Inorganic Quantum Dots in Organic Host Matrices for Efficient LEDs

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Much effort has been devoted to improving the performance of Organic Light Emitting Devices (OLEDs) by increasing their efficiency, narrowing or broadening their emission spectra, or polarizing their emission. In this work we examine the benefits of incorporating other material systems within organic host matrices to generate efficient hybrid organic/inorganic LEDs of saturated color. Specifically, we describe OLEDs incorporating CdSe nanocrystallites, or Quantum Dots (QDs).

It has already been demonstrated that nanocrystallites of CdSe coated with a ZnS passivation layer have photoluminescence (PL) quantum efficiencies of as high as 50%, matching that of the best organic lumophores. By changing the diameter of the CdSe core from 23 to 55Å, the luminescence wavelength can be precisely tuned from λ = 470 nm to λ = 640 nm with a typical spectral full width at half of maximum (FWHM) of less than 40nm. The narrow FWHM of QDs results in saturated color emission. This leads to efficient QD-LEDs even in the red and blue parts of the spectrum, since in QD emitting devices no photons are lost to infrared and UV emission. The broadly tunable, saturated color emission over the entire visible spectrum of a single material system is unmatched by any class of organic chromophores. Furthermore, environmental stability of covalently bonded inorganic nanocrystals suggests that device lifetimes of hybrid organic/inorganic LEDs should match or exceed that of all-organic LEDs, when nanodots are used as luminescent centers. The degeneracy of the band edge energy levels of QDs facilitates capture and radiative recombination of all possible excitons, whether generated by direct charge injection or energy transfer. The maximum theoretical QD-LED efficiencies are therefore comparable to the unity efficiency of phosphorescent OLEDs. The QD's excited state lifetime (τ) is much shorter (τ ~10ns) than a typical phosphor (τ>1ms), enabling QD-LEDs to operate efficiently even at high current density.

In this study, we incorporate inorganic quantum dots into electrically pumped molecular organic structures to prove their efficacy in OLEDs and examine the mechanisms of their ElectroLuminescence (EL). Our basic device structure is shown in the inset of Fig.1, along with a schematic drawing of a core-shell type QD passivated with TriOctylPhosphine Oxide (TOPO) caps. The QD solutions, prepared by the synthetic technique of Murray *et al* [C.B. Murray, et al., J. Am. Chem. Soc. 115, 8706 (1993).], have emission spectra that peak at λ=570nm, with an absorption maximum at λ = 559nm. The CdSe core diameter is approximately 38Å, and is overcoated with 1.5 monolayers of ZnS. The QDs are mixed in various concentrations into a chloroform solution of N, N'-diphenyl-N, N'-bis (3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD), which is then spin-cast onto clean, ITO coated glass substrates, resulting in a 40nm thick film. A 50nm thick film of tris- (8-hydroxyquinoline) aluminum (Alq_3) is then thermally evaporated onto the TPD:QD layer, and capped by a 1mm diameter, 75nm thick (10:1 by mass) Mg:Ag cathode with a 50nm Ag cap. The spin-casting and device manipulation during growth is performed in a dry nitrogen environment, with moisture and oxygen content of less than 5 ppm. All measurements are done in air.

The choice of organic host for the QDs is limited by material deposition methods. CdSe QDs are typically arranged into thin films by spin-casting from solution. While spin-casting is possible for molecular organics, and typical for polymer organics, it limits the available organic matrix materials to those that are highly soluble in solvents such as toluene, hexanes and chloroform, which are the preferred solvents for the TOPO capped QD colloids. In order to have a large range of possible solution mixtures and film thicknesses, it is necessary to have organic solubility in the range of 10mg/mL. Such is the case for TPD in chloroform. TPD has the added advantage of being a blue emitting material,

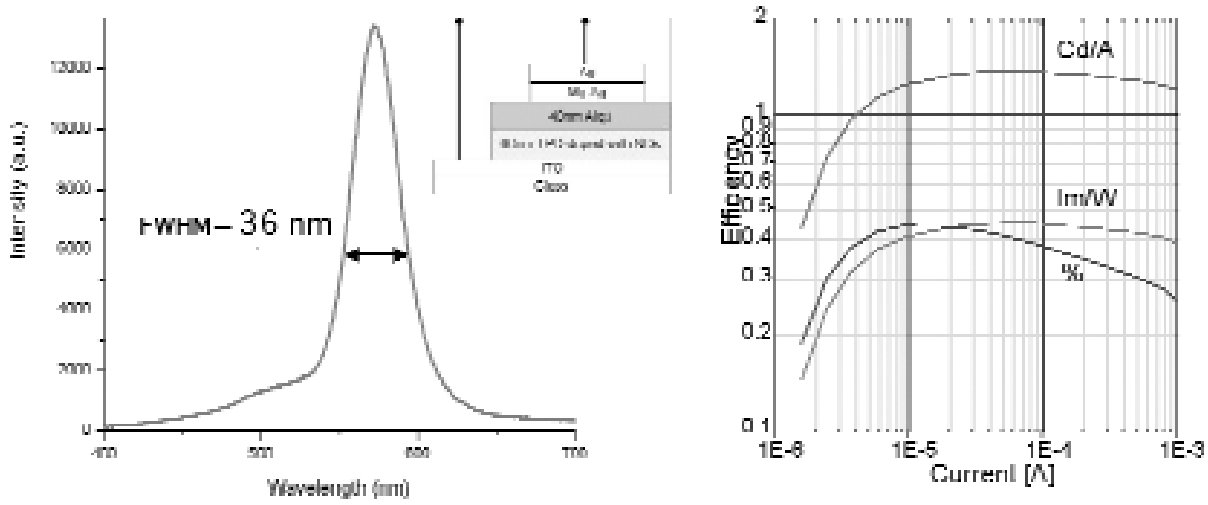

Fig. 18: Hybrid organic/inorganic light emitting device (HOI-LED). (Inset) HOI-LED cross section. (left) Electroluminescence spectrum at ~100 cd/m^2. (right) HOI-LED quantum efficiency in percent units, and luminescence efficiency in units of Cd/A and lm/W.reproducing the experimental data. A spectral shift towards lower energies is observed.

which can facilitate access to the entire visible spectrum by doping different sized QDs into this organic matrix.

A typical QD-LED emission is shown in Figure 18. The spectral peak at 570nm is due to the QDs, and the broader shoulder centered at 530nm we attribute to Alq_3 emission. The external quantum efficiency of QD-LEDs as a function of current is also shown in Fig.5, with the current-voltage plot for the same device shown in the inset. The peak quantum efficiency is 0.45% at 7mA/cm^2. At 125mA/cm^2, the LED luminance is 1500cd/m^2, which corresponds to a luminescence efficiency of 1.2 cd/A. This is a 20 fold improvement over the best previously reported QD-LED result [M. C. Schlamp *et al*., J. Appl. Phys. 82, 5837 (1997).]. Device yields over hundreds of devices are greater than 90%, indicating a robust material system.

The spectrum and efficiency of QD-LEDs strongly depends on QD concentration in the TPD matrix. For low concentrations of QDs the device behavior is similar to an undoped structure, and at extremely high QD concentrations we observe a morphology change in the QD doped layer that leads to poor device performance and low yields. The thickness of the TPD:QD layer also plays a critical role in determining the device properties. With a thick TPD:QD layer, the Alq_3 emission is completely suppressed at the expense of lower quantum efficiency and higher turn-on voltage of the device. Thinning this layer leads to an excess of hole injection, and thus enhanced Alq_3 emission.

The observed spectra also show a minimal dependence on current density. Deep trap emission from the QDs is always present as a weak EL tail red-shifted from the main emission peak, but it saturates at very low currents (<1mA/cm^2). This deep trap emission is enhanced when incorporating core only QDs, rather than the core-shell type QDs utilized in our best devices. With the less stable QDs, the deep trap emission saturates at much higher current densities (~100mA/cm^2), resulting in LEDs with significant

emission in the infrared. For optimum visible LED performance the overcoated dots are clearly preferred, though this observation may prove important as a means of characterizing the relative density of deep trap versus core level states.

The fundamental limits of QD-LED performance are significantly different than those of OLEDs. Our QD-LEDs have an emission FWHM of 36nm. In contrast, typical molecular organic LEDs have a FWHM of between 60 and 100nm, although emission of some polymers and phosphorescent molecules was shown to be as narrow as 26nm FWHM. However, in all of these cases the fundamental limit on bandwidth has already been achieved through materials preparation and purification. The vibrational structure of sterically flexible organics typically generates broad single molecule emission spectra at room temperature. The same is not true of the rigid, covalently bonded inorganic QD, for which single QD spectroscopy shows that the fundamental FWHM linewidth of a QD at room temperature is 14nm. It is the combination of spectral diffusion and size distribution of QDs in a sample that yields further line broadening. Consequently, our 36nm linewidth corresponds to a size distribution of about 5%. It is reasonable to expect that new techniques in QD preparation and processing could lead to narrower QD-LED line widths. This true color saturation would be ideal for many applications where efficient production of narrowband light is desired. In particular, the creation of a high luminescent efficiency red LED requires both high external quantum efficiency as well as narrowband emission, to prevent the bulk of emission from occurring in the infrared where our eyes have minimal response. The deep trap emission that is typical of QDs could be problematic in achieving this goal, but the devices reported here already show less than 1% of their total power emitted in the infrared. This deep trap emission saturates at very low current densities. The spectral FWHM reported here is already an improvement over conventional OLEDs, and yet the fundamental limit has not been attained.