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HIGH TEMPERATURE ZnSe:Mn/ZnS NANOPHOSPHORS WITH VERY HIGH QUANTUM EFFICIENCY FOR WHITE LEDs

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**HIGH TEMPERATURE ZnSe:Mn/ZnS NANOPHOSPHORS
WITH VERY HIGH QUANTUM EFFICIENCY FOR WHITE
LEDs**

by

BRIAN AKIRA AKINS

**B.S. ELECTRICAL ENGINEERING, UNIVERSITY OF NEW
MEXICO, 2009**

THESIS

Submitted in Partial Fulfillment of the
Requirements for the Degree of

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HIGH TEMPERATURE ZnSe:Mn/ZnS NANOPHOSPHORS WITH VERY HIGH QUANTUM EFFICIENCY FOR WHITE LEDs

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B.S. Electrical Engineering, University of New Mexico, 2009

M.S. Electrical Engineering, University of New Mexico, 2013

ABSTRACT

Efficient white LEDs are rapidly taking over many lighting and display applications, because of their improved color rendering and low power requirements. They are attractive replacements for traditional lighting from the point of view of both human perception and energy efficiency. Currently, the most efficient and common LED design consists of a blue LED and a yellow phosphor, which in conjunction produce white light. The LED phosphor is a yellow phosphor made of yttrium aluminum garnet doped with cerium (YAG:Ce). While it does strongly absorb blue light, its external quantum efficiency is only 75% under blue LED excitation at room temperature and it lacks sufficient red spectral content, resulting in cool white light under blue LED excitation.

This thesis investigates doped nanophosphors that have unique high temperature emission well above room temperature. A novel technique for colloidal synthesis of ZnSe:Mn/ZnS nanocrystals (NCs) is also presented here, using a growth doping technique that exhibits a bright emission peak at 587 nm with excellent thermal behavior and record high quantum efficiency. The 587 nm peak from the Mn dopant exhibits a record high

quantum efficiency of 90% with 418 nm excitation light, and has improved stability over previously reported synthesis due to the addition of a ZnS shell.

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LIST OF PENDING PATENT APPLICATIONS

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Chapter 1

Introduction

1.1. The Need for Daylight Quality Light Emitting Diodes (LEDs)

Starting in the late 1960's, LEDs began to dramatically improve their output intensity measured in lumens/LED at a rate that rivaled a similar improvement also seen in integrated circuits. This phenomenon was noticed by Roland Haitz of Agilent Technologies and was presented during a Strategies in Light conference in 2000 and coined Haitz's Law, shown in Figure 1.1.1. It states that LED lumen output per package increases by a factor of 20 every 10 years. Since then, LEDs have been predicted to replace all traditional lighting, which is estimated to consume 6.5% of total energy consumption [Haitz 2011].

Figure 1.1.1: Graph of LED flux/package vs. time, demonstrating Haitz's law [Steigerwald 2002].

In addition to energy arguments for daylight quality LEDs, there are health-related aspects of the drive to replace fluorescent lighting. The most obvious is the elimination of a bulb, which can easily break and expose the occupants of the room to the toxic mercury contained within the bulb, and requires special cleanup and disposal due to the presence

of mercury. A second point is that nocturnal light exposure has been linked to many pathological conditions, such as breast cancer [Davis 2001], colorectal cancer [Schernhammer 2003], cardiovascular disease, depression and anxiety disorders [Knutsson 2003], obesity, and type 2 diabetes [Giovanni 2003], [Kroenke 2007]. A third point is that human body clocks are highly sensitive to short-wavelength blue light in the wavelength range of 460 – 480 nm, as was discovered in 2001 [Brainard 2001], [Thapan 2001]. Light sources that are not tailored to emit a spectrum that more closely resembles the solar spectrum, as shown in Figure 1.1.2, have been found to cause nocturnal melatonin suppression [Kayumov 2005]. Many of the adverse health effects listed above, thought to be due to nocturnal light exposure, have been associated with melatonin suppression [Skene 2006].

Figure 1.1.2: Incident solar power spectrum upon the Earth vs. photon energy and wavelength, above the atmosphere and at sea level [Schubert 2006].

Light is known to be a potent regulator of human circadian and neuroendocrine physiology, with different photoreceptive systems mediating visual and neurobehavioral responses. Future lighting strategies will need to provide illumination for human neurobehavioral regulation as well as vision and vision comfort in both public and private buildings. For example, the aerospace community is interested in using lighting to support vision, circadian regulation, and alertness of astronauts in advanced human environments such as the International Space Station [Gronfier 2007].

It is now a well-established fact that very low levels of blue light are superior to high intense white light at shifting circadian rhythms, regulating melatonin levels, and producing a subjective alert response. Blocking or selectively filtering short-wavelength light has been shown to prevent nocturnal melatonin suppression in humans and to attenuate overall disruption of circadian endocrine rhythms and clock gene expression in rats.

1.2. Potential High Efficiency Low-Cost White LED Designs

Three methods have been devised in order to generate white light from a blue LED. The first method involves using three LEDs of the primary colors (red, green, and blue) in combination to generate white light; this device is called a RGB LED. It has the unique property of the ability to change its spectrum on demand by varying the output intensity of the red, green, or blue LED, or a combination of two, or all three at once. Although this method has the greatest control over the spectrum, it also has the lowest energy efficiency, because of the poor conversion efficiency of primarily the green, but also the red LED.

The second method uses an ultraviolet (UV) LED in combination with three phosphors, one to convert UV light to red light, one to convert UV light to green light, and one to convert UV light to blue light. This system will have a fixed emission spectrum, because it is determined by the ratios of the phosphors used and cannot be adjusted after fabrication of the LED white light source. In addition, it suffers from the second lowest energy efficiency, because it loses energy via Stokes shift losses due to the high energy UV light being down-converted to the lower energy red, green, and blue light.

Finally, the third system is called a binary complementary LED, which has been commercially mass produced and already exists in nearly all white LEDs. This is because of two important factors that are present in the binary complementary LED system. The first one is that this system has the highest energy efficiency, because it uses blue LEDs with a yellow phosphor and the blue LED has the highest energy efficiency of any color LED. Second is that the Stokes shift loss of energy is lower than that in the UV LED, because the Stokes shift is smaller in wavelength and energy, and it only occurs for one phosphor instead of three. Figure 1.2 summarizes these three LED systems, their spectra, and their performance in energy efficiency.

Figure 1.2: Potential white LED designs, with increasing energy efficiency from left to right, caused by the poor red & green LED efficiency and by Stokes shift losses with the RGB phosphors [Steigerwald 2002].

1.3. Potential Advantages of Colloidal Nanocrystals (NCs) as Nanophosphors

Colloidal NCs are attractive materials for use as nanophosphors in LEDs because they have many key advantages over traditional phosphors and wavelength converting materials such as fluorescent dyes. These advantages hinge on their unique properties that arise from their small nanometer scale size.

One such property is the size-dependent color tunability over the entire visible spectrum, which is illustrated in Figure 1.3, showing CdSe/ZnS nanocrystals emitting across the entire visible spectrum. Various colors of emitted light were created by growing increasing core sizes to go from blue to red emission. This property arises from the quantum confinement of carriers in the nanocrystal's volume and as the size of the nanocrystal is varied, the transition energy between the conduction band and the valence

band that carriers recombine across also varies. Then, when carriers are excited across the band gap by a photon of energy larger than the band gap, it creates an electron and hole pair that can then recombine causing the release photons, which, according to the NC size vary in energy and thus wavelength [Smith 2010].

Figure 1.3: CdSe/ZnS NCs synthesized at CHTM, with increasing core sizes left to right, emitting visible light of various colors under UV excitation.

A second set of attractive properties is the high quantum efficiencies and luminescence stability that colloidal NCs of many materials have been able to achieve. These properties arise from the careful design of the NC's structure to prevent undesired chemical changes and from the strong overlap of the electron and hole wave functions in the confined structure, when compared to a bulk crystal [Smith 2010].

The final useful property is that NCs of different sizes can be excited by the same excitation wavelength. Thus, by combining NCs of various sizes, a custom-tailored nanophosphor can be created to emit any visible spectrum desired, for example by combining the three primary colors to generate white light.

1.4. Advantages of Doped Cadmium-Free Nanophosphors

Doped cadmium-free nanophosphors have many advantages over their cadmium-containing counterparts. The first is that they are free of the toxic heavy metal cadmium, which poses health risks in the manufacture and use of the nanophosphor. Second, they can be engineered to have improved chemical stability, owing to the fact that the emission originates from atomic transitions in the dopant atom and not from the band-to-band transitions in the NC. A third and most important advantage is that doped NCs exhibit enhanced thermal stability and have been shown to emit light at very high temperatures [Xie 2009].

1.5. Colloidal NC Synthesis Setup

Colloidal synthesis of various high quality NCs requires a specific set of equipment. A Schlenk line, shown in Figure 1.5.1, is used to provide inert gas and vacuum to multiple three-neck flasks. The Schlenk line is a glass apparatus that has multiple pick off points connected to a two-way valve, which in turn connects to two glass tubes, one containing the inert gas under pressure from a gas cylinder, and the other connecting to a vacuum pump that is protected by a solvent trap.

Figure 1.5.1: Equipment setup used for NC synthesis inside a fume hood.

A three-neck flask is used to contain the solution and allow for connections to the Schlenk line and a thermocouple, and for injection of the precursor chemical solutions. The three-neck flask sits on a heating mantle, which provides heat and is placed on top of a magnetic stirrer, which uses a rotating magnet to move a magnetic stir-bar inside the three-neck flask. The thermocouple monitors the temperature inside the flask and is connected to a temperature controller, which is used to control the heat output by the heating mantle and is able to control the temperature inside the flask.

A final piece of equipment required, shown in Figure 1.5.2, is an inert atmosphere (argon) glovebox, where precursor solutions are prepared free from contamination by any undesired chemicals or gases, such as water and oxygen.

Figure 1.5.2: MBraun UNILab glovebox.

1.6. Colloidal NC Core Synthesis Technique

The colloidal NC cores reported in this thesis are synthesized using a nucleation-growth technique that has become the dominant method of synthesizing high quality NCs. The technique begins by preparing one precursor, which will be heated in coordinating solvents to the desired reaction temperature for formation of the core NCs. The second precursor for the core is prepared separately at a lower temperature and is injected into the heated solution containing the first precursor, causing nucleation and growth until the precursors are consumed. Next, the temperature reduced to allow growth and combination of small NCs into larger ones, focusing the size to a monodisperse solution (Ostwald ripening) and to repair defects in the NCs that occurred during growth (annealing) the temperature can be maintained or raised for a longer period of time [Murray 2001].

After the formation of the core NCs, they must be doped with the desired dopant atoms. Doping of the core NCs begins by preparing the dopant solution in the glovebox and then injecting it into the core solution at a reduced temperature to prevent new NCs from forming. The solution is maintained at the lowered temperature for a long time to allow diffusion of the dopant atoms into the core NCs [Chen 2004], [Shen 2009], [Acharya 2010].

1.7. Shell Growth Method: Single Ionic Layer Adsorption Reaction (SILAR)

Shell growth techniques for early syntheses of NCs tried to grow the entire shell layer in one step with a single injection of the shell precursors, containing the entire amount of precursors desired for a shell of a desired thickness. These early syntheses resulted in poor quality shells that had many defects such as islands, incomplete shells, and dislocations in the crystal structure.

The SILAR technique was developed to create complete high quality shells. Using this technique, shell precursors are injected in proportionally increasing amounts to only allow one monolayer of the shell crystal to grow on the core at a time. After injection of the shell precursor, the temperature is quickly dropped to the shell growth temperature. Next, the temperature of the solution containing the core NCs is raised to anneal the newly formed shell layer and prepare for the next shell precursor injection. This process is repeated as many times as necessary to grow a shell of the desired thickness [Chen 2004], [Shen 2009], [Acharya 2010].

Chapter 2

Synthesis and Characterization of InP:Cu/ZnSe NCs

2.1. Synthesis of InP:Cu/ZnSe NCs

The choice of InP:Cu/ZnSe nanocrystals is driven by their broad color tunability, cadmium-free composition, and bright emission well above room temperature. Figure 2.1 shows luminescence from InP:Cu/ZnSe NCs under UV light at a high temperature of 126 °C, taken during their synthesis. InP:Cu/ZnSe NCs can be tuned to emit over the broad spectral range from 630 to 1100 nm, and the expected quantum efficiency of InP:Cu/ZnSe colloidal nanocrystals is between 35-40% [Xie 2009].

Figure 2.1: Red emission from InP:Cu/ZnSe NCs, observed during synthesis at 126 °C when excited by a UV lamp.

The InP:Cu/ZnSe synthesis procedure was adapted from the synthesis published by [Xie 2009]. In a typical synthesis of the core NCs, the phosphorus precursor is prepared by adding 0.050 g of tris(trimethylsilyl) phosphine to 0.4 mL of 1-octylamine and 1.1 mL of 1-octadecene (ODE) in a glovebox. Next, 0.1168 g of indium acetate and

0.3517 g of myristic acid are added to 5.07 mL of ODE in a 100 mL three-neck flask. The flask is stirred at medium speed and heated to 188 °C under argon flow, and the phosphorus precursor is injected into the flask.

After allowing 10 minutes for the core to form, the temperature is lowered to 130 °C and the Cu dopant precursor (0.0126 g copper stearate in 1 mL of ODE) is injected into the flask. The temperature is increased at 2 °C / min till it reaches 210 °C for the doping of InP core NCs with Cu ions. The temperature is then lowered to 150 °C for shelling the InP:Cu core NCs with ZnSe.

The ZnSe shell synthesis begins with dissolving 0.711 g of zinc stearate in 11.25 mL of ODE and 0.089 g Se powder in 11.25 mL of trioctyl phosphine (TOP), all prepared in the argon-filled glovebox. Next, 1.2 mL of Zn precursor and Se precursor are separately added into the reaction flask, with a 10 minute time interval between the two injections at 150 °C. The temperature is raised to 220 °C for 30 minutes. The flask is then cooled to 150 °C and 1.65 mL of Zn precursor and 1.65 mL of Se precursor are injected separately, with a 10 minute interval between injections. Again, the temperature is raised to 220 °C for 30 minutes. Similarly, 2.1, 2.8, and 3.5 mL of each are added in the 3rd, 4th, and 5th injections. The flask is then cooled to room temperature.

For purification, 10 mL of hexane are added to the reaction solution. The final product, InP:Cu/ZnSe NCs, is purified by centrifugation with methanol until a clear methanol phase is obtained. The precipitated NCs are then collected and dispersed in hexane.

2.2. Characterization of InP:Cu/ZnSe NCs

Absorption measurements were performed using a Cary 5000 UV-VIS-NIR dual beam spectrophotometer. Samples for absorption were prepared by diluting the solution to an optical density of 0.2 at the peak excitation wavelength. PL characterization was performed using a Horiba Jobin Yvon Fluorolog-3 spectrofluorometer with a xenon lamp excitation light source, excitation monochromator, emission monochromator, and a Hamamatsu R928 photo multiplier tube (PMT). As synthesized InP:Cu/ZnSe NCs have a broad emission peak at 674 nm, which does overlap with their absorption spectrum, as shown in Figure 2.2.1 along with the emission from purified NCs in an aliquot vial when excited by a UV lamp. The overlap between the absorption and emission spectra means that the NCs will self-absorb, which will significantly limit their utility as a nanophosphor.

Figure 2.2.1: Absorption and PL spectra of InP:Cu/ZnSe NCs (left), and their emission after washing in an aliquot vial being excited by a UV lamp (right).

The quantum efficiency (QE) of the InP:Cu/ZnSe NCs was measured directly after synthesis using a Horiba Jobin Yvon Fluorolog 3 system with an integrating sphere attachment. The QE of the as-synthesized NCs measured at ~15% was somewhat below the expected QE of 35-40 % reported in [Xie 2009]. The raw measurement data are shown in Figure 2.2.2.

Figure 2.2.2: Excitation scatter spectra for InP:Cu/ZnSe NCs (left), and the corresponding fluorescence emission spectra (right), that resulted in a measured QE of ~15%.

Temperature dependence of the PL was measured using a thermoelectric heater/cooler attachment F-3004 on the Horiba Jobin Yvon Fluorolog 3 system. To perform this experiment, the InP:Cu/ZnSe and CdSe/ZnS NCs were solubilized in toluene, because of its high boiling point above 100 °C. Temperature dependence of the InP:Cu/ZnSe NCs PL is shown in Figure 2.2.3 (left), where InP:Cu/ZnSe NCs have a nearly linear decrease in PL intensity at the peak wavelength with increasing temperature, which is in stark contrast to CdSe/ZnS NCs PL intensity at the peak wavelength that shows an exponential decrease with increasing temperature. Also shown in Figure 2.2.3

(right) is the InP:Cu/ZnSe PL peak wavelength vs. temperature, which has a red shift with increasing temperature, with the maximum value of 7 nm.

Figure 2.2.3: PL intensity vs. temperature dependence for InP:Cu/ZnSe NCs compared to CdSe/ZnS NCs (left), and PL peak wavelength vs. temperature for InP:Cu/ZnSe NCs (right).

InP:Cu/ZnSe NCs were also structurally characterized by high resolution transmission electron microscopy (HRTEM) at UNM's Earth and Planetary Sciences TEM laboratory using a Jeol-2010F high resolution TEM. The TEM sample was prepared by placing a drop of the washed colloidal solution onto a 200-mesh carbon-coated copper grid and allowing the solvent to dry. The HRTEM images in Figure 2.2.4 show that the NCs are agglomerating, and have a very disperse size distribution, indicating that the synthesis procedure does not have good control over the final size of the NCs.

Figure 2.2.4: HRTEM images of InP:Cu/ZnSe NCs at 100k magnification - 20 nm scale bar (top), and at 500k magnification - 5 nm scale bar (bottom).

Energy dispersive x-ray spectroscopy (EDS) was performed using the Jeol-2010F high resolution TEM's EDS capability. The EDS spectrum is shown in Figure 2.2.5 confirms the presence of elemental In, P, Cu, Zn, and Se atoms in the composition of the NCs.

Figure 2.2.5: EDS spectrum of InP:Cu/ZnSe NCs.

Dynamic light scattering (DLS) measurements, using Brownian motion of the NCs in a known solvent to estimate the hydrodynamic size of the nanocrystals, were performed using a Wyatt Dynapro Titan DLS system. The DLS histogram shown in Figure 2.2.6 confirms the broad size distribution of the InP:Cu/ZnSe NCs observed in the HRTEM images.

Figure 2.2.6: DLS histogram of InP:Cu/ZnSe NCs.

Chapter 3

Synthesis and Characterization of MnSe/ZnSe NCs

3.1. Synthesis of MnSe/ZnSe NCs

The choice of MnSe/ZnSe nanocrystals is similarly driven by their color tunability, cadmium-free composition, and bright emission well above room temperature, as can be seen in Figure 3.1 taken during synthesis of the NCs. MnSe/ZnSe NCs can be tuned to emit over the spectral range from 575 to 610 nm. The quantum efficiency of MnSe/ZnSe colloidal NCs is expected to be ~50% [Pradhan 2007].

Figure 3.1: Green emission from MnSe/ZnSe NCs, observed during synthesis at 242 °C when excited by a UV lamp.

The MnSe/ZnSe synthesis procedure was adapted from the synthesis published in [Pradhan 2007]. A typical core synthesis begins with preparation of the Mn precursor stock solution by dissolving 0.569 g of stearic acid into 3.8 mL of methanol and heating the solution to 60 °C with moderate stirring. Then the flask is cooled to room temperature, and 0.363 g of tetramethylammonium hydroxide pentahydrate (TMAH) in 1.3 mL of methanol are added to it. The solution is stirred for 15 minutes. Next, 0.126 g of manganese chloride in 1.3 mL of methanol are added dropwise to the flask with vigorous stirring. The white precipitate is centrifuged with methanol, collected, and dried under vacuum.

The Se precursor stock solution is prepared by adding 0.19 g of powder Se to 0.5 mL of tributyl phosphine (TBP). Then, 0.050 g of the Mn precursor are added to 12.5 mL of ODE in a 100 mL three-neck flask. The temperature is set to 100 °C and the flask is purged with argon several times, before the temperature is raised to 280 °C. Next, 0.6 mL of octadecylamine (ODA) is mixed with 0.5 mL of TBPSe stock solution, heated to 70

°C, and injected into the reaction flask at 280 °C. Finally, the reaction is cooled to 260 °C and annealed for 60 minutes.

To shell the previously formed MnSe core NCs, the temperature is raised to 290 °C for ZnSe overcoating. To prepare the Zn precursor, 1 g of zinc stearate and 0.2 g of stearic acid are dissolved in 5 mL of ODE. 1.5 mL of Zn precursor is injected into the reaction flask, followed by a mixture of 0.25 g of ODA and 0.25 g of ODE. The remaining Zn precursor is injected by adding 1.5 mL at 15 min intervals, followed by (0.25 g of ODE) / (0.25 g of ODA) injection. The flask is then cooled to 260 °C and a mixture of 0.25 g of ODA and 0.25 g of ODE is injected into the flask. To shift the emission from ~575 nm to ~610 nm, 4.5 mL of dodecanethiol is added to the flask at 260 °C and heating is continued for 1 hour. The flask is then cooled to room temperature and the NCs are collected and purified by using centrifugation with acetone and are finally dispersed in chloroform.

3.2. Characterization of MnSe/ZnSe NCs

The synthesis of MnSe/ZnSe NCs was repeated several times, and every time after washing and dispersal of the NCs in chloroform the result was a non-fluorescent sticky brown sludge, as can be seen in Figure 3.2. This is suspected to be because the high temperatures of the synthesis, well above the known Mn diffusion temperature in ZnSe of 250 °C, allowed the Mn atoms to diffuse to the surface of the NCs, where they were not protected from oxygen, which is known to quench the Mn emission [Pradhan 2007].

Figure 3.2: Final product of MnSe/ZnSe NC synthesis.

Chapter 4

Synthesis and Characterization of ZnSe:Mn/ZnSeS NCs

4.1. Synthesis of ZnSe:Mn/ZnSeS NCs

The choice of ZnSe:Mn/ZnSeS nanocrystals is also driven by their color tunability, cadmium-free composition, and bright emission well above room temperature, as can be seen in Figure 4.1 taken during synthesis of the NCs. The synthesis for ZnSe:Mn/ZnSeS was adapted from [Chen 2004], [Shen 2009], [Acharya 2010] with significant modifications. The ratio of Mn to Zn precursors, the large excess of Se at the beginning of synthesis, variations of the time and temperature of the reaction, and the addition of S to the shell account for the significant modifications to the procedure that have resulted in this novel nanophosphor.

Figure 4.1: Yellow emission from ZnSe:Mn/ZnSeS NCs, observed during synthesis with UV lamp excitation at 240 °C (left) and at 22 °C (right).

A typical synthesis of the ZnSe core NCs begins with preparation of the Se precursor by adding 123 mg of selenourea and 10 mL of oleylamine into three-neck flask 1. The solution is heated to 100 °C under vacuum and then heated to 200 °C under argon, with vigorous stirring until the selenourea is completely dissolved, then it is allowed to cool to 100 °C. The core Zn precursor is prepared by adding 63 mg of zinc stearate (ZnSt_2) and 5 mL of octadecene (ODE) in three-neck flask 2. Then three-neck flask 2 is heated to 260 °C under argon. When the temperature is stabilized at 260 °C, all of the Se precursor is injected into three-neck flask 2. Then, three-neck flask 2 is cooled to 240 °C in preparation for addition of the Mn dopant precursor.

The Mn dopant precursor is prepared by adding 6.3 mg of manganese stearate (MnSt_2) to 0.5 mL of ODE. The mixture is injected into three-neck flask 2 at 240 °C, the temperature is maintained for one hour, and three-neck flask 2 is then heated to 260 °C.

The shell Zn precursor is prepared by adding 0.63 g of ZnSt_2 to 0.28 g of stearic acid (SA) and 10 mL of ODE to three-neck flask 3. The ZnSt_2 /SA/ODE solution is then heated under vacuum to 100 °C and then heated to 130 °C under argon for injection. To

begin, 0.96 mL of the $\text{ZnSt}_2/\text{SA}/\text{ODE}$ solution is injected into three-neck flask 2 at 260 °C, and after 10 min another 0.96 mL is injected into three-neck flask 2. The remainder of the shell is grown by progressively increasing injections of the $\text{ZnSt}_2/\text{SA}/\text{ODE}$ solution into three-neck flask 2. The injection temperature for three-neck flask 2 is 260 °C, and after each injection the temperature is rapidly lowered to 240 °C. The four subsequent injections have the volumes of 1.33 mL, 1.69 mL, 2.25 mL, and 2.81 mL, respectively.

The shell S precursor is prepared by adding 15 mg of powder S to 2 mL of ODE that is heated until the sulfur is completely dissolved. The S/ODE solution is then injected into three-neck flask 2 at 260 °C. Then, three-neck flask 2 is cooled to 240 °C for 30 minutes, and then cooled to room temperature. The resulting NCs are washed by centrifugation using acetone, until a transparent supernatant is obtained. The supernatant is then discarded, while the NC precipitate is collected using toluene and stored in a brown glass bottle.

4.2. Characterization of $\text{ZnSe:Mn}/\text{ZnSeS}$ NCs

Absorption measurements were performed using a Cary 5000 UV-VIS-NIR dual beam spectrophotometer. Samples for absorption measurements were prepared by diluting the solution to an optical density of 0.2 at the peak excitation wavelength of 453 nm. PL characterization was performed using a Horiba Jobin Yvon Fluorolog-3 spectrofluorometer with a xenon lamp excitation light source, excitation monochromator, emission monochromator, and a Hamamatsu R928 photo multiplier tube (PMT). As-synthesized $\text{ZnSe:Mn}/\text{ZnSeS}$ NCs have two broad emission peaks, one at 499 nm, which

does slightly overlap with their absorption spectrum, as shown in Figure 4.2.1, and a second peak at 587 nm, which has very low self absorption.

Figure 4.2.1: Absorption and PL spectra of ZnSe:Mn/ZnSeS NCs.

PL measurements of ZnSe:Mn/ZnSeS NCs using an excitation of 358 nm can be seen in Figure 4.2.2(b), and show 3 emission peaks, located at 400 nm, 499 nm, and 587 nm. The emission peak at 400 nm is from the ZnSe band-to-band emission and has a peak excitation at 358 nm. The 587 nm emission is from $\text{Mn}^{2+} {}^4\text{T}_1 \rightarrow {}^6\text{A}_1$ transition [Park 2007], [Ma 2010], and has a broad peak excitation plateau from 380 to 420 nm. Its emission at 418 nm excitation is shown in Figure 4.2.2(d). The 499 nm transition is hypothesized to be from ZnS traps on the surface of the NCs [Chen 2004], and has peak excitations at 453 nm and 483 nm. Its emission at 453 nm excitation is shown in Figure 4.2.2(c).

Figure 4.2.2: (a) Absorption spectra of ZnSe:Mn/ZnSeS NCs, (b), (c), and (d) their emission spectra at excitation wavelengths of 358 nm, 453 nm, and 418 nm, respectively.

Temperature dependence of the PL was measured using the thermoelectric heater/cooler accessory with samples in toluene. The ZnSe:Mn/ZnSeS NCs exhibit abnormal thermal behavior from competing thermal factors, one caused by the thermal release of trapped charges, and the other caused by the phonon-electron interaction [Park 2007]. The ~500 nm trap emission shows a peak in emission intensity at 45 °C, and then decreases almost linearly with increasing temperature, as shown in Figure 4.2.3 (left) in comparison to InP:Cu/ZnSe and CdSe/ZnS NCs. Also shown in Figure 4.2.3 (right) is ZnSe:Mn/ZnSeS NCs trap emission wavelength vs. temperature, which displays a

remarkable stability with only a 3 nm maximum red shift within the temperature range of 22 to 100 °C.

Figure 4.2.3: PL intensity vs. temperature for ~500 nm emission from ZnSe:Mn/ZnSeS NCs compared to InP:Cu/ZnSe and CdSe/ZnS NCs (left), PL peak emission wavelength vs. temperature for ~500 nm emission from ZnSe:Mn/ZnSeS NCs (right).

QE measurements of ZnSe:Mn/ZnSeS NCs were performed on freshly synthesized samples using the 4" integrating sphere attachment with the liquid sample holder accessory on a Fluorolog-3 system, with a Hamamatsu R928 PMT detector. The results of the QE measurements using the PMT were ~55% for the 499 nm surface trap emission and ~25% for the 587 nm Mn^{2+} emission. The raw data for the QE measurements are shown in Figures 4.2.4 and 4.2.5 for the 499 nm surface trap emission and the 587 nm Mn^{2+} emission, respectively.

Figure 4.2.4: Excitation scatter spectra for ZnSe:Mn/ZnSeS NCs (left), and the corresponding fluorescence emission spectra (right) that resulted in a measured QE of ~55% for the 499 nm surface trap emission.

Figure 4.2.5: Excitation scatter spectra for ZnSe:Mn/ZnSeS NCs (left), and the corresponding fluorescence emission spectra (right) that resulted in a measured QE of ~25% for the 587 nm Mn^{2+} emission.

Structural characterization of ZnSe:Mn/ZnSeS NCs was performed using a Jeol-2010F HRTEM. The HRTEM sample was prepared by placing a drop of the washed colloidal solution onto a 200-mesh carbon-coated copper grid and allowing the solvent to dry. HRTEM images in Figure 4.2.6 show rods 5 to 7 nm wide that vary in length from 10 to 20 nm.

Figure 4.2.6: HRTEM images of ZnSe:Mn/ZnSeS NCs at 100k magnification - 20 nm scale bar (top), and at 500k magnification - 5 nm scale bar (bottom).

DLS measurements of ZnSe:Mn/ZnSeS NCs were performed using a Wyatt Dynapro DLS. The results are shown in Figure 4.2.7, with peaks for 6.5, 8.5, and 12.5 nm hydrodynamic diameters of the NCs, resembling a Gaussian distribution. The size distribution for the ZnSe:Mn/ZnSeS synthesis is much better in comparison to the

InP:Cu/ZnSe synthesis, although it still is in need of improvement, as there is still a wide range of sizes.

Figure 4.2.7: DLS histogram of ZnSe:Mn/ZnSeS NCs.

The crystalline structure and composition of ZnSe:Mn/ZnSeS NCs were characterized by x-ray diffraction (XRD) on a Rigaku SmartLab system with Cu source operating at 40 kV - 44 mA, the step size was 0.02° at a scan rate of $4^\circ/\text{min}$ over the range $0 - 90^\circ 2\theta$. The XRD sample was prepared by placing several drops of the colloidal solution onto a zero background holder. The data were interpreted using the International Centre for Diffraction Data (ICDD) XRD/XRF powder diffraction file (pdf) database. The recorded peaks in the XRD measurement match very well the $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{Se}$ ternary semiconductor material, as shown in Figure 4.2.8, and confirm that the desired amount of Mn dopant has indeed been incorporated into the NCs.

Figure 4.2.8: XRD spectrum of ZnSe:Mn/ZnSeS NCs with very good matching of significant peaks to zinc manganese selenide with 95% of Zn and 5% of Mn.

Chapter 5

Synthesis and Characterization of ZnSe:Mn/ZnS NCs

5.1. Synthesis of ZnSe:Mn/ZnS NCs

ZnSe:Mn/ZnS NC synthesis is very similar to the ZnSe:Mn/ZnSeS synthesis, although the final shell precursor has been changed from elemental sulfur to thiourea. This change was made in order to use a sulfur precursor that had thiols already included, which could react at lower temperatures in order to grow a high quality ZnS shell instead of forming the ternary ZnSeS. Also, further modifications include the addition of two

additional zinc precursor injections after the addition of thiourea to grow two monolayers of ZnS shell onto the ZnSe:Mn NC cores.

Bright fluorescence was also observed during the synthesis of ZnSe:Mn/ZnS NCs, as shown in Figure 5.1. However, the modifications to this synthesis have changed the observed color of the fluorescence. While the flask in the ZnSe:Mn/ZnSeS NC synthesis appeared yellow under UV illumination, during the ZnSe:Mn/ZnS synthesis the flask appeared yellow – orange, because the Mn^{2+} emission has been enhanced.

Figure 5.1: Yellow - orange emission from ZnSe:Mn/ZnS NCs, observed during synthesis with UV lamp excitation at 240 °C (left) and at 22 °C (right).

The synthesis for ZnSe:Mn/ZnS was adapted from [Chen 2004], [Shen 2009], [Acharya 2010] with significant modifications. The ratio of Mn to Zn precursors, the large excess of Se at the beginning of synthesis, variations of the time and temperature of the reaction, and the addition of a ZnS shell account for the significant modifications to the procedure that have resulted in this novel nanophosphor with record high QE.

A typical synthesis of the ZnSe core NCs begins with preparation of the Se precursor by adding 123 mg of selenourea and 10 mL of oleylamine into three-neck flask 1. The solution is heated to 100 °C under vacuum and then heated to 200 °C under argon,

with vigorous stirring until the selenourea is completely dissolved, then it is allowed to cool to 100 °C. The core Zn precursor is prepared by adding 63 mg of zinc stearate (ZnSt_2) and 5 mL of octadecene (ODE) in three-neck flask 2. Then three-neck flask 2 is heated to 260 °C under argon. When the temperature is stabilized at 260 °C, all of the Se precursor is injected into three-neck flask 2. Then, three-neck flask 2 is cooled to 240 °C in preparation for addition of the Mn dopant precursor.

The Mn dopant precursor is prepared by adding 6.3 mg of manganese stearate (MnSt_2) to 0.5 mL of ODE. The mixture is injected into three-neck flask 2 at 240 °C, the temperature is maintained for one hour, and three-neck flask 2 is then heated to 260 °C.

The shell Zn precursor is prepared by adding 1.16 g of ZnSt_2 to 0.52 g of stearic acid (SA) and 18.4 mL of ODE to three-neck flask 3. The ZnSt_2 /SA/ODE solution is then heated under vacuum to 100 °C and then heated to 130 °C under argon with medium stirring. To begin, 0.96 mL of the ZnSt_2 /SA/ODE solution is injected into three-neck flask 2 at 260 °C, and after 10 min another 0.96 mL is injected into three-neck flask 2. The remainder of the shell is grown by progressively increasing injections of the ZnSt_2 /SA/ODE solution into three-neck flask 2. The injection temperature for three-neck flask 2 is 260 °C, and after each injection the temperature is rapidly lowered to 240 °C. The four subsequent injections have the volumes of 1.33 mL, 1.69 mL, 2.25 mL, and 2.81 mL, respectively.

The ZnS shell sulfur precursor is prepared by dissolving 0.086 mg of thiourea into 3 mL of ethanol, which is then injected into three-neck flask 2 at 70 °C. The ethanol is removed by putting the flask under vacuum, and then three-neck flask 2 is heated to 260 °C. Next, 3.65 mL of the ZnSt_2 /SA/ODE solution are injected into three-neck flask 2,

which is then cooled to 240 °C for 15 minutes. Three-neck flask 2 is then heated to 260 °C and 4.75 mL of the ZnSt₂/SA/ODE solution are injected. Three-neck flask 2 is then cooled to 240 °C for 15 minutes. Finally, three-neck flask 2 is cooled to room temperature. The resulting NCs are washed by centrifugation using acetone. The supernatant is discarded, while the NC precipitate is collected using chloroform and stored in a brown glass bottle.

5.2. Characterization of ZnSe:Mn/ZnS NCs

Absorption measurements were performed using a Cary 5000 UV-VIS-NIR dual beam spectrophotometer. Samples for absorption measurements were prepared by diluting the solution to an optical density of 0.2 at the peak excitation wavelength of 453 nm. PL characterization was performed using a Horiba Jobin Yvon Fluorolog-3 spectrofluorometer with a xenon lamp excitation light source, excitation monochromator, emission monochromator and a Hamamatsu R928 photo multiplier tube (PMT).

Absorption spectra and PL spectra excited by 365 nm light are shown in Figure 5.2.1 and demonstrate that the 589 nm Mn²⁺ emission from ZnSe:Mn/ZnS NCs does not strongly self absorb and that this nanophosphor would be an ideal material for use with LEDs. Similar to the ZnSe:Mn/ZnSeS PL, the ZnSe:Mn/ZnS PL has three emission peaks visible when excited by 365 nm light, although the band-to-band ZnSe emission has red shifted to 437 nm due to the ZnS shell, while the 497 nm surface trap emission and the 589 nm Mn²⁺ emission have both shifted slightly and typically vary within a 4 nm range from sample to sample.

Figure 5.2.1: Absorption spectra and PL spectra of ZnSe:Mn/ZnS NCs excited by 365 nm light.

A 2D excitation vs. emission map of ZnSe:Mn/ZnS NCs PL, shown in Fig. 5.2.2, was obtained at the Sandia/Los Alamos Center for Integrated Nanotechnologies using a Horiba Jobin Yvon Fluorolog-3 spectrofluorometer with a xenon lamp excitation light source, excitation monochromator, emission monochromator and a charge-coupled device (CCD) detector. The 497 nm surface trap emission is located in the upper left corner of the map, and the slope of the contour points to the size dispersity of the NCs. Towards the middle of the 2D map is the excitation-independent emission of Mn^{2+} at 589 nm. It is not sloped, because this emission is not sensitive to size dispersity.

Figure 5.2.2: 2D map of PL excitation vs. PL emission for ZnSe:Mn/ZnS NCs.

PL emission and excitation spectra for ZnSe:Mn/ZnS NCs 497 nm surface trap are shown in Figure 5.2.3, with the emission spectrum on the left excited by 453 nm light. The excitation spectra on the right show two excitation peaks at 453 nm and 483 nm. The raw spectrum is shown on the bottom, while the spectrum on the top has been corrected for variations in the lamp intensity. PL emission and excitation spectra for the 589 nm Mn^{2+} emission are shown in Figure 5.2.4, with the emission spectrum on the left excited by 418 nm light. The excitation spectra on the right show a broad peak excitation plateau from 380 to 420 nm, again with the raw spectrum on the bottom and the spectrum corrected for lamp intensity on the top.

Figure 5.2.3: PL spectra of ZnSe:Mn/ZnS NCs: emission spectrum excited by 453 nm light (left), excitation spectrum at 497 nm (right), with raw spectrum on bottom and lamp-intensity-corrected spectrum on top.

Figure 5.2.4: PL spectra of ZnSe:Mn/ZnS NCs: emission spectrum excited by 418 nm light (left), excitation spectrum at 589 nm (right), with raw spectrum on bottom and lamp-intensity-corrected spectrum on top.

PL lifetime measurements of the 497 nm trap emission shown in Figure 5.2.5 (left) indicate a fast lifetime, calculated with one exponential of 5.08 ns with 100.00% relative amplitude. Lifetime measurements of the 589 nm emission shown in Figure 5.2.5 (right) can be fitted with two fast lifetimes of 0.102 ns with 64.52% relative amplitude,

and 5.044 ns with 35.48% relative amplitude. Mn^{2+} has a third well-known long lifetime of 1.9 ms [Bol 1998] that could not be measured because of equipment limitations, but it explains the poorer fitting of the lifetime decay at longer times.

Figure 5.2.5: Lifetime measurements of ZnSe:Mn/ZnS NCs 497 nm surface trap emission with 460 nm LED excitation (left), and of 589 nm Mn^{2+} emission with 370 nm LED excitation (right). The blue trace is the system response calibration, red trace is the NC lifetime measurement, and green is the standard deviation of the lifetime fitting.

Initial QE measurements of ZnSe:Mn/ZnS NCs were performed on freshly synthesized samples using the 4" integrating sphere attachment with the liquid sample holder accessory on a Fluorolog-3 system, using a Hamamatsu R928 PMT detector. The data from the QE measurements for the 497 nm surface defect emission, shown in Figure 5.2.6, yield ~51% peak QE when excited with 453 nm blue light for a sample in toluene. The data from the QE measurements for the 589 nm Mn^{2+} emission, shown in Figure 5.2.7, a yield ~90% peak QE when excited with 409 nm blue light for a sample in chloroform.

Figure 5.2.6: Excitation scatter spectra for ZnSe:Mn/ZnS NCs (left), and the corresponding fluorescence emission spectra (right) that resulted in a measured QE of ~51% for the 497 nm surface trap emission.

Figure 5.2.7: Excitation scatter spectra for ZnSe:Mn/ZnS NCs (left), and the corresponding fluorescence emission spectra (right) that resulted in a measured QE of ~90 % for the 589 nm Mn^{2+} emission.

QE of the ZnSe:Mn/ZnS NCs was monitored over time to study how it changed with time and to judge the stability of these NCs. Two separate samples were monitored, as shown in Figure 5.2.8. The first sample (shown in black) was synthesized using the chemicals on hand and it was noted that the glovebox was very clean with water and oxygen levels both below 0.1 ppm. This sample of ZnSe:Mn/ZnS NCs started out with ~60 % QE and remained stable for the entire monitoring period of 13 weeks, which is

attributed to the lack of oxygen contamination. The second sample (shown in red) was synthesized using new chemicals, but it was noted that the glovebox was showing below 0.1 ppm water, and 2-3 ppm oxygen levels during synthesis. This sample of ZnSe:Mn/ZnS NCs started out with ~82% QE, increased up to ~90% after one week, and then began a steady decline to ~55 % QE after 6 weeks. The record high QE is attributed to the use of fresh chemicals, while the decline in QE is attributed to oxygen contamination during synthesis.

Figure 5.2.8: QE of 589 nm Mn^{2+} emission vs. time plot for two samples of ZnSe:Mn/ZnS NCs.

Color coordinates of the ZnSe:Mn/ZnS NCs were also measured during the QE measurements and are shown in Figure 5.2.9 in the standardized International Commission on Illumination's (CIE) CIE 1931 and CIE 1976 diagrams. The color coordinates of the 589 nm Mn^{2+} emission are excellent, because they are located very close to the edge of the diagram, and this indicates that they allow the maximum color mixing potential. The color mixing potential is all the colors in the area enclosed when a

color triangle is drawn between the three colors used to make white light [Hunt 2004], [Li 2013].

Figure 5.2.9: CIE Color coordinate diagrams for 589 nm Mn^{2+} emission from ZnSe:Mn/ZnS NCs. $x = 0.6022$, $y = 0.3855$; $u' = 0.3751$, $v' = 0.5403$.

Temperature dependence of the PL was measured using the thermoelectric heater/cooler accessory with samples in toluene. The ZnSe:Mn/ZnS NCs exhibit abnormal thermal behavior from competing thermal factors, one caused by the thermal release of trapped charges, and the other caused by the phonon-electron interaction [Park 2007]. The 497 nm surface trap emission shows a peak in emission intensity at 42 °C, the ~590 nm emission intensity decreases approximately linearly with increasing temperature, and the ~440 nm emission peaks at 37 °C, as shown in Figure 5.2.10 (left). Also shown in Figure 5.2.10 (right) is the PL peak wavelength vs. temperature for the three observed emissions from ZnSe:Mn/ZnS NCs. Note that the ~440 nm ZnSe band-to-band emission has the least stability and has a maximum red shift of 29 nm with an 80 °C

increase in temperature, while the ~500 nm surface trap and the ~590 nm Mn^{2+} emissions are very stable, with no significant red shifts with increasing temperature.

Figure 5.2.10: Intensity at three PL spectrum peaks from ZnSe:Mn/ZnS NCs vs. temperature (left), and PL peak wavelength vs. temperature (right), for the ~440 nm band-to-band emission in black, ~500 nm surface trap emission in blue, and ~590 nm Mn^{2+} emission in red.

Structural characterization of ZnSe:Mn/ZnS NCs was performed using a Jeol-2010F HRTEM. The HRTEM sample was prepared by placing a drop of the washed colloidal solution onto a 200-mesh carbon coated copper grid and allowing the solvent to dry. HRTEM images in Figure 5.2.11 show cubic particles 5 - 7 nm in diameter and rods that are 5-7 nm wide and vary in length from 10 to 20 nm.

Figure 5.2.11: HRTEM images of ZnSe:Mn/ZnS NCs at 80k magnification - 50 nm scale bar (top), and at 100k magnification - 20 nm scale bar (bottom).

DLS measurements of ZnSe:Mn/ZnS NCs were performed using a Wyatt Dynapro DLS. The results are shown in Figure 5.2.12, which shows a peak for a 15 nm hydrodynamic diameter of the NCs and a range of 11 to 21 nm. It also resembles a Gaussian distribution, and the size distribution for the ZnSe:Mn/ZnS synthesis is much better in comparison to the ZnSe:Mn/ZnSeS synthesis.

Figure 5.2.12: DLS histogram of ZnSe:Mn/ZnS NCs.

The crystalline structure and composition of ZnSe:Mn/ZnS NCs was characterized by XRD on a Rigaku SmartLab system with Cu source operating at 40 kV - 44 mA. The step size was 0.02° at a scan rate of $4^\circ/\text{min}$ over the range $10 - 80^\circ 2\theta$. The XRD sample was prepared by placing several drops of the colloidal solution onto a zero background holder. The results of the scan are shown in Figure 5.2.13. The data were interpreted using the International Centre for Diffraction Data (ICDD) XRD/XRF powder diffraction file (pdf) database. The peaks were found to match bulk crystal data for zinc selenide, zinc selenide sulfide ($\text{ZnSe}_{0.74}\text{S}_{0.26}$), and zinc manganese selenide ($\text{Zn}_{0.95}\text{Mn}_{0.05}\text{Se}$) materials. Although the ZnS shell did not appear in the XRD measurements, it may still be present because a two monolayer shell is nearly impossible to detect with XRD, as there is not enough long range order of the crystal for the diffraction to occur.

Figure 5.2.13: XRD spectrum of ZnSe:Mn/ZnS NCs with matching of significant peaks to ZnSe, ZnSe_{0.74}S_{0.26}, and Zn_{0.95}Mn_{0.05}Se.

From careful consideration of the XRD spectrum, a diagram of the actual ZnSe:Mn/ZnS structure was created and is shown in Figure 5.2.14 along with the structure previously believed to have been synthesized for comparison. The structure on the left is what the synthesis procedure was expected to produce, which included a ZnMnSe core with a ZnSeS shell, finally capped with a ZnS shell. The structure actually created is shown on the right, and includes a ZnMnSe core with a ZnSe shell and a ZnSeS shell, finally capped with a thin ZnS shell.

Figure 5.2.14: Structure of ZnSe:Mn/ZnS NCs: the intended structure (left) and the actual structure (right).

Chapter 6

Conclusions and Future Work

6.1. Conclusions

LEDs are rapidly becoming the light source of choice for many applications because of their energy efficiency, color tunability, and low cost when the operational lifetime and total power consumed over that time is considered. Nanophosphors are a key to creating daylight-quality low-cost LEDs that can recreate the solar spectrum or any other spectrum desired by down conversion of the high efficiency blue LED light.

InP:Cu/ZnSe NCs have been shown to produce a bright red emission well above room temperature, although they suffer from poor control over the size dispersity and agglomeration during and after synthesis. Furthermore, their QE still needs to be improved in order for them to be an attractive material as a nanophosphor for white LEDs.

MnSe/ZnSe NCs may be a promising future green nanophosphor, as they also fluoresce high above room temperature, but the synthesis investigated in this work has

not resulted in fluorescent NCs after washing. It may be possible to fix the problems with this material, and the motivation to do so is the green gap in LED technology and efficiency.

ZnSe:Mn/ZnSeS NCs exhibit fluorescence well above room temperature and a uniquely bright defect emission from the surface traps, and may have potential applications where the emission can be exploited, such as sensing. The Mn^{2+} emission from these NCs was fairly bright, although it would not make an ideal candidate for application as a nanophosphor in white LEDs when compared to ZnSe:Mn/ZnS.

ZnSe:Mn/ZnS NCs have been shown to be an ideal candidate for use as a nanophosphor material with record high, stable QE well above room temperature. They can be combined with blue InGaN/GaN LEDs to create a spectrally balanced white light emission. This novel nanophosphor exhibits three emission bands, one at 437 nm from the ZnSe band-to-band transition, one at 497 nm related to surface traps, and a bright 589 nm emission related to atomic transitions in the Mn^{2+} dopant. ZnSe:Mn/ZnS NCs also have a record high QE for the 589 nm Mn^{2+} emission of ~90% when synthesized with fresh chemicals, and a demonstrated stability for up to 13 weeks after synthesis if the reaction conditions are carefully controlled to eliminate oxygen contamination.

6.2. Future Work

It is very likely that ZnSe:Mn/ZnS NCs can be further stabilized over time and the QE pushed closer to 100% by growing thicker ZnSe shells of 7 - 10 monolayers. Similarly, growing thicker ZnS shells in the range of 3 – 10 monolayers may bring

improvements to the QE stability and enable red shifting of the excitation spectrum to the ideal wavelength of 450 nm from the current 418 nm peak excitation.

Also, another shell material such as SiO_2 would be ideal to further isolate the NCs from surface effects and to allow the surface chemistry to be compatible with polar materials such as polysiloxane, which is a commonly used encapsulation material for high power LEDs.

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