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High performance ITO-free white organic light-emitting diodes using highly conductive PEDOT:PSS transparent electrodes

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ABSTRACT

We report high performance white organic light-emitting diodes (OLEDs) based on high conductivity poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) films optimized by a solvent post treatment. The device stack is carefully optimized with high efficiency tandem structures including red, yellow/green, and blue emissive materials. The OLED with the PEDOT:PSS transparent electrode achieves a high power efficiency of 26.1 lm/W and an external quantum efficiency of 19.3%, which are comparable to the reference indium tin oxide (ITO)-based OLEDs. In addition, it is observed that the angular emission characteristic of PEDOT:PSS-based OLEDs is closer to Lambertian distribution compared to that of the ITO-based OLED. We show that the optimized device stack together with post-treated PEDOT:PSS transparent electrodes can realize high performance ITO-free white OLEDs.

1. Introduction

White organic light-emitting diodes (OLEDs) have shown great promise for highly efficient, energy-efficient displays and light sources. In general, OLEDs consist of multi-layered organic semiconductors sandwiched between a transparent electrode and an opaque metal electrode [1]. In general, high efficiency OLEDs have complex multi-layer system where organic semiconductor layers have different functions including charge injection, charge transport, exciton blocking, and recombination/emission etc. Beside the efficiency, the development of transparent electrodes is of great importance to realize flexible and low-cost applications. Indium tin oxide (ITO) is most widely used material as transparent electrodes due to its high electrical conductivity and optical transmittance as well as well-established fabrication process. It is well known that, however, ITO suffers from high costs, inherent brittleness, and high-temperature processing that lead to difficulty in the application in low-cost, flexible devices [2,3]. In this respect, many alternative transparent electrodes have been extensively investigated such as indium-free transparent conducting oxides [4], silver nanowires [5–8], metal grids [9,10], graphenes [11], carbon nanotubes [12,13], thin metals [14,15], and conductive polymers poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) [16]. Generally, silver nanowires show promising electrical and optical properties. However, the rough surface of silver nanowires often causes electrical shorts in devices. Therefore, various composite structures such as the silver nanowire/transparent conducting oxide or silver nanowire/polymer have been reported [7,8]. These structures effectively lower the surface roughness of silver nanowires and enhance the electrical performances. In contrast, the electrical properties of PEDOT:PSS are rather worse than other transparent electrodes. However, PEDOT:PSS films can be prepared by one-step solution process without buffer layer coating and its smooth surface is much favorable for the applications to organic devices. The conductive polymers have attracted a great of attention due to its decent conductivity and transmittance with an excellent mechanical flexibility [17]. In addition, the high work function of PEDOT:PSS anode (> 5.0 eV) can effectively inject holes into the hole transport and emission layers.

There has been many reports on organic optoelectronic devices employing the conductivity enhanced PEDOT:PSS transparent electrodes with various techniques [18–21]. Previously, we have reported that highly conductive PEDOT:PSS films can serve as high performance transparent electrodes for ITO-free organic photovoltaic cells as well as OLEDs [16,22]. The conductivity of PEDOT:PSS electrodes can be optimized by solvent treatment which results in favorable structural changes including a reduction of insulating PSS and well-connected conducting PEDOT networks [16,23,24]. Moreover, the electrical stability of post-treated PEDOT:PSS films are enhanced against humidity in air ambient due to the removal of hygroscopic PSS which absorbs water in ambient [16]. Our previous study shows that OLEDs with post-treated PEDOT:PSS films result in an improved device performance

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compared to the OLEDs based on the doped PEDOT:PSS films without post treatment [19,25].

Many studies on ITO-free OLEDs with PEDOT:PSS transparent electrodes have been reported and successfully shown its potential. However, most of PEDOT:PSS transparent electrodes have been utilized in OLEDs with single color emission. The application of PEDOT:PSS electrodes in white OLEDs together with achieving a high device efficiency is more challenging due to the complicated device stack in which the electrode-specific device structure is necessary. To realize the high efficiency ITO-free white OLEDs with PEDOT:PSS electrodes, optimization processes both for the device architecture engineering and for the conductivity enhancement of PEDOT:PSS are of great necessity and need to be performed together. Recently, high performance white OLEDs consisting of the phosphorescent red, green, and blue emitters result in 100% internal quantum efficiency with triplet-harvesting concepts [26]. Carefully chosen host/dopant materials of emitters for triplet harvesing and doped hole/electron transport layers for the efficient transport of holes/electrons can achieve the high device efficiency. Reineke et al. reported high efficiency white OLEDs with a power efficiency of 90 lm/W, which employ the patterned substrate for external outcoupling, reaching fluorescent tube efficiency [27]. The efficiency was further improved to 124 lm/W by including half-sphere outcoupling structures. Rosenow et al. introduced the triplet-harvesting system into stacked white OLEDs with phosphorescent green and yellow emitters, which can effectively harvest triplets [28].

In this work, we report highly efficient white OLEDs based on highly conductive PEDOT:PSS transparent electrodes. The device efficiency is boosted by using the optimized tandem structure based on red, yellow/green, and blue emissive multilayer system and the electrical performance of PEDOT:PSS transparent electrodes are enhanced by the solvent post treatment. The white OLED with PEDOT:PSS transparent electrodes developed in this work shows a power efficiency of 26.1 lm/W and an external quantum efficiency (EQE) of 19.6%. To the best of our knowledge, these are the highest efficiencies for white OLEDs with PEDOT:PSS transparent electrodes reported so far. We anticipate that this work represents a potential of PEDOT:PSS transparent electrodes for the realization of high performance ITO-free OLEDs.

2. Experimental

For the fabrication of PEDOT:PSS transparent electrodes, PEDOT:PSS formulation (Clevios PH1000, Heraeus) mixed with 6 vol% of ethylene glycol was spin-coated on glass substrates at 1500 rpm for 30 s. The thicknesses of resulting films were around 88 nm. Subsequently, the spin-coated films were baked on a hot plate at 120 °C for 15 min and the solvent post treatment with ethylene glycol bath was performed, as described in detail previously [16]. The organic layers for white OLEDs were deposited by thermal evaporation in a high vacuum chamber at a base pressure of 10^{-7} mbar. Doping was performed by co-evaportaion of host and dopant materials. Thicknesses of layers were monitored with calibrated quartz crystal microbalances. The device stack is shown in Fig. 1: glass substrate / ITO or PEDOT:PSS transparent electrodes / 35 nm (N,N,N',N'-tetrakis(4-methoxyphenyl)-benzidine) (MeO-TPD) : 2,2′-(perfluoronaphthalene-2,6-diylidene)dimalononitrile (F6-TCNNQ) (2 wt.%) / 10 nm 2,2′,7,7′-tetrakis-(N,N'-diphenylamino)-9,9′-spirobifluorene (Spiro-TAD) / 5 nm N,N'-di-1-naphthalenyl-N,N'-diphenyl-[1,1′:4′,1″:4″,1‴-Quaterpheny]l-4,4‴-diamine (4P-NPD) : Iridium(III)bis(2-methyldibenzo-[f,h]chinoxalin)(acetylacetonat) (Ir(MDQ)$_2$(acac)) (5 wt.%) / 3 nm 4P-NPD / 10 nm 4,7-diphenyl-1,10-phenanthroline (BPhen) / 90 nm BPhen : Cs (1:1) / 0.5 nm Ag / 75 nm MeO-TPD : F6-TCNNQ (2 wt.%) / 10 nm Spiro-TAD / 5 nm 4,4′,4″ tris (N-carbazolyl)-triphenylamine (TCTA) : fac-tris(2-phenylpyridine) iridium(III) (Ir(ppy)$_3$) : bis(2-(9,9-dihexylfluorenyl)-1-pyridine) (acetylacetonate) iridium(III) (Ir(dhfpy)$_2$(acac)) (91:8:1 wt.%) / 5 nm 2,2′2″-(1,3,5-benzenetriyl)-tris[1-phenyl-1H-benzimidazole] (TPBi) : Ir(ppy)$_3$: Ir(dhfpy)$_2$(acac) (91:8:1 wt.%) / 10 nm TPBi / 60 nm BPhen : Cs (1:1) / 100 nm Al. After evaporation process, devices were encapsulated in nitrogen atmosphere using glass lid. The current-voltage-luminescence characteristics were measured with a source-measure unit system and a calibrated Si-photodiode. Electroluminescence spectra was recorded with a calibrated spectrometer. The emission characteristics of the devices with viewing angles were examined with a spectrogoniometer.

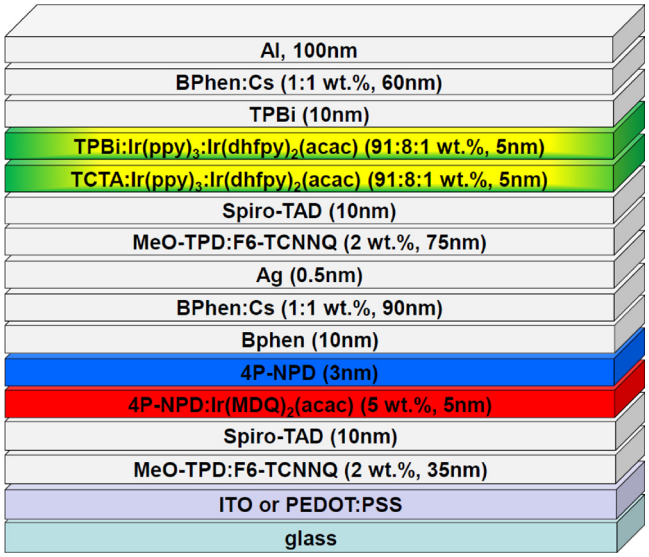

Fig. 1. (a) Schematic of the structures of OLEDs prepared in this work.

3. Results and discussion

Fig. 1 shows the device structure carefully optimized for high efficiency as described by Rosenow et al. [28]. A fluorescent blue and a phosphorescent red emitter are used for efficient triplet harvesting. The mixed phosphorescent units with a green and a yellow emitter are stacked on the triplet harvesting unit. This structure enables for a strong blue emission together with efficient triplet harvesting, which can reach an internal quantum efficiency of 100%. In addition, doped charge transport layers (HTL: F6-TCNNQ doped MeO-TPD and ETL: Cs doped BPhen) successfully achieve an ohmic contact between hole/electron transport layers and electrodes, resulting in the efficient charge injection and transport. Moreover, charges are effectively concentrated into the emissive layers thanks to the charge blocking layers of Spiro-TAD and TPBi, allowing the efficient radiative charge recombination. For ITO-free OLEDs, highly conductive PEDOT:PSS films are utilized as transparent electrodes. The conductivity of PEDOT:PSS films is improved from 719.9 S/cm (sheet resistance: 157.9 ohm/sq) to 1056.7 S/cm (sheet resistance: 155.1 ohm/sq) by the solvent post treatment, while transmittance does not change (average transmittance at 400–800 nm: 85.4%). The post treatment reduces insulating PSS and effectively forms conductive PEDOT networks, leading to the enhancement of conductivity of films as shown in our previous work [16,23,29].

Fig. 2 shows the current density-voltage-luminance characteristics for OLED with ITO (Device_ITO) and with PEDOT:PSS (Device_PEDOT:PSS). The characteristics of the devices are summarized in Table 1. The current density of Device_PEDOT:PSS is lower than that of Device_ITO caused by the more resistive property of PEDOT:PSS electrodes than that of ITO. Accordingly, Device_ITO exhibits the higher luminance compared to Device_PEDOT:PSS. Device_ITO and Device_PEDOT:PSS have a maximum power efficiency of 29.8 lm/W and 26.1 lm/W, respectively. The higher operating voltage of Device_PEDOT:PSS leads to the lower power efficiency of device than Device_ITO. Despite of the lower current density and the luminance of Device_PEDOT:PSS,