

Oxygen Plasma Surface Treatment onto ITO Surface for OLEDs Based on Europium Complex

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ABSTRACT

In this work, Organic Light-Emitting Diodes (OLEDs) based on Europium (III) complex were studied, especially those with an oxygen plasma surface treatment onto indium tin oxide (ITO) transparent electrode. An OLED with the same thin-film structure but with untreated ITO was fabricated for comparison purposes. Current density-voltage characteristics for treated devices demonstrated an increase from 0.4 to 3.3 mA/cm² and a decrease of the turn-on voltage from 28 to 22 V. Additionally, improved hole injection through the transparent electrode impacted on optical response, as luminous efficiency increased from 26 to 44 mcd/A with the advantage of no significant disturb on the europium typical electroluminescence emission spectrum. Emission peak was observed at a wavelength of approximately 614 nm, which is defined by the transition associated with spectroscopic terms (³D₀→⁷D₂) and CIE chromaticity coordinates of (0.50;0.36).

Index Terms: organic light emitting diodes; electroluminescence; electrical characterization; rare earth complexes; oxygen plasma surface treatment.

I. INTRODUCTION

Since the discovery of organic light-emitting diodes (OLEDs), the research on new materials and devices configuration has attracted much attention because of the large potential applications, in particular, on flat displays and on flexible ones [1]. Already commercial mobile phones from Samsung and flexible prototypes from LG with such displays have made appearance during the last Week Display in 2014 [2]. Nevertheless, there is still ongoing research for a higher color purity and internal efficiency associated with a very high emission intensity (approximately 1000 cd/m²) from more sophisticated organic materials. Rare earth and transition metal complexes are suitable candidates, especially those based on europium, terbium, rhenium and ruthenium [3-7].

Organic light emitting diodes (OLED) based on rare earth complexes have been studied since 1990 [8], due to its high internal quantum efficiency approaching 100% in radiative decay from triplet states [9]. More recent studies have shown that this kind of complex with a proper host semiconducting polymer [9] allows mechanisms of charge carrier transport both through singlet and triplet states simultaneously [10],

which increase the external efficiency. Although rare earth-based organic materials as Europium (III) complexes are a promising way to develop high efficient red emitters [3], they can also act together with other light emitting polymers to achieve white lighting [1]. Considering the thin film structure for OLEDs in which the emissive layer is made of an organic complex blended to a luminescent polymer, a complete understanding about charge carriers injection and transport is still lacking [11].

A previous work by Chan, Cheng and Hong [12] showed that the oxygen plasma surface treatment for OLEDs could lead to an increase of about 40% in electroluminescence. The explanation resided in the enhancement of injection processes that improved the OLED electrical behavior. Such a way to optimize injection of charge carriers has not yet been extensively studied for rare earth complexes, particularly for those based on Europium (III) [13]. In this context, OLEDs from a Europium (III) complex were investigated as a function of the transparent electrode surface treatment. It was verified that the electrode treatment by oxygen plasma improved ITO interface with the hole-transporting layer through an extra cleaning and by reducing ITO work function. A lower turn on voltage and an enhanced luminous

efficiency were a consequence of improved carrier injection from the anode and recombination in the emission layer.

II. EXPERIMENTAL

A. Device fabrication

OLEDs were prepared on patterned indium tin oxide (ITO, thickness of approximately 100 nm, sheet resistance of 30–60 Ω /square) onto glass substrates (Delta Technologies, CO, USA). Initial cleaning was made with neutral liquid detergent (Extran[®] MA 02, Merck Millipore, Darmstadt, Germany) under 50°C in a 10 min ultrasonic bath, followed by an isopropyl alcohol bath at boiling-point elevation and final drying on nitrogen blow. Anode was patterned by conventional micrometric photolithography from AZ1518 (Clariant, NJ, USA) positive photoresist, followed by an almost instantaneous wet etching in hydrochloric acid (HCl) catalyzed by zinc powder. A 10 min oxygen plasma treatment was performed in a reactor chamber under a pressure of 100 mTorr, an oxygen flow of 50 sccm and radio frequency power of 100 W. Process duration was chosen according to literature, which established a period between 2 to 10 minutes [12] that depends on the applied thin-film and device structure. Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, CLEVIOS[™], Leverkusen, Germany) as hole transport layer (HTL) was deposited immediately after oxygen plasma surface treatment. The emissive layer (EML) was obtained from tris(dibenzoylmethane) – bipyridine - europium (III) (Eu(DBM)₃bipy) dispersed in poly(9-vinylcarbazole) (PVK, molecular weight of 1,100,000) as host polymer in a mass proportion of (0.2:1 wt%), as reported elsewhere [14]. Spin coating of HTL and EML provided a thickness of approximately 500 Å and 2000 Å, respectively. Electron transport layer (ETL) was 100 Å-thick 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (butyl-PBD). Finally, as well as the ETL, a 1000 Å-thick aluminum film as cathode was thermally evaporated under a pressure of 10⁻⁶ Torr. All solvents were Chromasolv[®] grade from Sigma-Aldrich (MO, USA), except for ultrapure water (Millie-Q, 18.2 M Ω .cm). A schematic diagram of OLED organic materials and thin-film structure is provided in Fig. 1.

Samples of 25 mm × 25 mm × 1 mm displayed in Fig. 2 were composed of four OLEDs each with an emitting area of 9 mm² defined by the intersection between ITO anode and Al cathode. Atomic force microscope Nanoscope 3a Multimode 3 (Veeco/Bruker, NY, USA) according to [15] and an Alpha step 100 profilometer (Veeco, NY, USA) were employed to extract thin-film thickness.

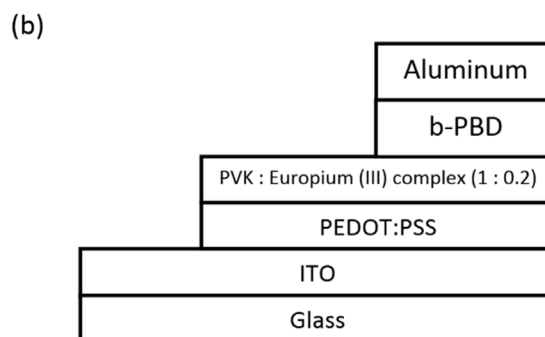
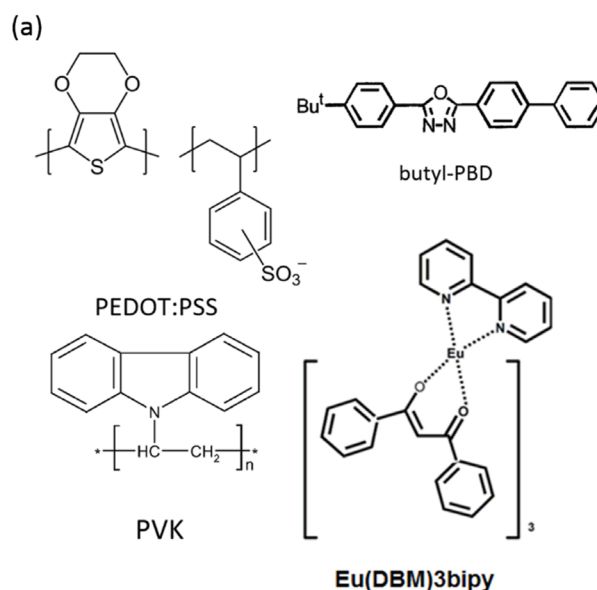


Figure 1. Schematic diagram of (a) organic materials and (b) layers composing an OLED.

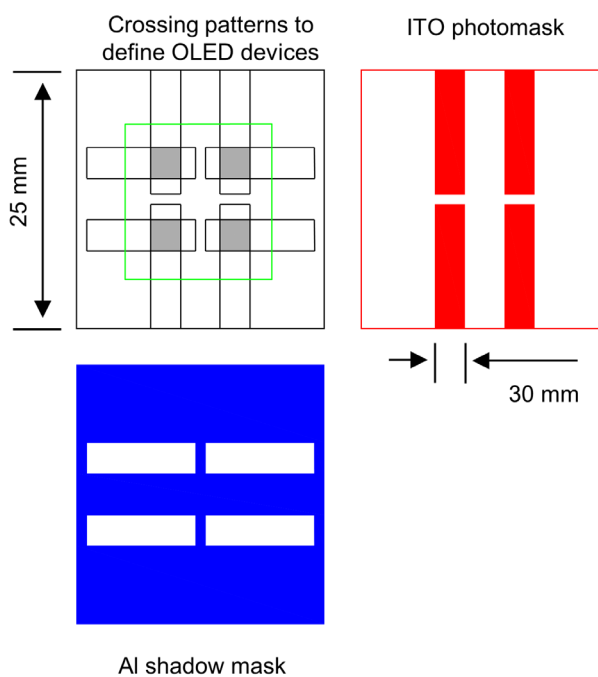


Figure 2. Schematic diagram of samples and OLED emitting area.

B. Electrical and optical characterization

Current versus voltage characteristics were recorded by a Keithley 2420C SourceMeter. Luminance was obtained through a Luminance-meter Minolta CS100A. Electroluminescence spectra were obtained from an Ocean Optics CCD spectrometer HR2000+ coupled to an optical fiber. All measurements were performed as illustrated in Fig. 3 at room temperature and after emitting area encapsulation with epoxy-attached glass in a glovebox system under N₂ inert atmosphere.

C. Equations and main device parameters

Turn on voltage (V_{on}) was obtained from the change of an ohmic to space charge limited current electrical transport in bulk, taking into account the current density versus voltage curve in logarithmic scale.

Maximum luminance (L_{max}) at normal viewing angle ($\theta = 0$ rad) and not integrated were extracted from electrical-optical characterization. It can be defined as the luminous intensity (i) over an area (A) by the following:

$$L = i(\theta = 0) / A \quad (1)$$

The ratio of current density (J) to luminance (L) determines the luminous efficiency (η_L):

$$\eta_L = J / L \quad (2)$$

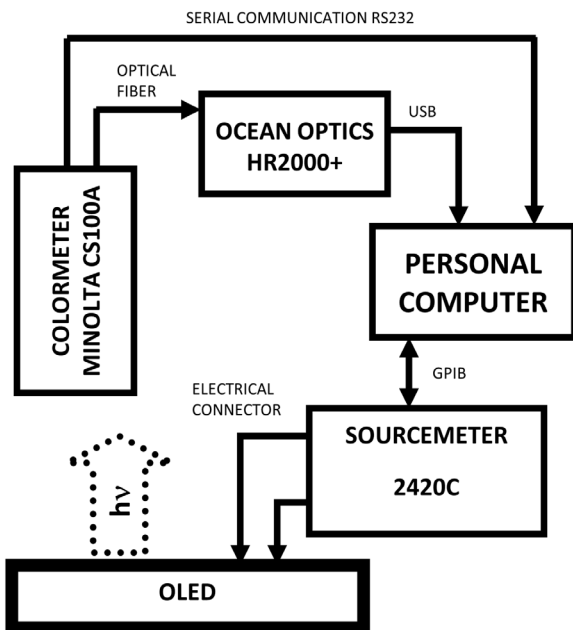


Figure 3. Schematic diagram of electrical and optical characterization.

Color coordinates plotted in the 1931 Commission Internationale de l'Éclairage (CIE) standard chromaticity diagram were calculated from electroluminescence spectrum and CIE standard values. More detailed information on OLED parameters extraction is given in [16].

III. RESULTS AND DISCUSSION

Current density-voltage characteristics in Fig. 4 show a turn on voltage decrease from 28 to 22 V for an ITO surface treated by oxygen plasma process, accompanied by a current density increase from 38 to 50 mA/cm² at 35 V. Considering the OLED thin-film structure under investigation and the energy diagram in Fig. 5, this phenomenon can be attributed to a barrier reduction between transparent electrode work function and the highest orbital molecular occupied (HOMO) from HTL, improving hole injection [13]

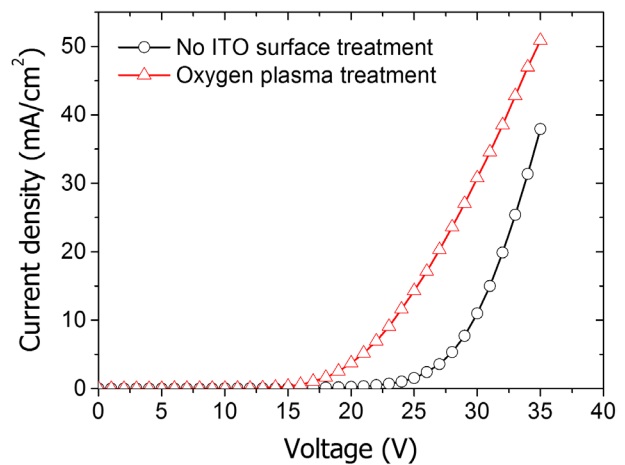


Figure 4. Luminance-voltage characteristics for treated (triangle) and untreated (circle) transparent electrode surface.

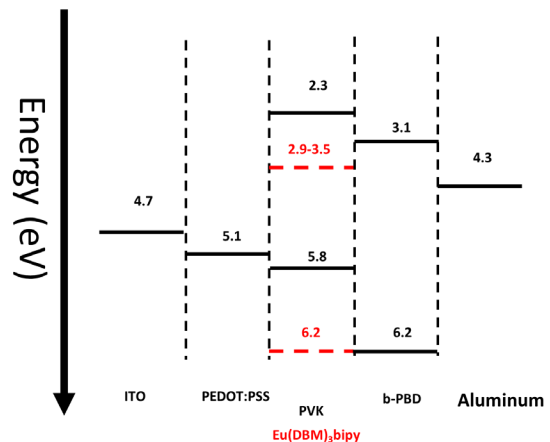


Figure 5. An energy diagram for the five-layer device with reference to the vacuum level. Energy levels of Eu complex from [18].

and therefore increasing the current density. Besides, according to Lu et al. [17], oxygen plasma is quite effective in removing organic contaminants on the ITO surface, as X-ray photoelectron spectroscopy (XPS) revealed a decrease in the surface content of carbon and an increase in the surface content of oxygen. Moreover, an observed reduction in contact angle can lead to a higher adhesion and homogeneity of PEDOT:PSS on top of the ITO anode.

An improved higher injection from transparent electrode together with a proper HTL can lead to a higher rate of generated excitons at the EML and, consequently, a higher rate of radiative decay, as seen in Fig. 6. The luminance response increased from 2.7 to 7.4 cd/m² at 30 V for OLEDs from O₂ plasma treated-ITO.

Calculated luminous efficiency reveals a high contrast between oxygen plasma-treated and untreated samples as shown in Fig. 7. This plot reveals that

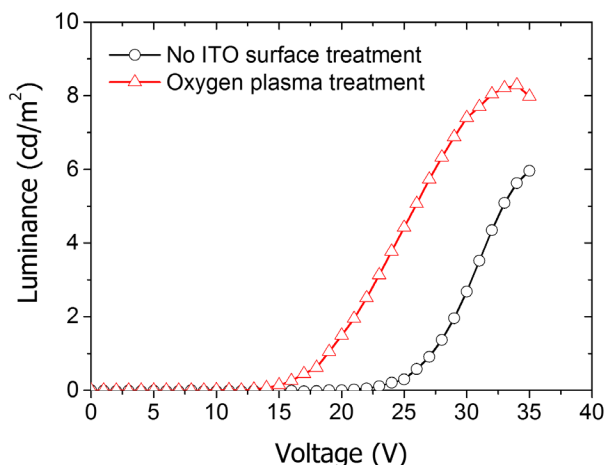


Figure 6. Luminance-voltage characteristics for treated (triangle) and untreated (circle) transparent electrode surface.

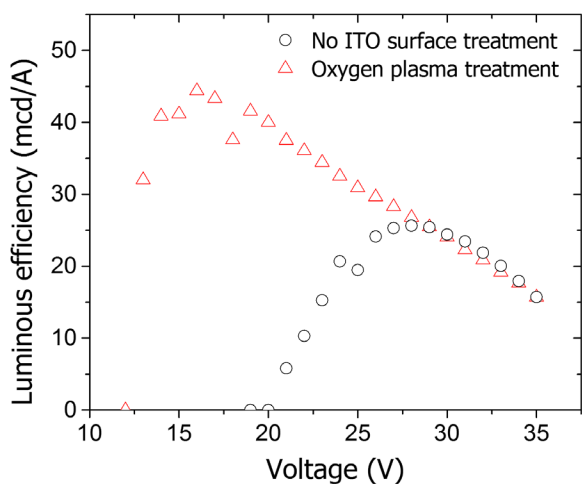


Figure 7. Luminous efficiency-voltage characteristics for treated (triangle) and untreated (circle) transparent electrode surface.

maximum luminous efficiency increased from 26 mcd/A at 28 V to 44 mcd/A at just 16 V. Data averaged for all produced devices indicated a proper reproducibility of the underlined phenomenon. Even though the behavior seems to be similar at high applied voltages (> 27 V), it is clear that the applied surface treatment enormously improves luminous efficiency at relatively low voltages (< 20 V). These results are important for the future development of rare-earth based OLEDs, as it shows a versatile way to overcome a traditional moderate luminous efficiency in such kind of electroluminescent devices.

Electroluminescence spectra in Fig. 8 point out that the main peak from europium emission related to ⁵D₀→⁷F₂ transitions (614 nm) increased for OLEDs after oxygen plasma treatment of the transparent electrode surface. Furthermore, improved electroluminescence response highlighted the europium emission, as it is clear that broadband emission from PVK host did not alter significantly. This behavior kept the pure color emission from europium complexes devices typically characterized by low values of full-width at half maximum (FWHM) [19].

The active (emissive) layer is a blend of a polymer and the Eu(III) complex. Considering the absorption and emission bands from both materials [20], we expect, from the overlap of the PVK emission band with some region of the Eu(III) complex absorption band, an energy transfer between the first to the second one. This explain the almost absence of the PVK emission. Furthermore, the energy levels from both materials, does not suggest a carrier trapping of electrical charges in Eu(III).

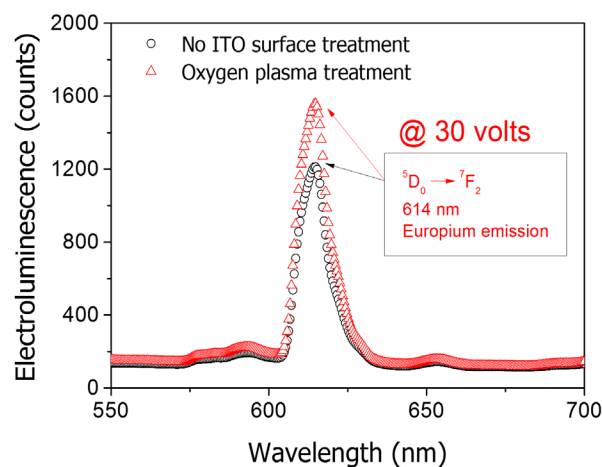


Figure 8. Electroluminescence spectra for treated (triangle) and untreated (circle) transparent electrode surface.

Table I. Summary of main OLED parameters.

O ₂ treatment	V _{on} (V)	J (mA/cm ²) @ 35 V	L (cd/m ²) @ 30 V	η _L (x10 ⁻³ cd/A)	λ _{max} (nm)	CIE coordinates
Yes	22	50	7.4	44 @ 16 V	614	(0.50; 0.36)
N/A	28	38	2.7	26 @ 28 V	614	(0.55; 0.36)

CIE chromaticity coordinates calculated from electroluminescence data changed from (0.55; 0.36) to (0.50; 0.36) after the transparent electrode surface was treated by O₂ plasma, as shown in Fig. 9. The slightly difference between these coordinates probably indicate an additional recombination in the host polymer, as the higher carrier injection from O₂-treated ITO seems to enhance the overall emissions. In general, excitons are generated in high rate in europium complex energy levels due to antenna effect [21]. However, there are also minor generated excitons that show radiative decay in the host polymer, which exhibits typical PVK broadband emission ranging from 400 to 470 nm [22]. Such result is in accordance with the assumption that no electrical carrier trapping mechanisms are involved in the energy transfer from the host to the guest.

Finally, OLED main parameters summarized in Table I reinforce a 22 % decrease in operating voltage, 32 % increase in current density, an almost tripled luminance and 70 % increase in luminous efficiency after performing an O₂ plasma treatment on ITO surface. Remarkably, without drastic changes to the maximum in electroluminescence spectrum and the chromaticity coordinates.

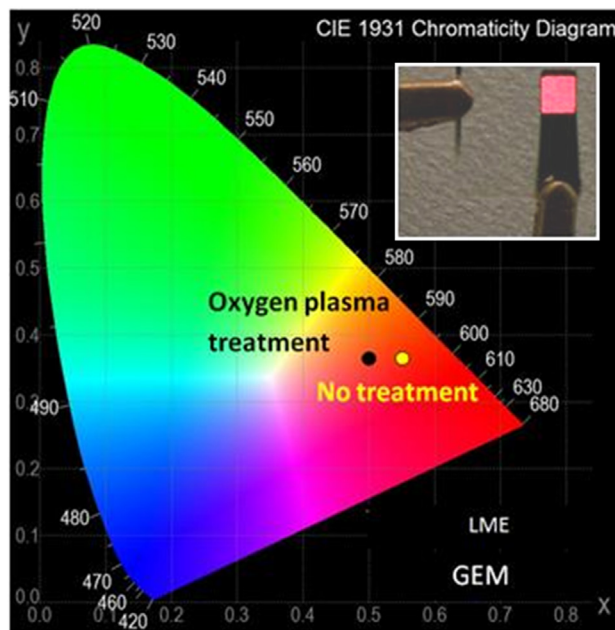


Figure 9. 1931 CIE standard chromaticity diagram with coordinates for treated and untreated ITO surface. Inset: Treated-LED photograph biased at 20 V.

IV. CONCLUSIONS

The effect of an oxygen plasma surface treatment on ITO transparent electrode in europium-based OLEDs was investigated. Pronounceable changes in turn on voltage, luminance, electroluminescence and luminous efficiency were noticeable. A decrease in turn-on voltage from 28 to 22 V was inferred from the current density-voltage characteristics. However, current density largely increased from 38 up to 50 mA/cm². Such a high current density implied in higher luminance, luminous efficiency and electroluminescence intensity at similar applied voltages. Beyond a simple surface cleaning to remove residual organic materials as after photolithographic processes, the oxygen plasma seems to effectively reduce the energy barrier between transparent electrode work function and HTL HOMO level, as no further changes were performed in OLED fabrication processes. In the particular case of a europium complex emitting layer, the ITO surface treatment did not affect the main OLED emission from europium energy levels transition ⁵D₀→⁷F₂, therefore allowing for high color purity with low FWHM.

ACKNOWLEDGEMENTS

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