

Enhanced efficiency of white polymer light-emitting diodes with inorganic nanodots

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Abstract—Enhanced efficiency of white polymer light-emitting diodes (PLEDs) was observed by incorporating polysilicic acid (PSA) nanodots into the hole-injection layer (HIL). The PLEDs employed three different phosphorescent dyes in a single emissive layer with a host polymer of poly(vinylcarbazole) (PVK). The optimal composition of the phosphorescent dyes has been found to accomplish the white emission. By incorporating 1.5 wt% of PSA nanodots into the HIL, the maximum efficiency has been found to increase about 65%, from 13.7 cd/A to 22.9 cd/A. This remarkable improvement in efficiency may be attributed to the introduction of the PSA nanodots, which leads to the better carrier balance in the PLEDs.

Key words: PLEDs, Efficiency, Polysilicic Acid, Nanodots, Carrier Balance

INTRODUCTION

White organic light-emitting diodes (WOLEDs) have drawn intense attention due to their potential applications in full-color flat panel displays, back-light sources for liquid-crystal displays (LCDs) and solid-state lighting (SSL) sources [1,2]. To accomplish the white emission, the proper mixture of three primary colors of red, green and blue (RGB) or two complementary colors (blue and orange) is required. A number of different approaches to fabricate WOLEDs have been reported previously, including multilayer structures capable of sequential energy transfer [3,4], multi-component emissive layers containing an appropriate ratio of RGB phosphorescent or fluorescent dopants [5,6], polymer blends containing RGB emitting species [7,8], and single polymer layer with broad emission [9,10].

Polymer light-emitting diodes (PLEDs) [5-11] offer an advantage of simple solution fabrication processes such as spin coating, screen, gravure, and ink-jet printing, in contrast to the small-molecule organic light-emitting diodes (SMOLEDs). However, white PLEDs are known to exhibit lower power efficiency (PE) and luminous efficiency (LE) as a disadvantage, when compared with the SMOLED counterparts fabricated by vacuum deposition process. For example, vacuum-deposited WOLEDs commonly show the LE over 10 lm/W [1], while those of white emissive PLEDs are usually below 10 lm/W [5,6], which means that PLEDs are still far from practical applications for solid-state lighting which requires the high LE.

To accomplish highly efficient white OLEDs, two different approaches could be utilized, of which the first is to utilize more efficient materials for the devices and the other is to optimize the architecture of the devices. The architectural approach includes reducing the energy barriers for carrier injection, balancing the carriers in the devices, confining the generated excitons in the emissive zone, and

facilitating the energy transfer from host to guest. As a new approach, the incorporation of inorganic nanodots into the devices has recently been found effective for improving the device efficiency [12,13]. Even though the nanodots could be incorporated by using a dry process, poor size or dispersion control may often result. To solve this problem, a wet process should be implemented. One advantage of a wet process is its feasibility for large areas and roll-to-roll fabrication [12]. To achieve a high power efficiency, the OLED device must be relatively thin, which greatly limits the use of larger size nanodots, especially those with a size comparable to or even greater than the thickness of the layer(s) in which they are to be incorporated.

Inorganic nanodots utilized in this study are polysilicic acid (PSA) nanodots, which are basically silica nanoparticles of average size 3 nm covered with hydroxyl ligand on their surface.

EXPERIMENTAL

In this study, we have fabricated single-layer white PLEDs with an emission layer containing three different phosphorescent iridium complexes. As a polymer host PVK has been employed. For an electron transporting moiety, OXD-7 (1,3-bis[(4-tert-butylphenyl)-1,3,4-oxadiazolyl]phenylene) has been used. To accomplish the white emission, three different phosphorescent emitters have been simultaneously doped in the single emission layer, which are 10 wt% bis(3,5-difluoro-2-(2-pyridyl)phenyl-(2-carboxypyridyl) iridium (III) (FIrpic) for blue emission, 0.2 wt% tris(2-phenylpyridine) iridium (III) (Ir(ppy)₃) for green emission, and 0.2 wt% tris(1-phenylisoquinoline) iridium (III) (Ir(piq)₂) for red emission. Therefore, the single emissive layer consists of PVK, OXD-7, FIrpic, Ir(ppy)₃, and Ir(piq)₂. The relative concentrations of PVK and OXD-7 are varied in order to balance the hole and electron transports within the light emitting materials. The emissive color was tuned by changing the ratio of FIrpic, Ir(ppy)₃, and Ir(piq)₂.

All the devices referred in this study were prepared by the following steps. The devices were fabricated on 150 nm-thick indium

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tin oxide (ITO) substrates, which were ultrasonically cleaned with TCE, acetone, methanol and deionized water sequentially, and then chemically etched to have a pre-designed pattern. The cleaned substrates were firstly exposed to oxygen and argon plasma for 5 min for surface treatment. As a hole injection layer, the PEDOT : PSS (poly(3,4-ethylene-dioxythiophene)-poly(styrenesulfonate)) layer of the thickness of 45 nm was spin-coated on top of ITO layer and baked at the temperature of 150 °C. Subsequently, a 60 nm-thick white emissive layer was spin-coated and baked at 80 °C. Finally, a 1 nm-thick LiF (lithium fluoride) layer and 100 nm-thick Al (aluminum) layer were deposited under 10^{-6} torr vacuum. The deposition rates of LiF and Al were set to 0.5 Å/s and 5 Å/s, respectively. The active area of all fabricated devices was 9 mm² and all the measurements were carried out at room temperature and ambient atmosphere without encapsulation.

To increase the efficiency further, we have introduced polysilicic acid (PSA) nanodots in the hole-injecting layer of PEDOT : PSS. The PSA nanodots were pre-dispersed in the PEDOT : PSS by means of pre-mixing in the solution state. The PSA nanodots were prepared by hydrolysis and condensation of sodium metasilicate [14–16], as described in the following. Firstly, 30 g of sodium metasilicate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$) was dissolved in 100 ml water and then the solution was mixed with 2.5 N 100 ml hydrochloric acid solution at 0 °C for 10 min. Secondly, 100 ml THF and 60 g NaCl were added into the mixed solution subsequently. After being stirred vigorously for 15 min, the reaction mixture was allowed to stand for 10 min. An organic layer (THF layer) was separated and dried with 30 g of anhydrous sodium sulfate. We varied the PSA concentrations in PEDOT : PSS and investigated the effect of incorporation on the emission efficiency of the devices.

RESULTS AND DISCUSSION

To achieve the white emission, a series of devices with different phosphor concentrations were fabricated and evaluated. The results are summarized in Table 1. The devices can be classified into two groups. First group (Devices A–C in Table 1) contains two different phosphors, which are FIrpic and $\text{Ir}(\text{piq})_2$. For the devices, the concentration of FIrpic was fixed at 10 wt% of the total organic materials in the emissive layer, and the $\text{Ir}(\text{piq})_2$ concentration was varied. Depending on the concentration of $\text{Ir}(\text{piq})_2$, the devices were named as Device A (0.1 wt%), B (0.2 wt%), and C (0.3 wt%). Fig.

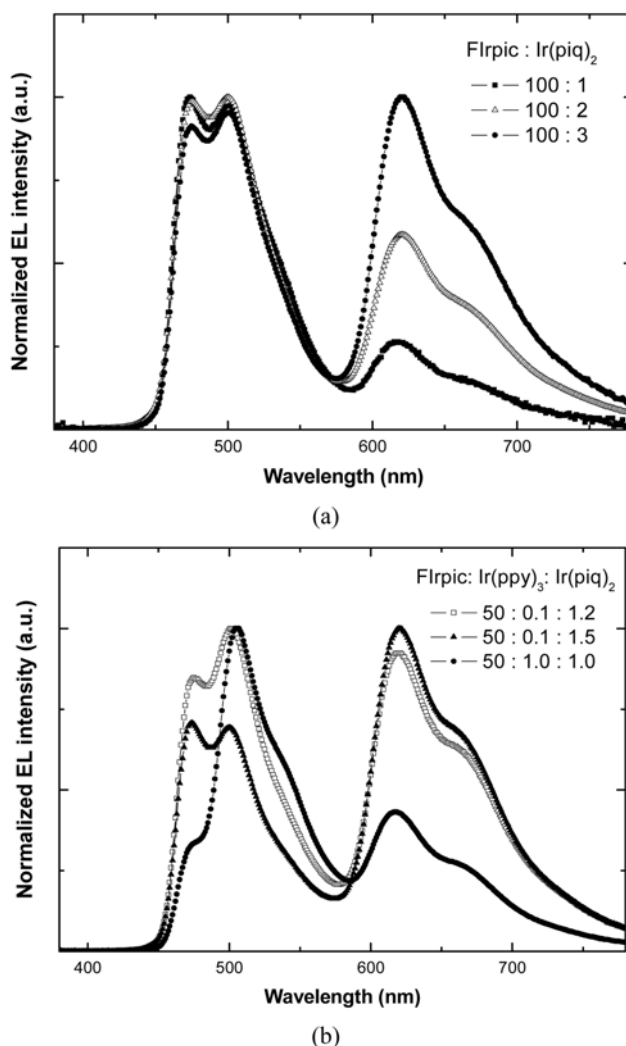


Fig. 1. EL spectra of (a) doubly-doped devices and (b) triply-doped devices with various doping ratios.

1(a) shows the EL spectra at the brightness of 1,000 cd/m² of these doubly-doped devices. Two intense peaks at 470 nm and 620 nm, with a shoulder peak at 500 nm were observed, which are assigned to the emission from FIrpic and $\text{Ir}(\text{piq})_2$. There is a monotonic increase of the red emission as the relative ratio of $\text{Ir}(\text{piq})_2$ to FIrpic

Table 1. Device performance of the white PLEDs doped with red, green and blue phosphorescent dyes

Device	Composition	CIE 1931 coordinates at 1,000 cd/m ²		Max. brightness [cd/m ²]	Max. current efficiency [cd/A]	CCT [K]
A ^a	100 : 1 ^c	0.232	0.398	1,780	1.93	9,500
B ^a	100 : 2 ^c	0.304	0.379	1,860	1.21	7,100
C ^a	100 : 3 ^c	0.374	0.375	1,300	1.7	4,100
D ^b	50 : 0.1 : 1.2 ^d	0.357	0.360	3,500	4.3	4,500
E ^b	50 : 0.1 : 1.5 ^d	0.405	0.341	4,800	4.7	3,200
F ^b	50 : 1 : 1 ^d	0.301	0.468	12,200	13.7	5,550

^aDoubly-doped devices

^bTriply-doped devices

^cFIrpic : $\text{Ir}(\text{piq})_2$ ratio; FIrpic is fixed at 10 wt% of the active layer blend

^dFIrpic : $\text{Ir}(\text{ppy})_3$: $\text{Ir}(\text{piq})_2$ ratio; FIrpic is fixed at 10 wt% of the active layer blend

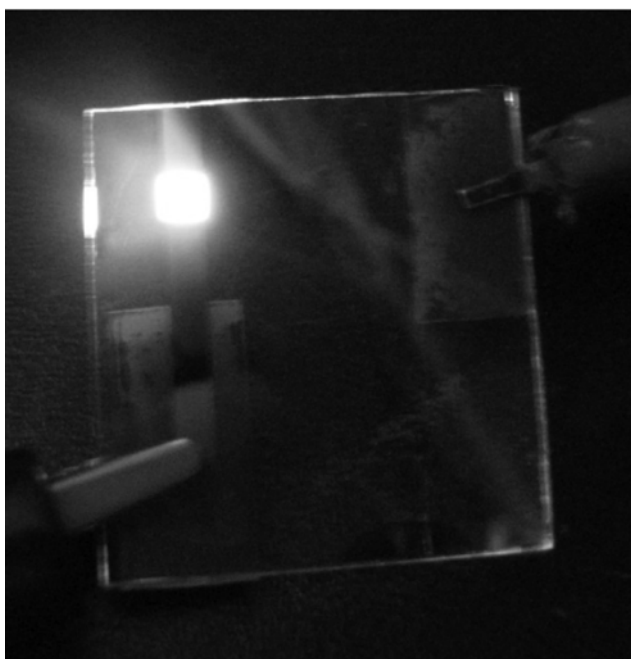


Fig. 2. Photograph showing the white emission of device F.

increases from 1 : 100 to 3 : 100. As shown in Table 1, the Commission Internationale de L'Eclairage (CIE) coordinates at 11,000 cd/m^2 change from (0.232, 0.398) to (0.374, 0.375); all are within or close to the white emission region. Especially, the EL colors of Devices B (0.304, 0.379), and C (0.374, 0.375) are close to the ideal CIE coordinate for pure white color.

The composition and performance of the second group of the devices (Devices D-F in Table 1), which contains the three different phosphors, are also included in Table 1. For the devices, the concentration of FIrpic was also fixed at 10 wt% of the total organic materials. The EL spectra of the devices with FIrpic : Ir(ppy)₃ : Ir(piq)₂ ratios of 50 : 0.1 : 1.2 (Device D), 50 : 0.1 : 1.5 (Device E), and 50 : 1 : 1 (Device F) are dominated by the narrow band gap green and red emitters despite their low concentrations (Fig. 1(b)). The CIE coordinates of all devices are located together with equi-energy white point (0.333, 0.333). One of these device emitting pictures is shown in Fig. 2.

From Table 1, we can conclude that the triply-doped devices show better performance than the doubly-doped counterparts. This can be understood since Ir(ppy)₃ is a very efficient green emitter with intense emission at 512 nm, where the photopic response of human

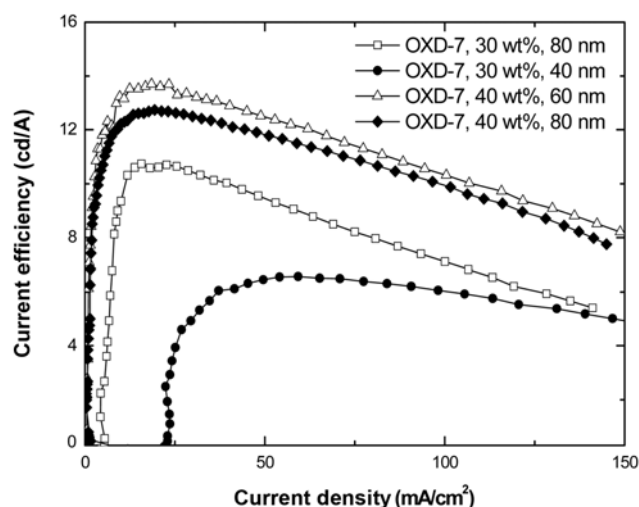


Fig. 3. Current efficiency versus current density characteristics of device F.

eyes is 344 lm/W , much stronger than for emission peaks of FIrpic (470 nm, 62 lm/W) or Ir(piq)₂ (620 nm, 260 lm/W).

For all the devices fabricated in this study, the concentrations of PVK and OXD-7 were fixed at 50 and 40 wt%, respectively. In cases with different concentrations, a different current efficiency of the devices resulted. For the device F, the current efficiency versus current density is shown in Fig. 3. The performance of the device with 40 wt% OXD-7 was found to be superior to that with 30 wt% OXD-7. We consider that the higher concentration of electron-transporting OXD-7 helps for the electrons to move more efficiently, leading to better performance, since the mobility of holes is much higher than that of electrons in typical PLED devices. The current efficiency was also dependent on the thickness of the single emissive layer. The optimized thickness was found to be 60 nm.

The effects of PSA nanodots with different concentrations in hole-injecting PEDOT : PSS layer on the performance of white PLEDs (Device F in Table 1) are summarized in Table 2 and Fig. 4. The device efficiency was found significantly improved when PSA nanodots were dispersed into the PEDOT : PSS layer. For example, the current efficiency of device 3 in Table 2 increased markedly from 13.7 cd/A to 22.9 cd/A with the incorporation of 1.5 wt% PSA nanodots into PEDOT : PSS layer. It was also found that the addition of 1.5 wt% PSA nanodots in the PEDOT : PSS layer shifted the CIE coordinate of the emission slightly from (0.332, 0.468) to (0.325, 0.479). This marked increase in efficiency may be attributed to the

Table 2. Effects of PSA nanodots with different concentrations in hole injection layer on the EL performance of the white PLEDs

Device	PSA concentration (wt% of PEDOT)	Turn on voltage [V]	CIE 1931 coordinates at 1,000 cd/m^2		Max. brightness [cd/m^2]	Max. current efficiency [cd/A], [V]	Current density at 1,000 cd/m^2 [mA/cm^2]
1	0	6.3	0.332	0.468	12230	13.7, 13.1	10.4
2	0.75%	6.0	0.325	0.479	11600	15.2, 10.8	8.0
3	1.50%	5.2	0.327	0.496	15000	22.9, 10.3	6.1
4	3%	4.8	0.362	0.51	15300	21.3, 9.6	5.7
5	5%	5.3	0.373	0.461	7450	20.4, 11.6	5.4
6	10%	5.3	0.325	0.507	3700	30.3, 11.8	4.7

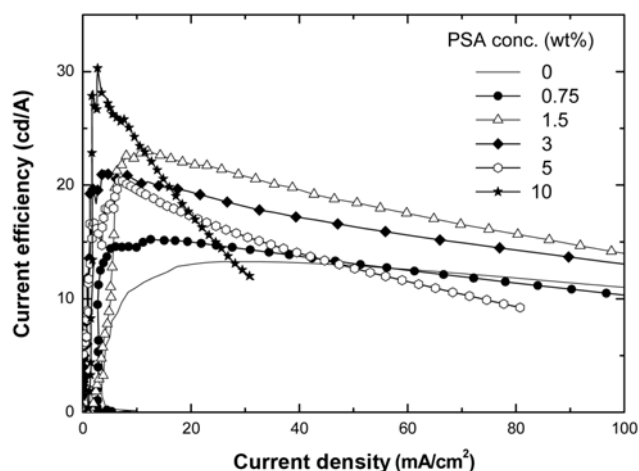


Fig. 4. Effect of PSA nanodot incorporation on the current efficiency of the phosphorescent white PLEDs.

enhanced balance of electrons and holes by changing the hole injection, since the incorporation of PSA nanodot into the hole injection layer can effectively trap holes, preventing excessive holes from pass-

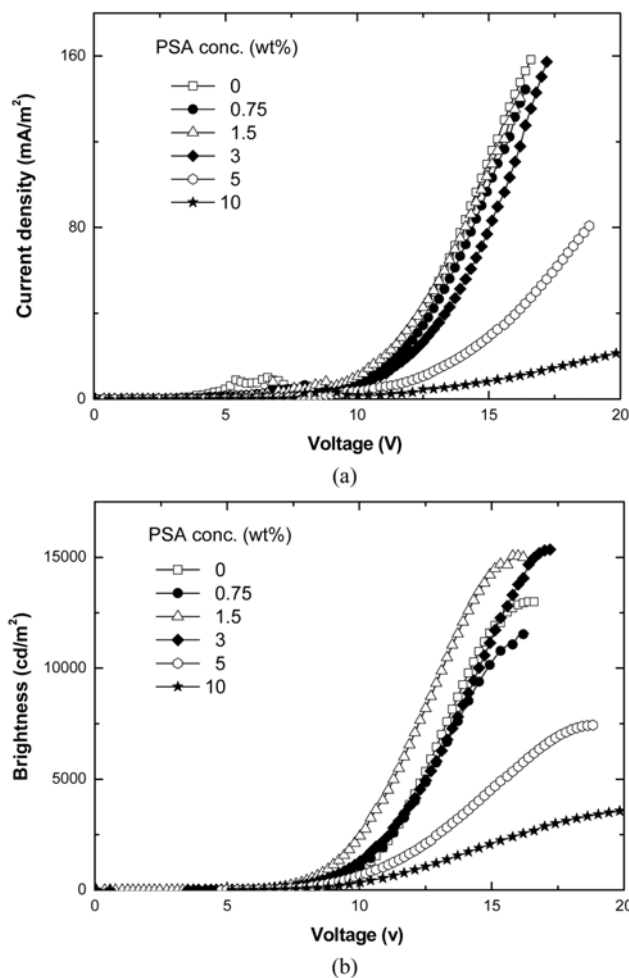


Fig. 5. Effect of PSA nanodot incorporation on the current density (a) and brightness (b) of the phosphorescent white PLEDs.

ing through the devices, which may lead to the lowering of device efficiency. The concentration of holes may thus be more equivalent to that of electrons inside the device, increasing holes-electrons recombination probability and electrons-photons conversion efficiency [17]. In the case of device 6, when 10 wt% PSA nanodots was added in HIL, the current efficiency increased to 30.3 cd/A with the increase of 120% from that of PSA-free device. However, such a high concentration of PSA nanodots would trap so many holes so that the current density is reduced significantly and as the result the brightness is also reduced correspondingly. As shown in Fig. 4, as the concentration of PSA nanodot in HIL increases above 3 wt%, the current efficiency drops faster with increasing current density.

Fig. 5 shows the effects of PSA nanodot concentration on the current density and luminance of the white OLEDs. The current density is observed to decrease as the nanodot concentration increases, indicating that the PSA nanodots had effectively reduced the injection of hole carrier. This result may be attributed to the fact that the PSA nanodots described here exhibited a negative charge on its surface, which would preferably trap the holes entering from the ITO anode. This trapping mechanism would consequently reduce the hole injection into the emissive layer, leading to better balance of electrons and holes in the emission region. Nevertheless, high concentration PSA would trap too many holes, leading to result in a quite low current density. For instance, in case of device 6 in Table 2, the current density was reduced from 10.37 to 4.73 mA/cm² at a brightness of 1,000 cd/m². Due to the low current density, the brightness of the device was seriously limited.

It is worth noting that the emission CIE coordinates slightly shifted when employing PSA nanodots to specifically optimized white PLEDs with three color component. It could be attributed to the fact that the employment of PSA changed the region of recombination zone of holes and electrons in the emitting layer [18], affecting the energy transfer between the PVK and the phosphors of Flrpic, Ir(ppy)₃ and Ir(piq)₂. Another important issue to mention is on the lifetime of PLEDs with PSA nanodots. We have not measured the lifetime of fabricated PLEDs with PSA nanodots in this study. However, from the literature we expect that the addition of nanodots could affect the device lifetime favorably [19]. It has been reported that the lifetime of PLEDs increased upon the addition of PSA nanodots. The lifetime improvement was attributed to the fact that fewer holes were injected into the emissive layer so that charge-accumulation-caused damage might be reduced, and the resultant higher device efficiency could somewhat reduce heat generated upon emission, preventing damage caused by the generation of excessive heat during operation [19].

CONCLUSIONS

Single-layer white PLEDs with enhanced efficiency were fabricated by blending polysilicic acid (PSA) nanodots into hole-injecting PEDOT:PSS layer. By incorporating 1.5 wt% PSA nanodots into the layer of specifically optimized PLEDs, the maximum current efficiency and luminance was found to increase from 13.7 cd/A to 22.9 cd/A and from 12,200 cd/m² to 15,000 cd/m², respectively. The enhancement may be attributed to improved balance of electrons and holes in the emission region as the result of hole-trapping effect of the incorporated PSA nanodots. The improved balance of

carriers also helps to reduce the operating voltage and current density.

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