Quantum Dot Conversion Layers Through Inkjet Printing


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Abstract
Quantum dot color conversion layers have the potential to greatly improve the efficiency and color performance of displays including and beyond liquid crystal displays. To fully realize these improvements, the quantum dots must be deposited and patterned at high resolution. One promising method for achieving this is through inkjet printing. In this paper we report on the fabrication and characterization of quantum dot inks, as well as films made from inkjet deposition of these materials.

Author Keywords
Quantum dot; color conversion; pixel; emissive display; LCD; display; micro-LED display; ink jet printing; patterning; color filter.

1. Objective and Background
The incorporation of quantum dots (QDs) has improved the efficiency and widened the color gamut of liquid crystal displays (LCDs).1 The current implementation of quantum dots in commercial products places the quantum dots in the backlight unit behind the LCD panel, typically in a Quantum Dot Enhancement Film (QDEF), and thus still relies on conventional LCD color filters to create red, green, and blue sub-pixels at the front of the screen. One method for further improving the performance of LCD panels both in terms of efficiency and color gamut is to move the quantum dot color conversion from a QDEF in the backlight into the color filter array (CFA) inside of the LCD panel itself. This significant architectural change replaces the color filter layer with a quantum dot conversion layer, thus creating a Quantum Dot Color Filter (QDCF).2 In addition, not only can QDCFs be used to replace the color filter layer in LCD panels, they can also be used as color conversion layers in OLED and micro-LED (μLED) displays.3,4

Quantum dot conversion layers can be deposited using conventional lithographic methods, but material usage, pixel pitch and yield requirements present many challenges. Inkjet printing, by contrast, uses a fraction of the material, and potentially allows for higher yield and cheaper manufacturing.5

2. Methods and Results
Materials and Methods: In order to create quantum dot conversion layers using inkjet printing, the QDs need to be formulated into a printable ink. These inks require high concentrations of QDs to achieve high color conversion efficiency in layers approximately 5 μm thick. At such high concentrations, completely Cd-free QDs must be used for RoHS compliance, which requires individual components in electronics to contain less than 100 ppm of cadmium within any homogenous layer of the system.6 In order to pattern the quantum dot layer onto each sub-pixel, the QDs and other ink components must be optimized for achieving the desired resolution and repeatability. This can be done by using inks with different curing mechanisms - thermal and UV. The work presented here will focus on thermal cure QD ink.

Ink Preparation: Green and red indium phosphide (InP) - zinc sulfide (ZnS) core-shell QDs were synthesized by traditional methods. The native ligands attached to the QD surface were then replaced by hydrophilic ligands through a ligand exchange process. This step makes the QDs compatible with the solvents or monomers.
typically used for printable inkjet inks. The process is illustrated in Figure 1. The QD dispersions were then mixed at high concentrations (15-50% loading) with other components to form a solution suitable for inkjet printing. Additionally, in order to achieve the desired level in certain optical properties (i.e. external quantum efficiency (EQE), blue light transmission), TiO2 scattering particles (5-20% loading) and a dispersant were added and dispersed thoroughly using a paint shaker.

Figure 1: QD production and dispersion process

To test the optical efficiency and reliability of QD ink films, the QD ink was coated onto glass substrates and then dried (100°C for 3 minutes in air) and cured (180°C for 10 minutes in nitrogen). These conditions are representative of the actual processing conditions for display manufacture. Uniform films of varying thickness were placed on a backlight with 450nm emission light. An integrating sphere was then placed on top of the QD ink film to collect the emitted photons as well as the amount of 450nm light transmitted through the film.

As expected, the amount of 450nm light transmitted through the film decreased as the thickness of the film increased (see Figure 2). In a final display, this blue light transmission reduces the color purity of the green or red sub-pixel, so a lower amount of blue light transmission is preferable. Although this can easily be accomplished using thicker films, other display factors may limit the maximum thickness of the QD film layer.

Figure 2 450nm light transmission as a function of film thickness

The external quantum efficiency (EQE) in this measurement is defined by the number of green or red photons emitted divided by the number of blue photons incident on the QD ink film. EQEs as high as 29.8% for green QD ink films and 38.2% for red QD ink films have been obtained after all of the above processing with films of thickness in the 4-9μm range (see Figure 3).

Figure 3. EQE as a function of film thickness
For reliability testing, these films were then encapsulated and exposed to high light flux at 50°C in order to approximate a 10x operational acceleration. Films were also placed in high temperature/dark storage (85°C) and high temperature/high humidity (65°C/95% RH) conditions. The optical performance for both green and red QD ink films shows little degradation after 1,000 hours.

QDCFR fabrication by inkjet printing: Using a commercial inkjet machine (Fujifilm DIMATIX DMP-2850) and inkjet printing head (DMC-11610), single color pixel arrays were fabricated on identical 30mm x 30mm black matrix substrates. The photo-patterned black matrices had a width of 20um, a thickness of 10.6um, and produced 280um x 80um pixels (see Figure 4). Since the emission from quantum dots is isotropic, the blue sub-pixel in an LCD display using a quantum dot conversion layer will require scattering to ensure angular color uniformity. The blue pixel array was printed with a clear ink containing scattering particles. The green and red pixel arrays were printed with QD ink. The blue, green, and red pixel arrays had film thicknesses of 6.2um, 6.0um and 6.1um respectively. Finally, a semi-transparent yellow pigment-containing filter was coated over the green and red pixel arrays, which reduces the blue light leakage through the printed features. Examples of the printed color filter devices made from thermal curing ink are shown in Figure 5.

Optical properties of inkjet printed films: The single color pixel arrays were placed on a blue LED backlight (with a nominal 450nm emission wavelength) and the peak emission wavelength, the full width-half maximum (FWHM) of the peak, and the amount of blue light transmission were measured (see Table 1).

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<tr>
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<th>Peak Wavelength (nm)</th>
<th>FWHM (nm)</th>
<th>Blue Transmission</th>
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<tbody>
<tr>
<td>Blue</td>
<td>449.2</td>
<td>20.5</td>
<td>30.4%</td>
</tr>
<tr>
<td>Green</td>
<td>546.4</td>
<td>40.0</td>
<td>0.4%</td>
</tr>
<tr>
<td>Red</td>
<td>640.6</td>
<td>39.1</td>
<td>0.2%</td>
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Table 1. Optical properties of single color pixel arrays.

Using the measured optical properties of the single color pixel arrays given in Table 1, a display comprising of those printed QD ink sub-pixels would have a DCI-P3 color gamut coverage of 87.7% and a BT2020 color gamut coverage of 75.7% (both values calculated in the CIE 1976 color space).

One of the primary features of quantum dots is the ability to tune the peak emission wavelength simply by adjusting the size of the quantum dots. Thus, improved color gamut coverage can be achieved by optimizing the peak emission wavelength for a particular color gamut (the peak emission wavelengths for maximizing DCI-P3 color gamut coverage are different than those for maximizing BT2020 color gamut coverage). In addition, reducing the FWHM of the emission can also improve the color gamut coverage by producing more saturated colors.

Recent QD ink formulations have achieved peak wavelengths for optimal DCI-P3 gamut coverage in a 6μm thick layer. Similarly, QD ink films with FWHM as narrow as 36nm have also been achieved. Table 2 shows the calculated color gamut coverage for the demonstrated QD ink film above, QD ink film with the same optical
properties as previously demonstrated but with optimized peak wavelengths, and QD ink film with both optimized peak wavelengths and improved FWHM.

<table>
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<tr>
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<th>DCI-P3</th>
<th>BT2020</th>
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<tbody>
<tr>
<td>Demonstrated</td>
<td>87.7%</td>
<td>75.7%</td>
</tr>
<tr>
<td>Optimized Wavelengths</td>
<td>98.7%</td>
<td>85.4%</td>
</tr>
<tr>
<td>Optimized Wavelengths + Improved FWHM</td>
<td>99.0%</td>
<td>87.6%</td>
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**Table 2.** Calculated color gamut coverage for demonstrated and optimized QD ink color conversion layers.

Optical Efficiency: Using an optical model for the photon conversion efficiency of displays incorporating quantum dots (see Ref. 2), the optical efficiency of an LCD display with a QDCF can be compared with an LCD display using conventional QDEF. For this analysis, typical values for the optical properties of commercial QDEF (EQE, peak emission wavelengths, and emission FWHM) were chosen for a display targeting the DCI-P3 color gamut. In the QDCF case, the display modeled also targeted a DCI-P3 color gamut, but used optical properties already achieved in QD ink film. At a final display white point of D65 for both cases, a QDCF using QD ink color conversion layers with demonstrated EQE values have a 75% higher photon conversion efficiency (see Table 3). Improvements to the EQE of QD ink film will only further increase the optical efficiency gain relative to QDEF.

<table>
<thead>
<tr>
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<th>Relative Optical Efficiency</th>
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<tbody>
<tr>
<td>QDEF</td>
<td>100%</td>
</tr>
<tr>
<td>QDCF</td>
<td>175%</td>
</tr>
</tbody>
</table>

**Table 3** Optical efficiency comparison between QDCF and QDEF

3. **Impact**

We have demonstrated the viability of inkjet-printed QD color conversion layers for LCD and emissive displays. Cadmium-free quantum dots can be made compatible with materials and processes used for inkjet printing. We have also fabricated patterned arrays using inkjet printing, with feature sizes relevant to large area displays. The efficiency, color gamut and viewing angle of displays can be improved while reducing manufacturing costs through minimal material usage. Inkjet printing of QD color conversion layers has the potential to disrupt the incumbent LCD technology, as well as accelerate the development of emerging display technologies such as μLEDs.

4. **References**