Method for fabrication of saturated RGB quantum dot light emitting devices

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ABSTRACT

Creation of patterned, efficient, and saturated color hybrid organic/inorganic quantum dot light emitting devices (QD-LEDs) is dependent on development of integrated fabrication and patterning methods for the QD layer. We show that micro-contact printing can be applied to QD deposition, generating micron-scale pattern definition, needed in pixilated-display applications. We demonstrate saturated color QD-LEDs with external quantum efficiencies in excess of 1%. Combining this technique with the use of wide optical band gap host materials, and a new synthetic route for the creation of blue emitting (CdS)ZnS nanocrystals, it is now possible to fabricate QD-LEDs with saturated color emission in the red, green and blue regions of the spectrum.

Keywords: nanocrystal, quantum dot, light emitting device, micro-contact printing, QD-LED.

1. INTRODUCTION

The luminescence of inorganic core-shell semiconductor nanocrystal quantum dots (QDs) can be tuned across much of the visible spectrum by changing the size and semiconductor core material of the QDs while preserving a spectral full width at half maximum (FWHM) as narrow as 30nm and photoluminescence efficiency of 50%[1]. Organic capping groups, surrounding the QD lumophores, facilitate processing in organic solvents and their incorporation into organic thin film light emitting device (LED) structures[2]. Prior work shows that hybrid organic/inorganic QD-LEDs can indeed be fabricated with high brightness and small spectral FWHM[3], and that this process can be generally applied to the fabrication of QD-LEDs containing a wide range of particle core materials, sizes and overcoating shell thicknesses[4]. This has served to demonstrate that integration of QDs into organic LEDs has the potential to enhance the performance of thin film light emitters, and promises to be a rich field of scientific endeavor.

1.1. Motivation

Organic light emitting devices (OLEDs) have been identified as a dominant new technology poised to realize the next generation of flat panel displays (FPDs). OLED performance is exemplified by wide viewing angles, high color contrast, and low power consumption as compared to emissive liquid crystal displays[5]. Indeed, internal quantum efficiencies can approach 100% when organic phosphorescent molecules are used as the emitting materials[6]. A significant challenge of today's OLED technology remains the identification and synthesis of organic lumophores compatible with electrically pumped device structures[7]. Only a handful of efficient and long-lived organic phosphors have been incorporated into laboratory devices, while the ongoing research is aimed at the chemical design of new molecules, especially in the blue part of the spectrum[8]. As such, inorganic quantum dots (QDs) have generated interest in the OLED community as efficient alternative lumophores, whose saturated color emission can be tuned across the visible spectrum[4].

Because FPDs are the prime motivators for this line of investigation, it is important to have a complete picture for how QD-LEDs would fit into the mix of FPD technologies. In order to do this, however, a roadmap for the realization of QD-LED FPDs must exist. While prior work has focused on proof of concept demonstrations of individual QD-LED pixels, this work relied upon fabrication techniques that are not compatible with production of full-color emissive displays[9]. Additionally, all of the efficient LED demonstrations have been utilizing the well developed (CdSe)ZnS

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Light-Emitting Diodes: Research, Manufacturing, and Applications IX, edited by
Steve A. Stockman, H. Walter Yao, E. Fred Schubert, Proc. of SPIE Vol. 5739
(SPIE, Bellingham, WA, 2005) · 0277-786X/05/$15 · doi: 10.1117/12.590708

core-shell QD material system, and while this has yielded proof of concept demonstrations of high performance devices it does not demonstrate the crucial element of an efficient blue emitter[10]. It is possible to synthesize blue emitting CdSe core particles, but these nanocrystals tend to be less efficient and more difficult to process than the larger green and red materials.

1.2. Quantum Dots as Lumophores

Inorganic semiconductor QDs are nanocrystals that are of smaller diameter than the Bohr exciton in a bulk crystal of the same material. By reducing the size of the nanocrystal core, quantum confinement effects lead to an increase in the band edge exciton energy. As shown in Figure 1 for CdSe nanocrystals, quantum confinement increases the exciton energy from a bulk bandgap of 1.7 eV (corresponding to wavelength, λ = 730 nm and the red edge of the visible spectrum) to any value up to 2.75eV (corresponding to λ = 450 nm and blue luminescence)[11]. By utilizing different core materials with correspondingly different bulk bandgaps, one can tune the band edge QD emission over much different ranges of the spectrum. In the case of PbSe nanocrystals this tuning range is from 1.2-2.4μm yielding near infrared emission[12]. A large body of work has shown that QDs of almost any wavelength from ultraviolet to infrared are achievable.

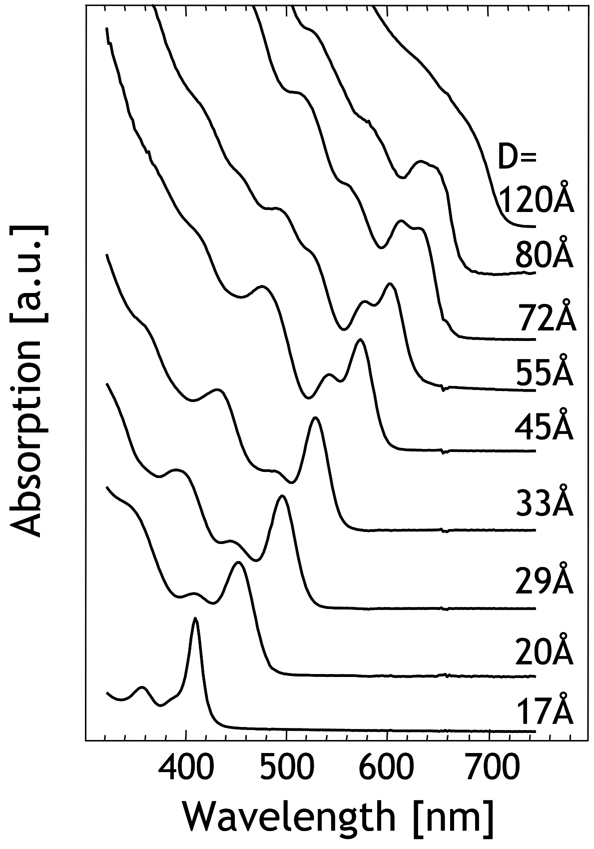

Figure 1: Absorption spectra of quantum dot solutions demonstrating a size tuning series of CdSe core QDs. (After reference 11.)

In addition to tuning QD properties via the core material and size, QDs offer other levers for manipulation of their basic properties. The QD shell material and thickness may be designed (see Figure 2), as well as which capping molecules passivate the inorganic surface of the QD[13]. In this way QDs, unlike typical organic small molecules, can be designed for a specific wavelength and application without effecting the solubility and processing properties of the material. The use of a shell layer also isolates the QD from its environment, and increases the material stability. This inherent difference between material sets makes QDs an attractive choice for the lumophore in thin film light emitting devices.

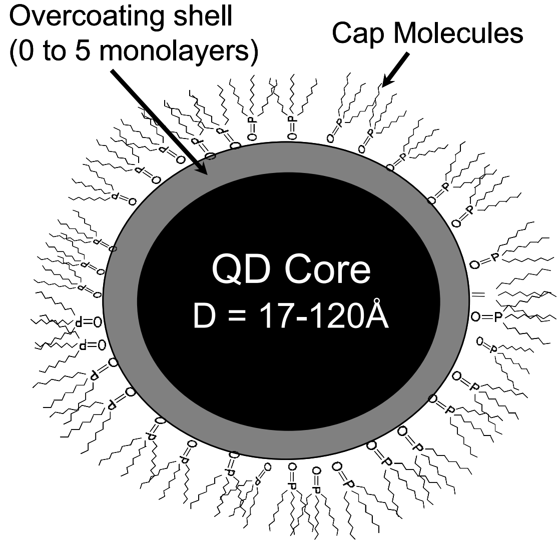

Figure 2: Cartoon of a core-shell-cap semiconductor nanocrystal quantum dot.

Because of the narrow luminescence spectrum that is the norm for high quality preparations of QDs, a large color gamut is accessible to LEDs using QDs as the primary lumophore. Figure 3 shows the Commission International d'Eclairage (CIE) chromaticity diagram, the cathode ray tube television

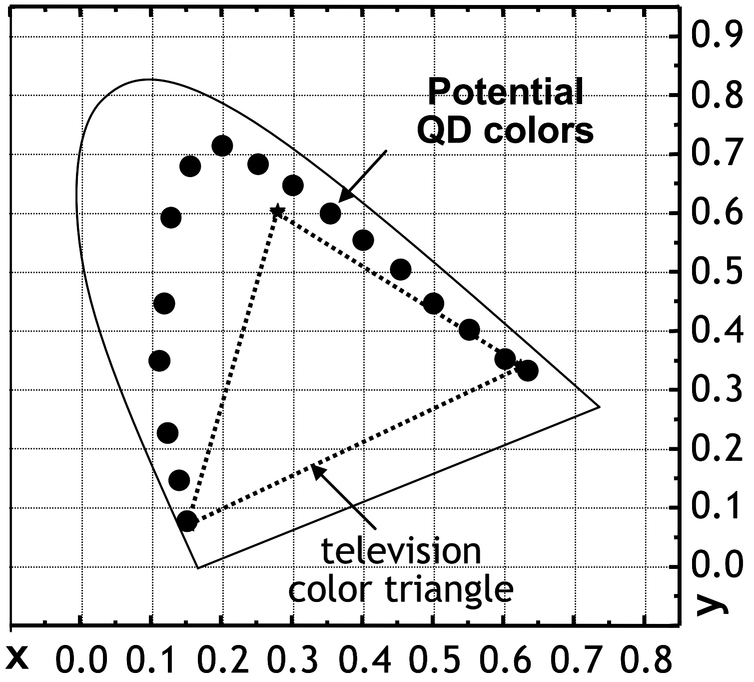

Figure 3: CIE chromaticity diagram depicting the cathode ray tube color standard and the potential QD emission colors.

color standard which is defined in reference to it, and the colors of QDs plotted in this coordinate system. The area encompassed by this arc of QD points demonstrates the quality of color saturation that is possible. This is in contrast to organic small molecules, whose broadband emission encompasses a smaller area on the CIE chart.

2. MATERIALS DEVELOPMENT – BLUE LUMINESCENT NANOCRYSTALS

λ [nm]	Relative Sensitivity	CIE Coord.
380	0.00004	
400	0.0004	
420	0.004	
440	0.023	0.16, 0.014
460	0.06	0.14, 0.035
480	0.139	0.11, 0.13
500	0.323	0.047, 0.46

Table 1: Human eye sensitivity and CIE coordinate for blue light emission.

The ability to synthesize semiconductor nanocrystals with narrow size-distributions and high luminescent efficiencies has made QDs an attractive alternative to organic molecules in applications such as optoelectronic devices[2, 14] and biological fluorescence labeling[15-17]. Efficient red and green emitting QD-LEDs have been realized with (CdSe)ZnS core-shell nanocrystals, but blue QD-LEDs remained elusive due to a lack of blue emitting core-shell material. The ideal blue emission spectrum of an LED for a flat panel display application would have a narrow bandwidth and a wavelength such that its coordinates on the CIE chromaticity diagram would lie to the outside of the current National Television System Committee (NTSC) standard color triangle. For a gaussian emission spectrum with a full width at half maximum (FWHM) of 30 nm and a maximized perceived power, the ideal wavelength of blue emission for display applications is ~470 nm. This choice represents a trade off between perceived power of the emission, and the perceived blueness of the emission, as shown in Table 1. Wavelengths bluer than 470 nm become difficult for the human eye to perceive, while those redder than 470 nm have coordinates that lie inside the standard NTSC color triangle. In a recent work, core-shell QD materials were synthesized that met these ideal spectral characteristics and show potential as an active material in a blue emitting QD-LED.

In order to choose a semiconductor core material for achieving this ~470nm emission wavelength, first a list of the known semiconductors and their bandgaps was assembled. This list was quickly pared down to only those candidates with a bulk band gap within a one eV of the energy of interest (Table 2). Finally, the strengths of each candidate were assessed, and the ideal choice became apparent, CdS. This is because of known difficulties in synthesizing stable and efficient materials at the required sizes for each of the other core materials.

Semiconductor Core	**Problems**
CdSe	NCs are too small (<2 nm in diameter)
ZnSe	Band gap is too blue (440 nm)
ZnTe	Difficult to synthesize large (>4.5 nm) NCs
CdS	***None***

Table 2: Identified candidate materials for blue luminescent nanocrystal cores.

In contrast, early work suggested that CdS cores tuned to around 460-480nm could in fact be synthesized with narrow size distributions and reasonable quantum yields[18]. However, bare CdS cores tend to emit deep-trap white luminescence that overwhelms the blue emission. A procedure for the growth of CdS nanocrystal cores of appropriate size, with narrow size distributions, and a robust, reproducible method for overcoating these cores with ZnS was what was missing. Our recent report of core-shell (CdS)ZnS nanocrystals exhibiting bright blue (quantum efficiencies = 20-30 %) and narrow band edge luminescence (FWHMs ≤ 28 nm) from 460 nm to 480 nm, filled in this gap[10]. That same report also demonstrated preliminary results of blue EL from these core-shell nanocrystals by embedding them in an organic thin film device.

3. DEVICE DESIGN

Once efficient, stable, and narrowband QD materials have been identified in the red, green, and blue portion of the spectrum, we can turn our attention to the design of QD-LEDs utilizing these novel materials sets. The motivation for this is to use the unique emission properties of the QDs in an electroluminescent device. However, the electrical conduction properties of QD thick films are known to resemble those of insulators, motivating us to use the QDs solely as lumophores within our devices, and to isolate them from playing any part in conduction of charge carriers within the device. This is shown in the energy band diagrams of Figure 4. For a thick film of QDs, the energy barriers to electron or hole conduction are large. However, if we design a device which utilizes only a single

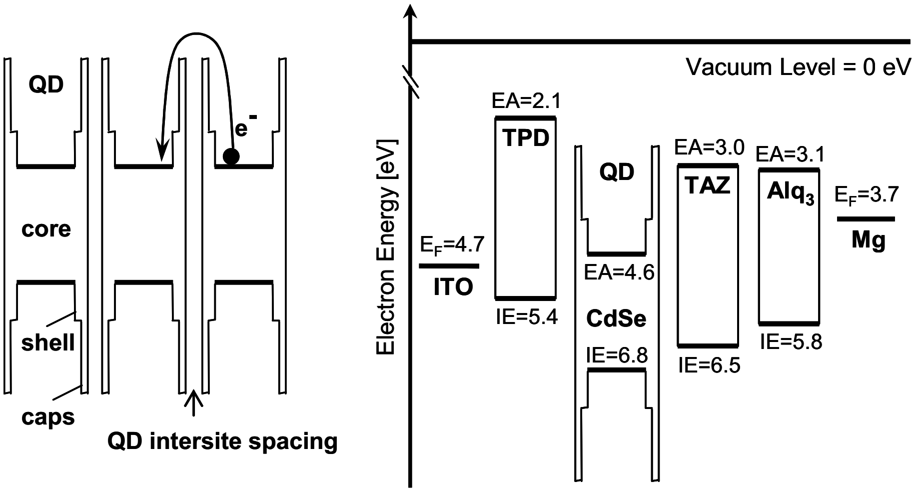

Figure 4: Energy band diagrams for QD multilayers versus a device designed around a single monolayer of QDs. For multilayers of QDs, electrons must overcome large energy barriers for transport to occur. In the case of a single monolayer of QDs, the QDs do not need to participate in conduction processes – their role as lumophore is isolated from that of charge conduction layers. (After reference 3.)

monolayer of QDs, located where the electrons and holes meet within the layered structure (the exciton formation zone), no charge carriers ever need to be conducted by the QDs. Instead, excitons are formed on the QD monolayer, and the light emission is due to the QD lumophores.

4. FABRICATION

A discussion of the available fabrication methods to assemble such a device follows. Since the QDs are solution processible, we naturally seek out wet processing techniques that would take advantage of this property. The two methods discussed below have been successfully employed in the fabrication of efficient QD-LEDs based on the proposed device structure depicted in Figure 5.

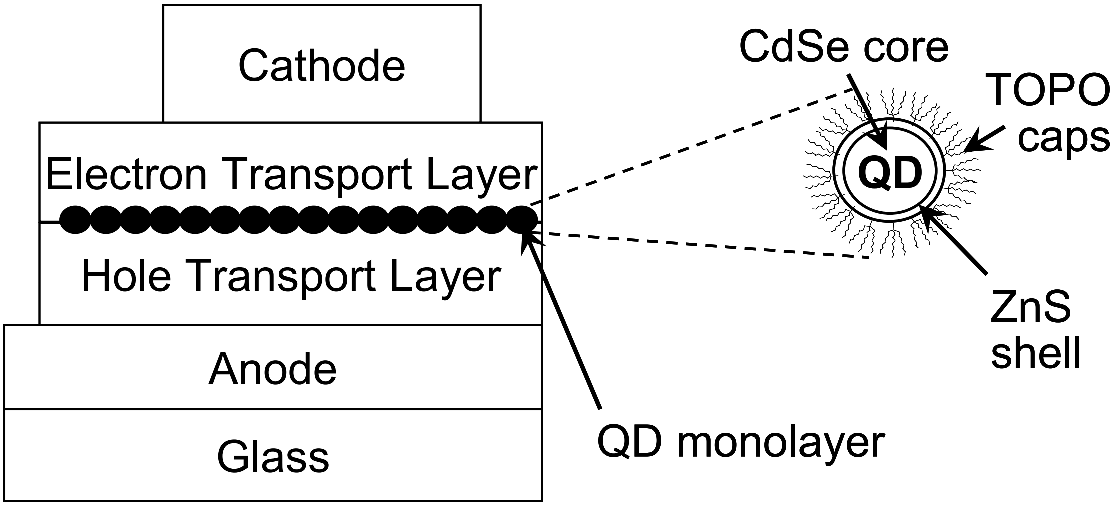

Figure 5: Diagram of the proposed device design. Using a single monolayer of QDs separates them from any role in conduction, allowing the creation of low voltage QD-LEDs.

4.1. Phase Separation

Phase separation is a well-established method for forming large area (> cm^2), ordered monolayers of colloidal nanocrystal quantum dots (QDs)[9]. The QD thin films are formed in a single step by spin-casting a mixed solution of aromatic organic materials and aliphatic-capped QDs. The two different materials phase separate during solvent drying, forming the desired QD monolayer assembled on top of the organic semiconductor contact. Previous work has shown the robustness and flexibility of this phase separation process, as well as how the properties of the resulting films can be controlled in a precise and repeatable manner. Parameters such as solution concentration, solvent ratio, QD size distribution and QD aspect ratio can all affect the resulting thin film structure. Controlling these factors allows the creation of QD-LEDs with high efficiency and high color saturation.

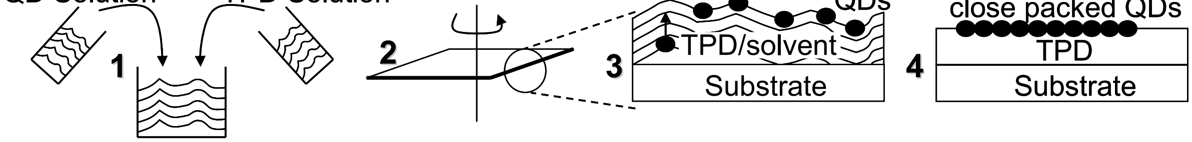

Figure 6: Process flow for phase separation technique applied to the assembly of a QD monolayer on top of an organic hole transporting semiconductor contact. (After reference 9.)

The fabrication of a monolayer sheet of close-packed QDs by phase separation during spin-casting is in essence a very simple process, as depicted in Figure 6. The process relies upon the solvation of both the organically capped semiconductor QDs and the organic material to be used as an underlayer in a compatible solvent system. During solvent drying, the QDs phase separate from the organic underlayer material, and rise towards the surface of the film. When drying is complete, the organic material is in the form of a homogenous thin film, which is coated by a layer of QDs such as shown in Figure 7. For typical solvent systems, the film is dry well before equilibrium is achieved, and thus the film formation is arrested in a non-equilibrium condition. The exact structure and composition of the layer is completely determined by the composition of the spin-casting solution (for a fixed set of processing conditions). Hence, the material purity of the QD sample is of critical importance to the phase separation process.

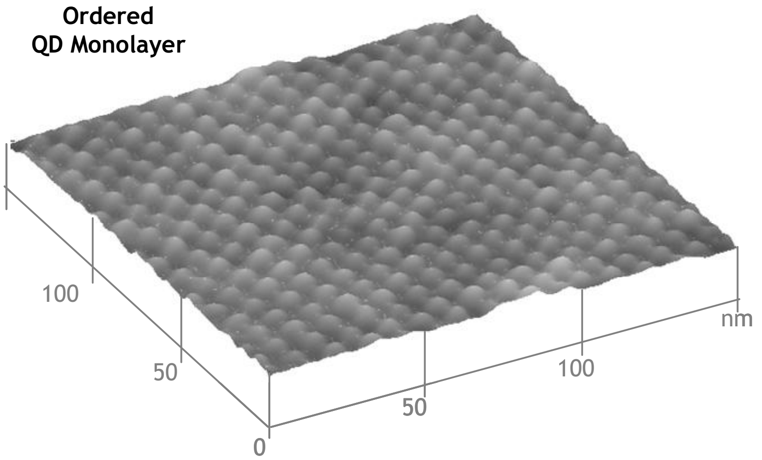

Figure 7: AFM image of a QD monolayer assembled via the phase separation process. Despite being frozen in a non-equilibrium state, the degree of ordering is high.

It has been demonstrated that the phase separation process is not critically dependant on any one component of the system. Phase separation and assembly of QD monolayer sheets occurs for a large number of substrates, solvents, organic underlayer materials, QD core materials, QD organic capping groups, QD diameters, QD size aspect ratios, spin-casting parameters and environmental conditions. The only known constraints on the phase separation process are 1) that there is a solvent or solvent system which dissolves both QDs and organics in the needed concentrations, and 2) that the solvent and organic layer wet the substrate surface.

However, this technique is far from ideal for all experiments and device applications. Phase separation requires that we co-deposit an organic thin film with the QD monolayer, something which is not always desirable. Additionally, this organic underlayer must be homogeneous, a constraint which limits the number of device designs which we can access. We are also only able to use organic materials that are highly soluble, and while this is not necessarily a limitation in the long term, currently the majority of organic small molecular semiconductors which have been studied are optimized for vapor phase deposition, not solubility. Finally, this technique successfully assembles QD monolayers over entire surfaces, but does not allow us to laterally pattern the red, green and blue QD monolayers adjacent to each other, something which is clearly desirable should we want to make a full color QD-LED display.

4.2. Micro-contact printing

Thus a fabrication process that would allow for in plane patterning of QD monolayers is desirable, provided that it not place additional constraints on the materials or device designs that it can be used with. Indeed, the ideal QD fabrication technique would involve the dry (solvent free) application of an already patterned QD film to any substrate, removing all solubility and surface chemistry requirements on the substrate which are typical and to some extent assumed within the field. To satisfy this need, we have extended the method of micro-contact printing to QD monolayer deposition.

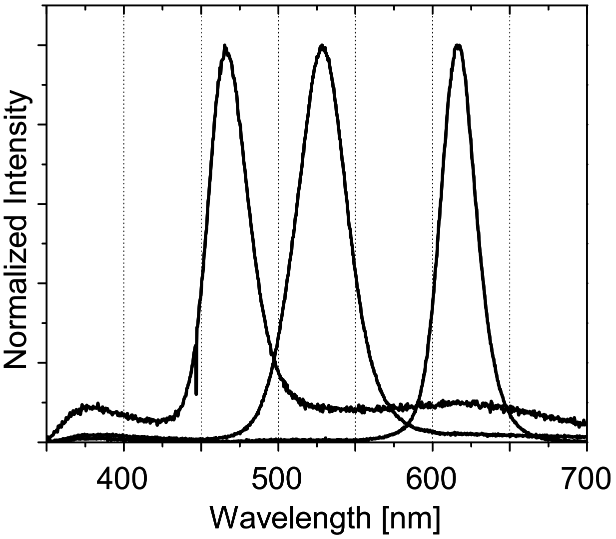

Figure 8: Emission spectra of red, green, and blue QD-LEDs fabricated via micro-contact printing. (After reference 20.)

Figure 8 shows device electroluminescence spectra for red, green, and blue QD-LEDs fabricated using our QD micro-contact printing technique. Red, green, and blue emitting QDs were all printed onto a thermally evaporated thin film of 4-4'-N,N'-dicarbazolyl-biphenyl (CBP) (HTL). The micro-contact printing of QDs is a dry process that no longer introduces impurities into our hole transport layer fabrication, allowing all of the organic layers in the device to be deposited under ultra-high vacuum conditions, exposing the organics only once to nitrogen environment for the deposition of the QD layers, and all in the absence of solvent. The QD deposition is followed by the deposition of the hole blocking layer (HBL) 3-(4-Biphenylyl)-4-phenyl-5-tert-butylphenyl-1, 2, 4-triazole (TAZ) and the electron transport layer (ETL) tris-(8 hydroxyquinoline) aluminum (Alq_3), and finally an evaporated Mg:Ag/Ag cathode (50:1 Mg:Ag by weight) to complete the device fabrication.

The ability to separate the deposition of the organic HTL/HIL from that of our QD monolayers has allowed us to explore the use of other molecules for the HTL/HIL and in particular the large band gap organic semiconductor, CBP. Previously our QD-LEDs used N,N'-diphenyl-N,N'-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD) as the HTL, due to its good solubility in chloroform and chlorobenzene compared to many other HTL candidates. We have found that the larger band gap CBP molecule produces far better color saturation in our devices, as exemplified by Figure 8. The greater observed color saturation could be attributed to the larger downhill energy transfer process now available with the use of CBP[19], which results in a decrease in the intensity of organic emission and an increase in intensity of QD emission, leading to the larger ratio between the QD electroluminescence (EL) and organic EL. The observed increase in ratio of QD EL to organic EL in our devices is also possibly due to the ever increasing photoluminescence (PL) quantum efficiencies of the QDs themselves.

The color saturation of red and green QD-LEDs is represented by their position on the CIE diagram relative to the current High Definition Television (HDTV) standard color triangle as seen in Figure 9. The blue QD-LED CIE color coordinates lie just inside the HDTV standard color triangle and is a result of the red tail seen in the blue QD-LED EL spectrum. Currently the red EQE is 1% using QDs with PL quantum efficiencies of 70% after processing and preparing for device use, our green emitting QD-LEDs have EQEs of 0.5% using QDs with PL quantum efficiencies of 40%, and our blue EQE is 0.25% using QDs with PL quantum efficiencies of 20%. All three color QD-LEDs have reproducible, stable, current-voltage (IV) characteristics, with turn on voltages of 2-5 V and operating voltages of 8-12 V. Display brightness (100 cd/m^2) is achieved at ~2 mA/cm^2 and ~10 V for these QD-LEDs.

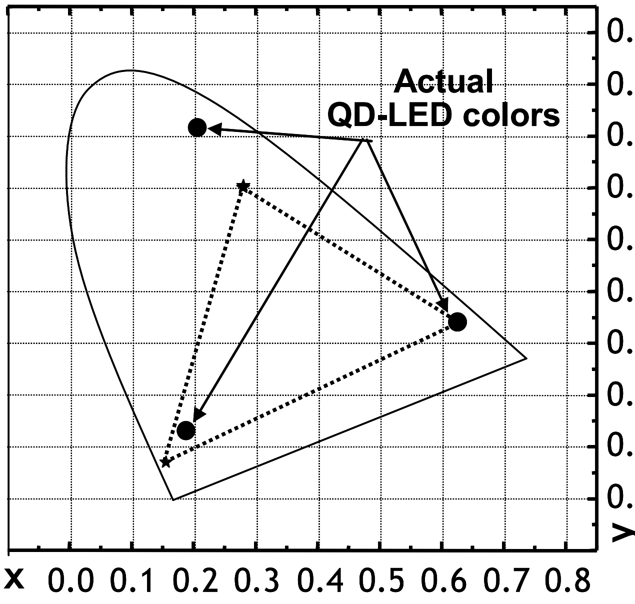

Figure 9: CIE diagram showing actual QD-LED color coordinates relative to the NTSC color triangle (dotted lines). (After reference 20.)

5. CONCLUSIONS

In conclusion, we demonstrate red, green, and blue emitting QD-LEDs that are efficient, highly color saturated, and which can be patterned laterally for full color display applications by means of micro-contact printing of single layers of nanocrystals. The use of micro-contact printing of nanocrystals to fabricate LEDs has tremendous potential for flat panel display technology. However, phase separation of QDs from organics could still have niche roles in QD-LED fabrication where cost is of extreme importance, and lateral patterning is not necessary, for example in the construction of white light emitting QD-LEDs for general lighting application. In this case, the development of a highly soluble, high bandgap molecular organic semiconductor remains. The completion of a toolkit of easily processed, highly emissive, stable QD materials has allowed QD-LEDs to reach technological significance.

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