Manipulating Optical Properties of Luminescent Nanoparticle Substrates through Ink Jet Printing

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ABSTRACT

Photoluminescent particles (PLPs) were deposited on nanofiber substrates in controlled amounts allowing for the fabrication of photoluminescent nanofibers (PLN). In this work, color control of composite PLN materials for solid-state lighting fixtures has been achieved through ink jet printing. Dovetailing of several critical factors was necessary to realize a suitable PLN. Factors of particular importance were: (1) controlling the location and quantity of PLPs deposited, (2) producing suitable ink formulations for use with nanofiber substrates, and (3) matching nanofibers with compatible chemistry and desirable optical properties.

Keywords: solid state lighting, ink jet printing, nanofibers, photoluminescent particles

1 INTRODUCTION

Nanofiber substrates are suitable host materials for photoluminescent particles (PLPs) provided that PLPs, such as quantum dots (QD) or phosphors with specific emission wavelengths, can be deposited in controlled amounts. The resulting photoluminescent nanofiber substrates (PLNs) are amenable to use in light-emitting diode (LED)-based solid state lighting (SSL) devices. Application of PLPs to nanofibers with a materials printer imparts a sufficient degree of control over the concentration and placement of luminescent particles that enables lighting devices of desired colors, including white light, to be built.

Published works concerning the deposition of QD PLPs have reported the use of techniques such as contact printing methods, stamp transfer, and noncontact printing methods [1]. Ink jet printing, a non-contact method, is of particular interest because it uses minimal materials, can cover large sample areas, does not damage the nanofiber substrates, and is capable of precisely depositing multiple layers of material if necessary. QDs are expensive; therefore, limiting material consumption is a nontrivial benefit of ink jet printing. Some technical challenges associated with ink jet printing of QDs involve balancing (1) solution properties necessary for sustainable, high quality printing, (2) solution properties necessary for stable, high concentration QD suspensions, and (3) compatibility of ink-substrate chemistries. Many researchers have reported the problematic "coffee ring" effect [2] that leads to non-uniform deposition of particles. This is of particular concern in light emitting devices, since variation of the concentration of PLPs across the surface would likely produce color non-uniformities. In this work, suitable PLP inks were formulated and deposited in controlled, uniform amounts onto nanofibers using a 2800 model Dimatix material printer (DMP 2800). When tested in prototype lighting devices with high brightness, blue LEDs as an excitation source, the fabricated PLNs had luminous efficacies in excess of 50 lumens/watt and produced emissions at neutral white colors with high color rendering indices [3]. The controlled deposition of various PLPs, in specific quantities on nanofibers substrates of various morphologies and surface chemistries has afforded the fabrication of PLNs which are suitable for use in lighting devices. Incorporation of PLN nanocomposites that achieve specific correlated color temperature (CCT) and color rendering index (CRI) properties has been critical to the fabrication of these novel SSL devices.

2 METHODS

Solutions of poly(methyl methacrylate) (PMMA) (Scientific Polymer Products, Inc.) and Nylon (Sigma Aldrich) were prepared using formulations favorable for electrospinning nanofibers. The solution chemistry and electrospinning conditions were tailored to fabricate nanofibers with specific morphologies, such as smooth or porous surface structures and fibers of target sizes, as characterized by average diameter. These solutions were electrospun in two types of chambers. Chamber 1 was a needle-spinneret chamber developed at RTI which was designed to control parameters that influence fiber properties. These parameters effect structure-property relationships such as temperature, humidity, balance of electrical pull to solution feed rate and electric field formation. Chamber 2 was an Elmarco NanoSpider LabTool, a commercial, multi-jet system that allowed larger samples to be spun quickly. Chamber 1 was primarily used to develop nanofiber morphologies, whereas chamber 2 was used to spin high-throughput, device size samples.

Large rectangular nanofiber mats, approximately 1 x 2 feet, were electrospun using the Elmarco tool and cut into shapes for use in prototype lighting devices developed at RTI. Several surface treatments were applied to these substrates via a choice of deposition methods such as spray coating and vapor phase polymerization.

QD inks were developed with solutions properties amenable to ink jet printing with a DMP 2800. QDs (Evident Technologies, Troy, NY) were dispersed in long carbon chain organic solvents with low vapor pressures. Target solution properties, as recommended by Dimatix, are low vapor pressure, viscosity in the range of 10-12 cPs, surface tension in the range of 28-33 dynes/cm, and good particle suspension. On average, the inks developed in this study had a viscosity of 8-10 cPs, surface tension of 28 dynes/cm and low evaporation rates.

PLNs were fabricated using red and green QD inks that were jetted in predetermined amounts onto bare and surface treated PMMA and Nylon nanofiber substrates. Pattern resolution was observed under UV light and with optical microscopy. Measured optical properties of the PLNs including quantum efficiency, reflectance, and color were taken using an integrating sphere equipped with an Ocean Optics USB2000 fiber optics spectrometer. Quantum efficiency was measured using the Diffuse Incident Light Method (DILM) [4], and reflectance was measured using procedures described in CIE-130-1998. Color, as determined by chromaticity coordinates, and other lighting parameters of the PLN were measured using the SpectraSuite software that operates the Ocean Optics spectrometer.

3 RESULTS AND DISCUSSION

In order to understand the stability of QD suspensions in various solvents, a series of inks were prepared with varying carbon chain length additives and organic solvents. The QDs used in this study were made from cadmium selenide with a zinc sulfide shell (i.e., CdSe/ZnS) and were capped with hexadecylamine ligands to render them soluble in organic solvents. Since the goal was to produce an ink that would deposit sufficient quantities of QDs for use with high brightness LEDs, obtaining high QD loadings in the suspension while maintaining suspension stability was critical. Formulations based on short chain organic solvents did not provide sufficient stability for the ink. This phenomenon was apparent in the precipitation (Figure 1, vial 1) and the aggregation of QDs, resulting in a chalky appearance (Figure 1, vial 2). Sustainable dispersions of high concentration QD inks usable in the DMP 2800 were obtained by using organic solvents having long carbon chains and low vapor pressure (Figure 1, vial 3).

DMP 2800 Cartridges capable of ejecting 10 picoliter ink droplets were used. The drop visualization system on the DMP2800 was used to observe drop formation on the cartridge nozzles (Figure 2). This droplet imaging allowed jetting parameter to be adjusted so that droplet formation and trajectory were suitable.

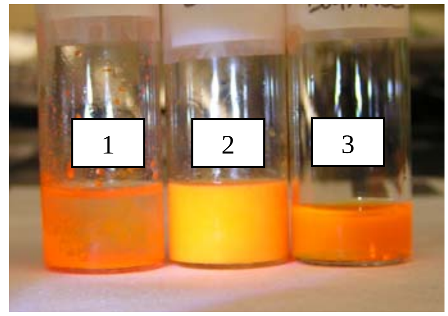


Figure 1. Quantum dots can precipitate out of solution, which can be prevented with a careful choice of printing solvent. This image shows various organic-based solutions of QDs.

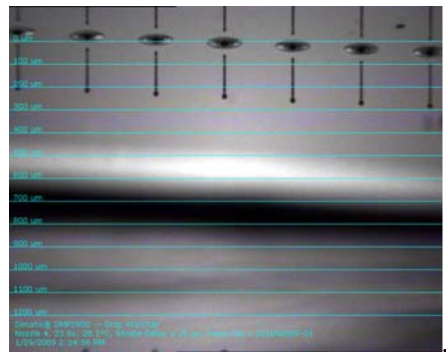


Figure 2. RTI's QD inks jetting from DMP 2800 material printer.

Nanofiber substrates, made from either nylon or PMMA were used as host materials for PLPs. These substrates were formed using the process of electrospinning in one of two different spinning chambers, as described above. Polymer solution formulations and electrospinning conditions provided control of fiber morphology. Fibers with average diameters between 100-1000 nm, having porous or smooth surface characteristics, and cylindrical or ribbon-like cross sections were used as printing substrates for the QDs. Images of typical nanofibers examined in this study are shown in Figure 3.

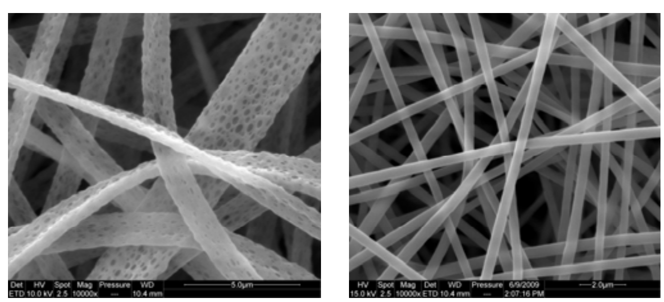
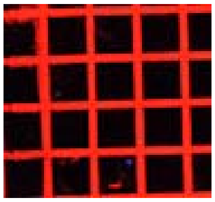
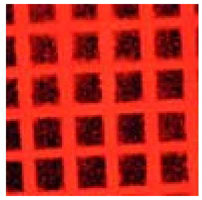


Figure 3. SEM micrographs of different fiber morphologies

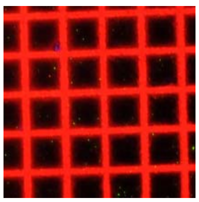
Initial studies focused on QD inks that were jetted onto bare nanofiber substrates. As shown in Figure 4, an initial printing of a single layer produced good resolution, although there was some variation of the width of the printed lines (Figure 4A). However, sequential printing of multiple layers resulted in a significant degradation in pattern resolution (Figure 4B). The reasons for these effects are being investigated further, but can likely be explained by the degree of affinity of the QDs and solvents for the nanofiber surface as well as the nano and macro features of the nanofiber substrate. .



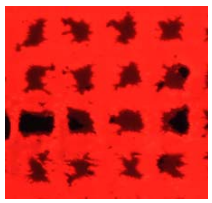
(A) Untreated nylon fibers, 1x layers of QDs



(B) Untreated nylon fibers, 10x layers of QDs



(C) Nylon fibers, 10x layers of QDs with surface treatment (method 1).



(D) Nylon fibers, 10x layers of QDs with surface treatment (method 2).

Figure 4. Surface treatments on nanofiber substrates effect pattern resolution.

In order to improve pattern resolution for multiple layers, several surface treatments were examined. As shown in Figure 4C, surface treatment 1 produced a significant improvement in the ability of the QD ink to hold a high resolution pattern on the nanofiber substrate. In contrast, surface treatment 2, actually produced a degradation in print quality (Figure 4D).

In producing white light for general illumination applications, proper blending of blue, green, and red light is critical to achieving high quality lighting. This is represented graphically using x,y chromaticity coordinates following the 1931 CIE convention. A typical chromaticity diagram is shown in Figure 5. High quality white light is produced when the x and y values lie near the Planckian Locus, which is the color point of black body radiators operating at various temperatures. In Figure 5, the Planckian Locus is represented as a black arc in the middle of the chromaticity diagram with the corresponding CCT values (in degrees K) indicated.

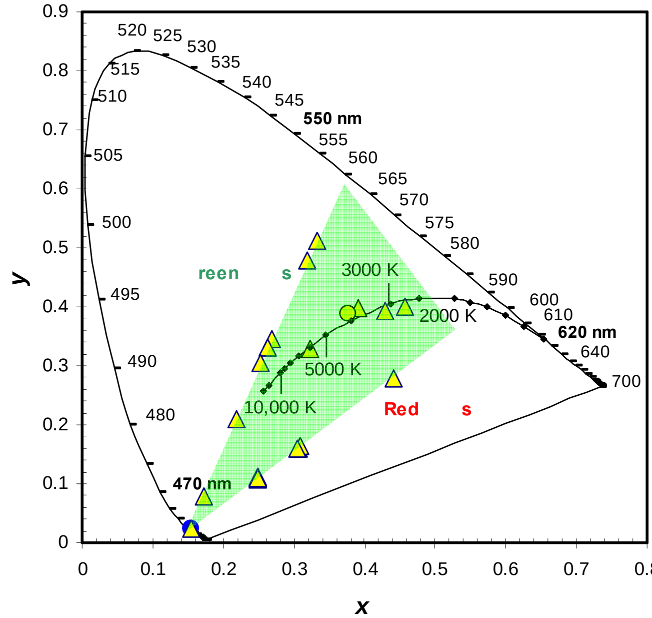


Figure 5. Chromaticity Diagram, after the 1931 CIE convention, containing examples of typical green and red PLNs fabricated at RTI. The green triangle shows the range of colors possible by blending PLNs of different colors.

To produce white light, PLNs containing green and red luminescent particles were deposited on the same nanofiber substrate using ink jet printing. These PLNs were incorporated into SSL devices such as the one shown in Figure 6. By adjusting the relative percentages of green, red, and blue emissions, a variety of white light illumination sources were produced. Using the chromaticity diagram in Figure 5, green PLNs of differing green luminescent particle concentrations form a straight line from the excitation wavelength (450 nm) to the dominant wavelength of the luminescent particle in the PLN. Likewise, red PLNs of differing red emitting particle concentrations lie along a straight line from the excitation wavelength to the dominant wavelength of the red particle. These two lines form the boundaries of the triangle highlighted in green in Figure 5. Any point within this triangle, including those on the Planckian locus, can be produced by appropriate blends of blue, red, and green emissions. Examples of white light produced by blending emissions from red and green PLNs (excited by a blue LED) are indicated by the points along the Planckian locus in the chromaticity diagram.

Figure 6. Prototype lighting device used to test the performance of PLNs made using ink jet printing.

4 CONCLUSIONS

Sustainable, high concentration PLP inks have been formulated and applied to nanofiber substrates. The substrates were electrospun using RTI's chambers and solution formulations. The resulting nanocomposites developed in this work are being used to create PLNs for SSL applications. These types of flexible polymeric PLNs are able to diffuse light and provide conformal panel lighting for inorganic LED-based luminary devices. The polymeric substrate of a PLN is low cost and mass producible. The LED-based, PLN-containing luminary device can be as efficient as a compact fluorescent light, with better color quality and lower environmental impact. Once optimized, the composite PLN structure fabricated in this work will provide enhanced flexibility to the designers of SSL fixtures.

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