Optimization of polymer light emitting devices using TiO$_x$ electron transport layers and prism sheets

Yu-Hsuan Ho$^{a,b}$, Yung-Ting Chang$^c$, Shun-Wei Liu$^d$, Hsiao-Han Lai$^a$, Chih-Wei Chu$^a$, Chih-I Wu$^c$, Wei-Cheng Tian$^b$, Pei-Kuen Wei$^{a,e,*}$

$^a$Research Center for Applied Sciences, Academia Sinica, Taipei 115, Taiwan
$^b$Graduate Institute of Electronics Engineering, National Taiwan University, Taipei 106, Taiwan
$^c$Graduate Institute of Photonics and Optoelectronics, National Taiwan University, Taipei 106, Taiwan
$^d$Department of Electronic Engineering, Mingchi University of Technology, New Taipei 24301, Taiwan
$^e$Institute of Optoelectronic Sciences, National Taiwan Ocean University, Keelung, Taiwan

**Abstract**

The internal and external efficiency of polymer light emitting devices were found can be simultaneously improved by insertion a high refractive index material, titanium oxide (TiO$_x$), to the emission layer and a prism sheet attached to the substrate. The TiO$_x$ layer increased the internal efficiency due to a better electron injection and hole confinement. However, it led a wider angular emission profile with more photons trapped in the substrate. By using the prism sheet, those trapped light was efficiently coupled to the air. The extraction efficiency enhancement was increased from 33.1% to 54.4% and the overall current efficiency was improved up to 86%.

**1. Introduction**

Due to the large refractive index mismatch between organic layers ($n = 1.7–1.9$), glass substrate ($n = 1.52$) and air, substantial photons trapped in the organic light emitting devices are usually critical problems to constrain the external quantum efficiencies. In general, lower than one third of the generated photons can escape from emitting devices. One third of these photons are guided in the glass substrate and the others are trapped in the organic layers. Many researches had been proposed to increase the coupling ratio of external mode (coupling to air) by extracting trapped photons from substrate mode and high-index guided mode [1–3]. The surface modifications at the air/substrate interface with microlens arrays, micro-pyramid arrays, silica micro-spheres and photonic crystals all had been reported to efficiently extract the light confined in the substrate [4,5]. Other techniques, such as the fabrication of the micro/nanostructures into devices or insertion of low index material were also proposed to couple light out of the high-index guided mode [6–8].

In addition to the surface modification for extracting the trapped photons, the device efficiency can also be improved by using the micro-cavity effect in the organic layers [9]. However, the modification of the electron-transport or hole-transport layer also leads to the degradation of internal quantum efficiency and rapid increase of operation voltage. In this work, we combined both surface roughening and cavity-tuning methods to achieve an optimal increase of current efficiency. A solution based sol–gel and spin-coating process was applied to inset a titanium oxide (TiO$_x$) on the emissive polymer. The HOMO and LUMO levels were measured to be 7.1 and 3.6 eV, respectively, which can assist to the electron injection, transport and the hole blocking [10]. The large refractive index ($n = 2.41$) of TiO$_x$ also provides an effective means to tune the optical cavity mode in the emitting layers [11]. By combination the TiO$_x$ layer with the prism sheets, the...
extraction efficiency enhancement was increased from 33.1% to 54.4% without any device electricity degeneration. In addition, 86.0% improvement of current efficiency was achieved.

2. Device fabrication

The devices were attached with prism sheets by index matching oil as illustrated in Fig. 1(a). The prism sheet had an apex angle of 90° and the prism pitch was 50 μm. This prism sheet acts as the backlight enhancement film (BEF) which can efficiently extract the substrate guiding wave. For the emitting layers, the glass substrates were coated with 250 nm-thick indium tin oxide (ITO) and then soaked into concentrated HCl for 15 min to pattern the transparent ITO anode. After UV-O₃ plasma treatment, hole injection layer (Poly (3,4-ethylenedioxythiophene) – poly (styrenesulfonate), PEDOT:PSS), hole transport layer (Poly (9,9-diocetylfluorene-co-N-(4-butylphenyl)-diphenylamine, TFB) and emission layer (polyfluorene derivative Green B) were spin-coated onto this ITO anode sequentially. The thickness of the first three organic layers was set to be around 120 nm, which is thought to be the suitable thickness for green light emission [9]. We used a solution based sol–gel process to deposit TiOₓ around 120 nm, which is thought to be the suitable thickness of the TiOₓ layer to the transparent anode. Fig. 1(a) shows the effective distance of the dipole from the metal cathode, R₁ is the reflectivity of organic layer to the opaque cathode, R₂ and T₂ are the effective reflectivity and transmission of the organic layer to the transparent anode. L is the total optical length of the cavity (including anode, organic layers, and cathode). When the total thickness of the organic layers was increased, the resonant wavelength was also increased and resulted in the red shift of the emission spectra. The calculated optical response was shown in Fig. 3(a). The optical response is the experimental electroluminescence (EL) spectrum divided by the intrinsic spectrum of the emitter, which represents whether constructive or destructive interference in the device layered structure. Fig. 3(b) shows the calculated EL spectra of the OLEDs with different TiOₓ thickness. When the TiOₓ thickness increased, the EL spectrum red shift and broadening were also observed in the simulation result.

3. Measurement results

Fig. 2 showed the characteristics of these devices including electricity, current efficiency and emission spectra. As depicted in Fig. 2(a), the current density of the device increase significantly by the insertion of the TiOₓ layer (10 nm) compared with the device without the TiOₓ layer. Due to the better electron-injection, the devices with TiOₓ layer implementation showed better or comparable electrical characteristics to the control device (TiOₓ: 0 nm). With a better hole confinement and carrier balance, the devices with TiOₓ all had higher current efficiencies. They were 8.01 cd/A for control device, 10.02 cd/A (TiOₓ: 10 nm), 10.35 cd/A (TiOₓ: 20 nm) and 9.40 cd/A (TiOₓ: 30 nm). The thicker TiOₓ layers resulted in a longer cavity length and made the emission spectra broadening and red shift. As illustrated in Fig. 2(c), the peak wavelength shifted from 532 nm to 540 nm and the FWHM (Full width at half maximum) was increased from 68 nm to 78 nm. The optical effect could be explained by Fabry–Perot equation [12–13].

\[
|E_{out}(\lambda)|^2 = \frac{|E_{in}(\lambda)|^2 \times T_2 \times \left[1 + R_1 + 2\sqrt{R_1 \cos(\pi L/a)}\right]}{1 + R_1 R_2 - 2\sqrt{R_1 R_2 \cos(\pi L/a)}},
\]

where \(E_{out}(\lambda)\) is the output intensity, \(E_{in}(\lambda)\) is the free space luminous intensity, \(x\) is the effective distance of the dipole from the metal cathode, \(R_1\) is the reflectivity of organic layer to the opaque cathode, \(R_2\) and \(T_2\) are the effective reflectivity and transmission of the organic layer to the transparent anode, \(L\) is the total optical length of the cavity (including anode, organic layers, and cathode). When the total thickness of the organic layers was increased, the resonant wavelength was also increased and resulted in the red shift of the emission spectra. The calculated optical response was shown in Fig. 3(a). The optical response is the experimental electroluminescence (EL) spectrum divided by the intrinsic spectrum of the emitter, which represents whether constructive or destructive interference in the device layered structure. Fig. 3(b) shows the calculated EL spectra of the OLEDs with different TiOₓ thickness. When the TiOₓ thickness increased, the EL spectrum red shift and broadening were also observed in the simulation result.
When we applied the TiO\textsubscript{x} layer into the devices, the emission pattern was broadened as shown in Fig. 4(a). The wider emission pattern implies more light impinged at the substrate/air surface with a larger incident angle and more photons were trapped in the device. If we plotted the relation of the FWHM of the emission profile versus the corresponding TiO\textsubscript{x} thickness, a positive correlation was observed as shown in Fig. 4(b). Before the insertion of the TiO\textsubscript{x} layer, the angular FWHM was 60.2° which was similar to a Lambertian light source. When 30 nm TiO\textsubscript{x} layer was inserted, the angular FWHM was increased to 64°. After the application of a prism sheet onto the device, a higher luminous enhancement was obtained for larger angular FWHM. The higher luminance came from the increase of extracted photons at larger incident angles and the reduction of the total reflection of the normal incident light. The additional inclined surface could help to couple out the light with large incident angle, but the one in small incident angle would be trapped due to the total internal reflection occurred at the inclined surface. This kind of trade-off concern had been reported in some other works [14]. Using the cavity tuning layer to change the emission profile in cooperation with surface roughening techniques can maximize the out-coupling efficiency of these emission devices. As illustrated in Fig. 4(b), the luminous enhancement ratio increased from 33.1% to 54.4% after the TiO\textsubscript{x} layer was inserted. Although thicker TiO\textsubscript{x} layer had a higher extraction improvement, too thick TiO\textsubscript{x} layer also depressed the electricity and internal quantum efficiency. There is an optimal condition for the TiO\textsubscript{x} layer with prism sheet attachment. Fig. 5 shows the current efficiency and efficiency enhancement ratio for different thickness of TiO\textsubscript{x} layers with and without the prism sheet. As depicted in Fig. 5(a), the best efficiency occurred as the thickness of TiO\textsubscript{x} was 20 nm and the angular FWHM was 62.8°. In this case, the current efficiency increased from 8.0 cd/A to 15.0 cd/A, which indicates that the efficiency enhancement was up to 86.0%.

![Fig. 2. Characteristics of the emitting devices with cavity tuning layers, TiO\textsubscript{x}, thickness of 0, 10, 20, and 30 nm. (a) Current density vs. bias voltage, (b) current efficiency vs. current density, and (c) EL spectra.](image)

![Fig. 3. Calculated optical response (a) and electroluminescence spectra (b) of the devices with different TiO\textsubscript{x} thickness.](image)
4. Conclusion

In summary, the extraction efficiency enhancement is not only influenced by the extraction ability of the micro- or nanostructure but also the emission profile. We used a high-index n-type material, TiO$_x$, to tune the emission profile in cooperation with the prism sheet to achieve the best extraction efficiency. The current efficiency improvement of individual techniques of TiO$_x$ layer implementation and prism sheet attachment was 33.1% and 29.3%, respectively. By combining both techniques, the overall current efficiency was increased up to 86.0% higher than the summation of the individual improvement. The optimal enhancement was attributed to the simultaneous improvement of both electron–hole balance and light extraction.

Acknowledgement

This work was supported by National Science Council, Taipei, Taiwan, under Contract No. NSC-100-2120-M-007-006 and NSC-100-2221-E-001-010-MY3.

References