Bright, Large Pixel, Flexible Quantum-Dot Light-Emitting Diodes for Photomedicine

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Abstract

Herein, we report flexible deep-red quantum-dot light-emitting diodes on ITO/PEN substrates with narrow bandwidth, long shelf-life, external quantum efficiency up to 8.3%, and high brightness of 42214 cd/m^2 (8 mm^2 pixel at 5.8 V) equivalent to 19.6 mW/cm^2.sr, which are ideal light sources for photomedicine, i.e. photodynamic therapy and photobiomodulation.

Keywords

Quantum dots, flexible quantum dot light emitting diodes, polyethylene naphthalate, shelf-life, photodynamic therapy, photobiomodulation

1. Introduction

Quantum dot light emitting diodes (QLEDs) have highly desirable properties for display, lighting and photomedicine applications, such as emission wavelength tunability (by controlling the QD size), high color purity, wide color gamut and high-power density [1-3]. Besides the optoelectronic properties, solution-processed QLEDs also offer simple/low-cost processing and high stability of the active materials [4]. QLEDs can also exhibit light weight and thin form factors when made on flexible substrates. Given all these properties, flexible quantum dot light emitting diodes (FQLEDs) are receiving special attention from the display industry [4,5]. However, limited device stability has been a formidable barrier holding their entry into display.

The authors' team first proposed photomedicine as a near term, high value-added target market for FQLEDs [6,7]. In particular, wearable and ergonomic FQLEDs with narrow emission bandwidth and high radiance at deep-red wavelengths are a promising alternative light source for practical and low-cost application in emerging photomedical therapies, i.e., photodynamic therapy (PDT) and photobiomodulation (PBM), also known as low level light therapy (LLLT). Efficacy of PDT treatment in cancer and other diseases, and beneficial clinical effects of PBM have been already proved [8]. However, the current commercial light sources (lasers or LED arrays) have fundamental limitations preventing widespread adoption of PDT and PBM, among them: bulkiness and high cost of laser systems, and poor flexibility/irradiance uniformity of LED arrays.

Recently, pioneer studies in PDT and PBM developed by our group revealed comparable results when using QLEDs or inorganic LEDs as red-light emitting sources [6]. Specifically, similar cell metabolism increase was observed under irradiation of different cell cultures with both sources. In the same work, both QLED and LED sources achieved photo-destruction of 3D tumor nodules, with enhanced PDT efficacy under QLED irradiation. QLED based antibacterial PDT and preliminary FQLEDs have also been developed and reported by our group [7]. This last in-vitro study demonstrated that QLED based PDT can effectively kill Methicillin-resistant *Staphylococcus aureus*, an antibiotic-resistant bacterium. The QLED photomedicine work also stimulated the revival of early OLED photomedicine studies [9], and led to recent demonstration of flexible microcavity OLED based in-vitro studies in PBM based wound healing [10] and antimicrobial PDT [11].

As the research on QLED based phototherapy continues, and its effectiveness has been demonstrated, the development of more stable and more efficient large-pixel FQLEDs is required for widespread acceptance and final commercialization into the health-care and photomedicine markets. In this last delivery, we report the performance of FQLEDs made on two commercial conductive substrates: Ag-stacked film on polyethylene terephthalate (PET) and ITO film on polyethylene naphthalate (PEN). The PEN based substrate promises better solution-process compatibility and gas barrier, since the ITO on PEN FQLEDs showed superior shelf-life and more stable performance. In addition, these devices can simultaneously sustain high current density and brightness without burning at low driving voltage, confirming better thermal stability of PEN based FQLEDs. Ultimately, we demonstrated deep-red emitting FQLEDs with external quantum efficiency up to 8.3%, low roll-off efficiency, low turn-on voltage (1.9 V) and high brightness of 42214 cd/m^2 at low voltage (5.8 V), equivalent to radiance of 19.6 mW/cm^2.sr

2. Results and Discussion

Using similar structure to that one of previously reported ultrabright deep-red inverted QLEDs [12], we followed essential steps to move from rigid to flexible QLEDs. New conductive substrates - with different treatment conditions - and flexible encapsulation were then proposed keeping the following structure: FCS/ZnO:Cs_2CO_3/CdSe-ZnS-CdZnS QDs/Spiro-2NPB/HAT-CN/Al. Where, FCS stands for the flexible conductive substrate acting as the cathode; ZnO:Cs_2CO_3 is a composite layer used as electron injection and transport layer, simultaneously; CdSe-ZnS-CdZnS core-shell-shell QDs are used as the material of the emissive layer (EML), 2,2',7,7'-tetrakis[N-naphthalenyl(phenyl)-amino]-9,9-spirobifluorene (Spiro-

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2NPB) as the hole transport layer (HTL), 1,4,5,8,9,11-hexaazatriphenylene-hexacarbonitrile (HAT-CN) as the hole injection layer (HIL), and aluminum (Al) as the anode. The specifications of the two FCSs are as follows: 1) an Ag-stacked film on PET purchased from TDK Japan, and 2) an indium tin oxide (ITO) film on PEN purchased from South China Xiangcheng Technology (SCXT). Both substrates had same thickness (125 µm), with no barrier and similar transmittance. Most importantly, the sheet resistance and maximum resistance temperature of the

Table 1. Properties of the two conductive substrates used for fabrication of FQLEDs (taken from data sheets)

	Ag stacked film on PET - TDK	ITO on PEN SCXT
Sheet resistance (Ω/sq)	3.7	6 - 8
Transmittance (%)	82.4	≥ 80
Tmax (°C)	125	150 - 200
Thickness (µm)	125	125
Barrier layer	No	No

ITO/PEN substrate were approx. twice larger and 25-75 °C higher, respectively, based on the manufacturer's data summarized in Table 1.

Fabrication of the hybrid organic-inorganic QLEDs was then carried out inside an N_2 filled glove-box, using a combination of solution process and vacuum evaporation techniques. Briefly, the flexible substrates were first baked inside a vacuum oven at 50 °C. Control devices without any baking were also made for comparison. Later, the substrates were treated inside an oxygen plasma chamber for a short time, in order to eliminate organic impurities and make the surface more hydrophilic. Right after plasma treatment, the ZnO:Cs_2CO_3 solution was spin-coated on the substrates. Subsequently, QDs in chlorobenzene were spin-coated on top of the ZnO nanoparticles (NPs). Both materials, the ZnO NPs and the CdSe-ZnS-CdZnS QDs were synthesized in our lab as reported elsewhere using the precipitation method [13] and the hot injection route [14], respectively. After spin-coating, the substrates were transferred inside a thermal evaporation chamber for deposition of the organic layers and the top metal contact. Finally, a Spiro-2NPB layer (100 nm), a HAT-CN layer (20 nm) and the Al electrodes (100 nm) were thermally

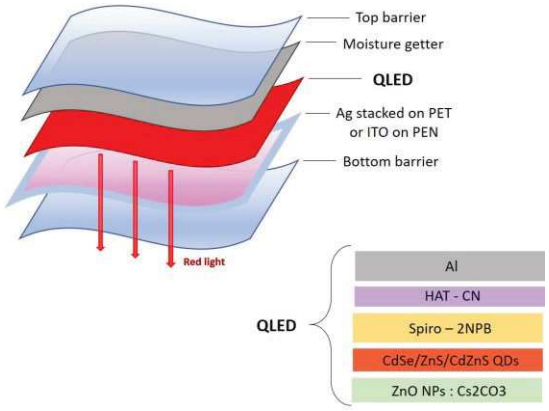

Figure 1. Final structure of flexible QLEDs after the encapsulation step. And multilayer structure of the inverted QLEDs.

evaporated under high vacuum (6 x 10^{-7} – 1 x 10^{-6} mbar).

For encapsulation of the devices, a flexible getter was first laminated on top, and later, barrier films from the Holst Centre [15] were laminated on top and bottom of each

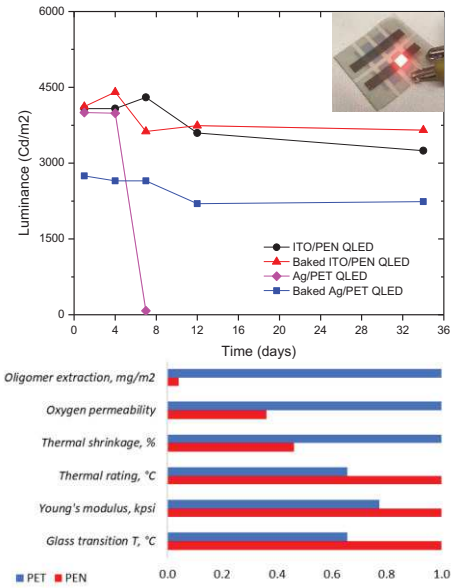

Figure 2. Luminance evolution of FQLEDs (at 3.0 V) to evaluate the shelf-life inside a glove-box (O_2: 5 ppm / H_2O: < 0.1 ppm), previous to encapsulation. Inset: picture of ITO on PEN QLED (substrate size: 3x3 cm^2) with 16 mm^2 pixel. And bar chart representing relevant properties of PET and PEN (normalized data).

device as depicted in Figure 1. Each barrier is a thin-film stack based on an organic coating for planarization (OCP) between two inorganic layers of amorphous hydrogenated silicon nitride (SiN).

Before encapsulation and J-L-V characterization outside the glovebox, we tested the shelf-life of the devices (see inset in graphic of Figure 2). Four different FQLEDs were kept inside a glovebox (O_2: 5 ppm / H_2O: < 0.1 ppm) for approximately 1 month, and luminance under 3 V was recorded at day: 1, 4, 7, 12 and 34. The evolution of the luminance is shown in the graphic from Figure 2, where the curves correspond to four FQLEDs made under different conditions: Ag/PET QLED and ITO/PEN QLED control devices, and Ag/PET QLED and ITO/PEN QLED subjected to baking. The result of this experiment demonstrates that the baking step -before start processing the substrates- is more critical for the Ag/PET film, since luminance of the Ag/PET QLED with no baking drastically decayed after 1 week. While the luminance for both the ITO/PEN QLED and the baked ITO/PEN QLED did not change significantly after 34 days. Additionally, some dark spots appeared on the baked Ag/PET QLED after 1 week, but no dark spots were observed over this period for the ITO/PEN QLEDs. This can suggest that the water absorbed inside PET substrates before the fabrication process, can be later released by desorption when the devices are finished, gradually affecting the upper layers of the device. In contrast, the retained amount of water in the PEN substrates

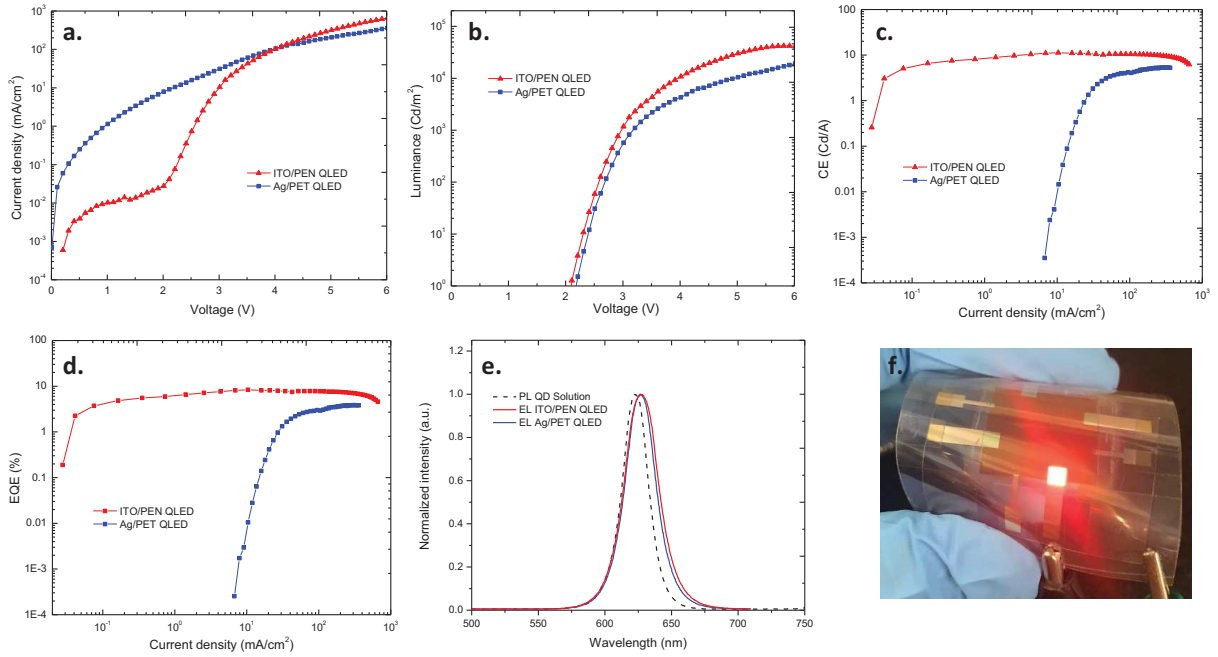

Figure 3. Performance of the FQLEDs made on ITO/PEN and Ag/PET (substrates size: 5x5 cm^2), a) current density vs. voltage (J-V); b) luminance vs. voltage (L-V); c) current efficiency vs. current density (CE-J); d) External quantum efficiency vs. current density (EQE-J). e) Normalized PL spectrum of the QDs solution, and EL spectra of the FQLEDs; f) Encapsulated ITO/PEN QLED with pixel (8 mm^2) driven at 3.5 V in air.

seems lower, given the high luminance sustained by the ITO/PEN QLED with no baking, even after 1 month. This therefore confirms the good gas barrier properties of PEN. A comparison of the most relevant properties between the used PEN (DuPont Teijin Films) and PET is represented in the bar chart from Figure 2. The superior properties of PEN are mainly ascribed to the two condensed aromatic rings of the PEN monomer structure, one additional ring in comparison to PET. Besides good gas barrier properties, PEN is expected to have higher chemical and hydrolytic resistance, making the PEN based substrates more compatible to solution process fabrication and ideal for all-solution processed QLEDs [16,17]. Unlike PET, which is particularly vulnerable to chlorobenzene, PEN can exhibit good resistance to the solvents used during our solution process, i.e. methanol, 2-propanol, and 2-methoxyethanol for spin-coating of ZnO NPs, and chlorobenzene for spin-coating of QDs.

According to the shelf-life results, we made FQLEDs of the best devices using each substrate: baked ITO/PEN QLED and baked Ag/PET QLED. After encapsulation of these FQLEDs, the characteristic curves J-V and L-V were measured (see Figure 3a-b) using a Bo-Test SMU with silicon photodetector -calibrated with a Konica Minolta LS-110 luminance meter. Then, the current efficiency (CE) and external quantum efficiency (EQE) were obtained and plotted as shown in Figure 3c-d. The most important parameters from the J-L-V characteristics were summarized in Table 2. Conversion from measured luminance (photometric units) to radiance (radiometric units) was carried out using a numerical integration approach, the electroluminescence (EL) spectrum intensity of the QLED I(λ) and the empirical function for photopic response V(λ), which are functions of the wavelength. It is worth noting that regardless the lower sheet resistance of the Ag-stacked film reported by the manufacturer, the ITO/PEN QLEDs showed better performance than the Ag/PET QLEDs. As observed in the J-V curve, the current density of the Ag/PET QLEDs increases faster at low voltage but later it is surpassed by the current density of the ITO/PEN QLED at 4.1 V. Considering that the turn-on voltage is the same for both QLEDs (1.9 V), a higher luminance of the ITO/PEN QLED over the measured range can arise from better charge balance under the J-V regime of this device, as evidenced with the CE-J curves of Figure 3C. Consistently, both the CE and EQE peaks of the ITO/PEN QLED (11.3 cd/A and 8.3%, respectively) are early reached at 3.0 V, and low roll-off efficiency is observed. Most importantly, the EQE only drops to 7.5 % (9.6 % decrease) when luminance of 20000 cd/m^2 is reached at 4.5 V. Normally, the fluence rate or irradiance required for in-vitro and in-vivo PDT/PBM studies is $\leqslant$ 10 mW/cm^2. Ideal irradiance on a target surface can be obtained varying the driving voltage of the QLED and the distance between the QLED and the irradiated surface. Then, for example, an 8 mm^2 QLED pixel with radiance of 9.3 mW/cm^2.sr at 4.5 V

Table 2. Most relevant parameters obtained from the J-L-V performance of the FQLEDs

	$V_{turn-on}$ (V)	L_{max} (cd/m^2)	Equiv-Radiance (mW/cm^2.sr)	CE_{max} (cd/A)	EQE_{max} (%)	EQE (%) @ 20000 nits
Ag/PET QLED	1.9	19040 (6.0 V)	8.8	5.3	3.8	3.8 (6.0 V)
ITO/PEN QLED	1.9	42214 (5.8 V)	19.6	11.3	8.3	7.5 (4.5 V)

can produce an irradiance of 10 mW/cm^2 on a target surface located at a distance of ~3 mm from the QLED.

A peak emission wavelength of 627 nm and narrow full-width at half-maximum (FWHM) of 29 nm were obtained from the EL spectrum of the ITO/PEN QLED plotted in Figure 3e. From the same Figure, a red-shift (4 nm) with respect to the peak wavelength of the QD solution photoluminescence (PL) spectrum is observed. Finally, the maximum brightness of 42214 cd/m^2 at low voltage (5.8 V) make these ITO/PEN QLEDs feasible for other large-pixel applications, with opportunity for further optimization. The encapsulated devices can hold 80% of the initial luminance after 1 week out of the glove-box. An encapsulated ITO/PEN QLED with pixels of 8 mm^2 and only 1.4 g in weight is shown in Figure 3f. We believe, that an integrated barrier layer between the ITO film and PEN substrate will significantly improve the lifetime of these devices in air, with no need for bottom lamination. Moreover, the Joule-heat induced temperature rise under continuous operation at high current density need to be addressed [18].

3. Impacts

In summary, we present in this work a bright flexible deep-red quantum dot light emitting diode with long shelf-life. A radiance of 9.3 mW/cm^2.sr reached at low voltage (4.5 V), narrow spectrum and emission wavelength in the range 620-670 nm, make these ITO on PEN QLEDs ideal for application in photomedicine as wearable light sources. A close-packed array of pixels (8-9 mm^2) can uniformly irradiate on a surface, similar as using a single large pixel. The devices can be stored for long time either in inert atmosphere or in vacuum sealed bags. With further improvements, we believe this low-cost, lightweight and flexible QLED can be introduced as a disposable light source for ambulatory treatment on PDT and PBM. Moreover, the high brightness 42214 cd/m^2 at only 5.8 V creates an opportunity for other flexible large-pixel applications.

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