency (both typically ~5-10% in these measurements) could significantly improve the efficiency of these devices. Although not addressed in this work, photo stability is an important consideration for the encapsulated nanocrystal films. Non-shelled CdSe nanocrystals have been shown to degrade via the photo-oxidation of surface selenium atoms [15] unless the nanocrystals are kept in an inert atmosphere [16]. Thus, it will be important for future devices to be fabricated under inert conditions and for the nanolight LEDs to be packaged in a material that is impermeable to oxygen.

### IV. CONCLUSION

The thickness of white CdSe nanocrystal phosphor films and choice of LED excitation wavelength play significant roles in the overall power and color quality of nanocrystal phosphor LEDs. Films that are too thin do not absorb the majority of the LED excitation light, compromising the emitted white light power and unbalancing the white light spectrum. Films that are too thick suffer from nanocrystal self-absorption, which compromises both the color quality and emitted power. It was found that the nanocrystal film absorbance approached 100% and the emission intensity was maximized for film thicknesses near 150 µm when excited via 365 nm and 385 nm LEDs. While these films exhibited good white light color quality (CRI > 80, CIE coordinates near pure white), slightly thinner films resulted in an emission color even closer to pure white light. While the overall trends will remain the same, ongoing research efforts to increase the efficiency may result in different optimal film thicknesses or excitation LED wavelengths. For example, a higher w/w concentration of CdSe in BP-PFCE polymer could be used to improve the emission intensity. In doing this, the optimal thickness would likely change due to increased absorbance at the same thickness as well as increased re-absorption of the nanocrystal emission, altering the color characteristics. Further increases in the efficiency of UV LEDs, in addition to the quantum efficiency of white-light CdSe nanocrystals, could result in higher quality solid state lighting devices.

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### REFERENCES


