Quantum Dot Electroluminescence to Achieve Saturated Colours for REC2020 Compatibility

Poopathy Kathirgamanathan(PK) and Muttulingam Kumaraverl

Organic Electronics Group, Wolfson Centre, Department of Chemical Engineering, Brunel University London, Uxbridge, UB8 3PH, UK. e-mail: p.kathir@brunel.ac.uk
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ABSTRACT

Electroluminescent colloidal quantum dots have the potential to offer saturated colours satisfying the new more demanding REC 2020 (ITU-R-BT 2020) standard. This paper reports our attempt to match the REC 2020 colour co-ordinates with red (CdSe/Znse/ZnS) and (InP/ZnS) QDs. Using solvent based surface engineering of sol-gel derived ZnO electron injector layer, we achieved a current efficiency of 32.6 cdA^{-1} and a power efficiency of 18.6 lmW^{-1} at 1000 cdm^{-2} for Cd based QDs. We also report dark red electroluminescent InP/ZnS QDs ((x,y = 0.672, 0.325)) with a maximum current and power efficiency of 3.6 cdA^{-1} and 4.7 lmW^{-1} respectively.

1 INTRODUCTION

Researchers engaged in displays are actively searching for materials that would satisfy the new demanding display specification ITU-R-BT-2020 for high definition TVs. The usual fluorescent and phosphorescent emitters only achieve roughly 90% of NTSC standards. Typical quantum dots include CdSe/ZnS, InP/ZnS and $CuInS_2$. The toxicity of Cd necessitates that less toxic alternatives are sought. Amongst these, InP/ZnS is regarded as the most promising candidate due its narrowness of emission and the possibility to manufacture stable quantum dots by alloying (1-23). Quantum dots offer saturated colours, narrow emission (FWHM, 25-30 nm) as opposed to standard OLED emitters with FWHM of 50-60 nm) and control over the emitted wavelength by varying the quantum dot size and composition. Rare earth chelates and Perovskites offer even narrower emission peaks (FWHM < 20 nm), but their device efficiencies and lifetimes are too low at present (6,8,12). While the efficiency of green QLEDs have exceeded that of PHOLEDs, the red and the blue are yet to achieve sufficiently high efficiencies. The life-times of QLEDs are not yet long enough for commercial acceptance.

This paper reports our successful effort to achieve the REC2020 colour co-ordinates for red with world record efficiency and reasonably long life time to be a serious contender to Red PHOLEDs.

Inverted devices **(Figure 1)** were fabricated using "home made ZnO nanoparticles (ZnO-M1)" by sol-gel method (particle size 3 -5 nm).

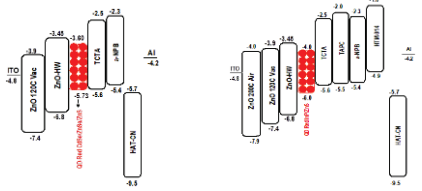


Figure 1. Energy level diagram of CdSe/ZnSe/ZnS (Left) and InP/ZnS (Right) devices.

Recent report by Ippen et al (25) of world class external quantum efficiencies for InP/ZnS systems of 16.9% (red), 13.0% (green) and 9% (blue) for the ZnSe based QD-EL (conventional device structure (ITO/PEDOT/TFB/QD /ZnMgO/Al) opens up the possibility of achieving even higher efficiencies if the quantum dots can be optimised with respect to the core/shell thickness/shell /organic ligand and appropriate charge transport layers developed or adapted. The authors claim that thy achieved these high efficiencies by optimising the shell layer thickness and minimising the interfacial strains by alloying (e.g. InP/ZnSeS/ZnS/Ligand). Mude et al reported (27) an external quantum efficiency of 10% upon aging inverted devices (ITO/ZnMgO/QD/TCTA /TAPC/ HATCN/Al) for 70 days.

While the performance of QLEDs based on CdSe/ZnS has improved dramatically over the last 5 years (Figure 2), the development QLEDs based on InP/ZnS is at its infancy.

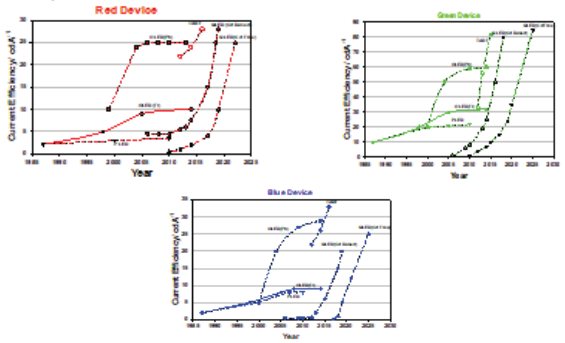


Figure. 2 Development of OLED, PHOLED, TADF , QLEDs (Cd based) and QLEDs (Cd Free).

The objective of the present work is aimed at optimising the efficiency of QD-EL devices by fine-tuning the energy level , minimising the barrier height and optimising the mobility of electron injector/ transport layer (ZnO-NP) in the inverted QLEDs by surface engineering of the ZnO-NP film by simple low temperature processing. The approach that we have adopted is to do surface treatment of ZnO films with solvent based surface engineering.

2 EXPERIMENT

We fabricated devices based on red CdSe/ZnSe/ZnS (RQD) (PL Efficiency in hexane 90±5 %) and InP/ZnS (PL Efficiency in hexane 45±3 %).

Type A: ITO/ZnO (NP) (40 nm, Brunel)/Red-CdSe /ZnSe /ZnS (25 nm) /TCTA (10 nm)/HTL (α-NPB or HTM-14)/ HATCN (10 nm)/Al

Type B: ITO/ZnO (NP)-**HW** (40 nm, Brunel) washed with hexane/ Red-CdSe/ZnSe/ZnS (25 nm) /TCTA (10 nm)/ HTL (α-NPB or HTM-14)/HATCN (10 nm)/Al

Type C: ITO/ZnO (NP)(40 nm, Brunel)/Red-InP/ZnS (20 nm) cast from hexane/TCTA/HTL((α-NPB or HTM-14) /HAT-CN (10 nm)/Al

Type D: ITO/ZnO-NP-**HW** (40 nm, Brunel)/Red-InP /ZnS (20 nm) cast from Octane solution/TCTA/HTL((α-NPB or HTM-14)/HAT-CN (10 nm)/Al

Type E: ITO/ZnO-NP-**HW** (40 nm, Brunel)-Washed with hexane/Red-InP/ZnS (20 nm) cast from Octane solution /TCTA/HTL((α-NPB or HTM-14)/HAT-CN (10 nm)/Al

The ZnO-NP (Sol-Gel) films (spin coated 3000 rpm) were annealed either at 120 ^{0}C in vacuum for 30 minutes or annealed in air at 220 ^{0}C in the furnace. All other layers including TCTA, α-NPB and HTM -14 (supplied by Merck) were evaporated (1 As^{-1}) and HATCN (evaporated at 0.5 As^{-1}) in an ULVAC OLED plant (Solciet, purchased from ULVAC, Japan) onto a patterned ITO/glass (100 mm x 100 mm) under a vacuum of 10^{-5} Torr. Deposition of the cathode also took place under vacuum ahead of device encapsulation in a nitrogen-filled glove box. QD films were dried at 80 ^{0}C in a vacuum oven for 10 minutes.

3 RESULTS & DISCUSSION

The average particle size of 7.6 ±1.7 nm (Red CdSe/ ZnSe /ZnS QD) and 8 ±1 nm InP/ZnS (Red) and 6±1 nm were obtained by TEM (Figure 3).

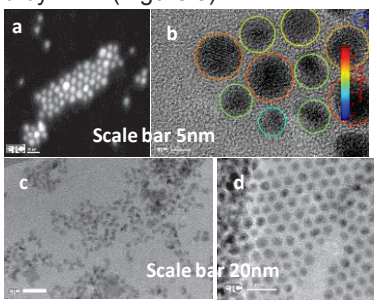


Figure. 3 a and b TEM- (CdSe/ZnSe/ZnS) . Fig. 3 (c)- Red InP/ZnS & Fig. 3 (d). Green InP/ZnS.

Figure 4 shows the absorption and the emission spectra of the red CdSe/ZnSe/ZnS and compared with red InP/ZnSe.

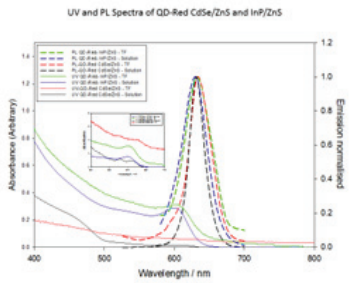
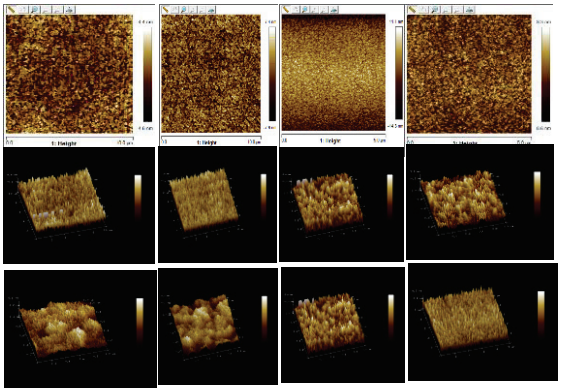


Figure. 4 Absorption and Emission Spectra of CdSe /ZnSe/ZnS and InP/ZnS in solution and thin films

The AFM images **(Figure 5)** shows the ZnO-NP film annealed at 120 ^{0}C for 30 minutes **(Figure 5 A)**, ZnO-NP-HW annealed at 120 ^{0}C for 30 minutes and then washed (treated) with hexane and then annealed at 80 ^{0}C for 30 minutes **(Figure 5B)**, ZnO-NP + QD **(Figure 5 C)** and ZnO-NP (HW) +QD **(Figure 5 D)**. The hexane causes the ZnO-NP surface to become rougher (R_a increasing from 1.16 nm to 1.85 nm). On depositing the QD onto ZnO-NP, R_a further increases to 2.90 nm and QD on ZnO-NP-HW, R_a reduces to 1.95 nm which is only marginally higher than the R_a of ZnO-NP-HW.



ZnO(120°C)	ZnO(120°C) +Hex Wash	ZnO(120°C) +QD	ZnO(120°C) +Hex Wash+QD
Rq :1.46nm	Rq :2.33nm	Rq :3.65nm	Rq:2.43nm
Ra :1.16nm	Ra :1.85nm	Ra :2.90nm	Ra :1.95nm

Figure. 5 AFM images of the ZnO-NP film annealed at 120 ^{0}C for 30 minutes **(Figure 5 A)**, ZnO-NP-HW annealed at 120 ^{0}C for 30 minutes and then washed (treated) with hexane and then annealed at 80 ^{0}C for 30 minutes **(Figure 5B)**, ZnO-NP + QD **(Figure 5 C)** and ZnO-NP (HW) +QD **(Figure 5 D)**.

It was interesting to note that crystallinity of ZnO-NP and ZnO-NP-HW films were found to be 61% and 93% respectively (Thin Film XRD is shown in **Figure 6).** The increase in crystallinity is consistent with the increase in the roughness of ZnO-NP on washing with hexane.

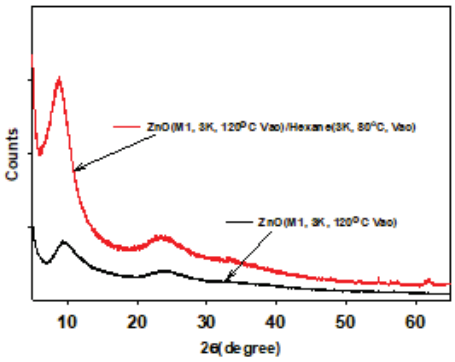


Figure 6: XRD of ZnO-NP (virgin) film and ZnO-NP-Hexane Wash (HW)

On treating the ZnO-NP with hexane (wash), the conduction and valence band are raised with respect to ZnO-NP-Virgin (see **Figure 7)** as determined from XPS/PES and from optical absorption edge (E_g). Further, we determined the mobility from the SCLC region of the electron only devices of (ITO/Al/ZnO-NP (virgin)/Al) and (ITO/Al/ZnO-NP-HW/Al) to be 3 x10^{-5} $cm^2V^{-1}s^{-1}$ and 9 x10^{-5} $cm^2V^{-1}s^{-1}$. The increase in mobility is also consistent with the increase in crystallinity.

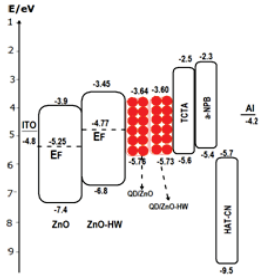


Figure 7. Energy level diagram of ZnO-NP (Virgin) and ZnO-NP-HW (Hexane washed/treated ZnO-NP)

3.1 Electroluminescent Devices Based on Red CdSe /ZnSe/ZnS.

Figure 8 illustrates the performance data for the devices Type A ITO/ZnO (NP) (40 nm, Brunel)/ Red-CdSe/ZnSe/ ZnS (25 nm) /TCTA (10 nm)/HTL (α-NPB or HTM-14)/ HATCN (10 nm)/Al and **Type B:** ITO/ZnO (NP)-**HW** (40 nm, Brunel) washed with hexane/ Red-CdSe/ZnSe/ZnS (25 nm) /TCTA (10 nm)/HTL (α-NPB or HTM-14)/HATCN (10 nm)/Al. The device performances are summarised in Table 1.

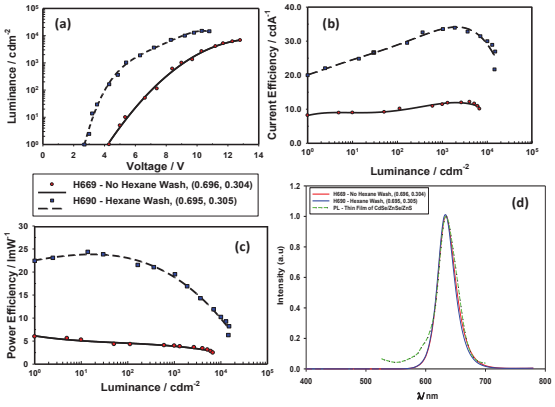


Figure. 8 Device Performance of **Type A and Type B (a)**. Luminance vs. Voltage, **(b).** Current Efficiency vs. Luminance., **(c).** Power Efficiency vs. Luminance., **(d).** Electroluminescence vs. photoluminescence spectra

Table 1. Device Performance for CdSe/ZnSe/ZnS devices. Type A and Type B.

Device I.D	Device Structure	CIE (x,y)	$V_{t\text{-}on}$ /V(a)	V_d/ V(b)	Current Efficiency /cdA^{-1}(b)	Power Efficiency /lmW^{-1}(b)	Max. Current Efficiency /cdA^{-1}	Max. Power Efficiency/ lmW^{-1}
Type A	ZnO-NP	(0.696, 0.303)	4.5	10.3	11.8	3.6	12.1	5.7
Type B	ZnO-NP –HW (Hexane Wash)	(0.695, 0.305)	2.8	5.5	32.6	18.6	32.6	23.4
Type B	ZnO-NP-HW, Thermal aging of the QLEDs at 40°C for 24 hours	(0694, 0.306)	2.7	5.0	31.5	19.8	33.0	22.5
Type B	ZnO-NP-HW, Thermal aging of the QLEDs at 40°C for 120 hours	(0.693, 0.305)	2.3	4.4	30.7	21.9	35.2	35.1

(a). At 1 cdm^{-2} , (b). At 1000 cdm^{-2}

Table 2: Device Performance for red InP/ZnS devices. Type C, Type D and Type E

Device I.D	Device Structure	CIE (x,y)	$V_{t\text{-}on}$ /V(a)	V_d/ V(b)	Current Efficiency/ cdA^{-1}(b)	Power Efficiency /lmW^{-1}(b)	Max. Current Efficiency/ cdA^{-1}	Max. Power Efficiency/ lmW^{-1}
Type C	ZnO-NP/InP/ZnS cast from hexane	(0.672, 0.325)	2.4	3.4	2.5	2.4	3.6	4.7
Type D	ZnO-NP-HW /InP/ZnS cast from Octane	(0.683, 0.313)	2.2	3.7	0.8	0.5	1.0	0.8
Type E	ZnO-NP/InP/ZnS cast from Octane	(0.683, 0.313)	2.2	4.6	0.6	0.5	0.6	0.6

(a): At 1 cdm^{-2}, (b). At 100 cdm^{-2}

3.2 Electroluminescent Devices Based on Red InP/ZnS

Electroluminescent devices of Type C: ITO/ZnO (NP)(40 nm, Brunel)/Red-InP/ZnS (20 nm) cast from hexane/TCTA/HTL((α-NPB or HTM-14)/HAT-CN (10 nm)/Al, **Type D**: ITO/ZnO-NP-**HW** (40 nm, Brunel)/Red-InP/ZnS (20 nm) cast from Octane solution/TCTA/HTL((α-NPB or HTM-14)/HAT-CN (10 nm)/Al and **Type E:** ITO/ZnO-NP-**HW** (40 nm, Brunel)-Washed with hexane/Red-InP/ZnS (20 nm) cast from Octane solution/TCTA/HTL((α-NPB or HTM-14)/HAT-CN (10 nm)/Al are shown in Figure 9. The device performances are summarised in Table 2.

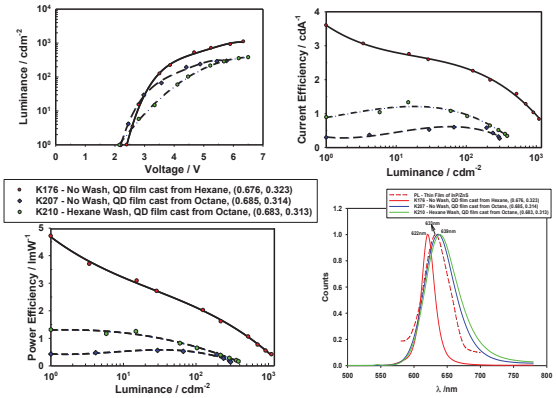


Figure 9. Comparison of InP/ZnS Device Performance: Type C, Type D and Type E

4 CONCLUSIONS

Using solvent based surface engineering of sol-gel derived ZnO-NP electron injector/electron transport layer, we achieved 2.76 fold increase in current efficiency to 32.6 cdA^{-1} and 5.17 fold increase in power efficiency to 18.6 lmW^{-1} at 1000 cdm^{-2} for Cd based QLEDs. We also report dark red electroluminescent InP/ZnS QDs ((x,y = 0.672, 0.325)) with a maximum current efficiency of 3.6 cdA^{-1} and 4.7 lmW^{-1}. We believe that the solvent based surface engineering has wide applicability and offers the scope for further improvement in QD –EL efficiency of InP/ZnS QD-EL.

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