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ITO-free large-area top-emission organic light-emitting diode by blade coating

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ABSTRACT

Large-area top-emitting organic light-emitting diodes (TEOLEDs) with multi-layer structure are successfully demonstrated using the solution-processable blade coating on ITO-free substrate. The semitransparent cathode of TEOLED is composed of lithium fluoride (LiF), aluminum (Al) and silver (Ag). The composition of 3 nm Al and 10 nm Ag has a transmittance of 56% and a sheet resistance of 11 Ω/□. It is applied to the green phosphorescence device with an emissive area of 2 cm by 2.5 cm. The maximum current efficiency is 25.2 cd/A with high light-emission uniformity within 10% variation. The large-area TEOLEDs show comparable current efficiency as the small-area devices with an emissive area of 2 mm by 2 mm (having the same device structure) and better efficiency than traditional large-area bottom-emitting devices. Cesium fluoride (CsF) and n-doped electron transport layer are applied to improve electron injection. At 6 V, the luminance is raised from 141 cd/m^2 to 502 cd/m^2 and 304 cd/m^2, respectively. In n-doped device, a simple Al/Ag cathode is used without LiF.

1. Introduction

Organic light-emitting diodes (OLEDs) have been actively studied in the past several years due to their potential for solid-state lighting and flat panel display applications [1–7]. Indium tin oxide (ITO) is commonly used as the transparent electrode for OLEDs due to its high transmission in visible wavelength range, good electrical conductivity, and high work function. However, since indium is a scarce material, it leads to the high cost of ITO. In addition, during OLEDs' operation, indium migrates from ITO into the emission layer and this reduces OLEDs' lifetime [8,9]. On the other hand, top-emitting OLEDs (TEOLEDs) of conventional architecture consists of a reflective anode and a semitransparent cathode, where light emits through the semitransparent cathode. The reflective anode is usually of high reflectance, excellent electrical conductivity, and relatively cheap metals, e.g., Al, Ag, etc. Thus, using these metals to replace ITO can help to save costs, and potentially raise lifetime. They could also be fabricated on opaque and flexible substrates, such as metal foils and plastics.

For TEOLEDs, the deposition for organic layers is mainly vacuum evaporation in small-area devices [10–19]. However, the material utilization of vacuum evaporation is low that limits OLED products from wide development. Furthermore, for OLED lighting, large-area device with uniform luminance is necessary. Metal grid is applied for large-area OLED by vacuum process [20], but the process is complex and the grid may cause uniformity constraint. It is highly desired to realize a large-area TEOLED in a simple sandwich structure by solution process on an ITO-free substrate. The solution-processable blade coating method is developed for fabricating multi-layer organic semiconductors. Blade coating has the advantage of depositing multiple layers with minimal dissolution due to its rapid drying process. Compared with 10% material utilization to spin coating, blade coating is almost 100% that saves considerable costs. Furthermore, the method can be easily scaled up to large area with high throughput. From previous studies, multi-layer bottom-emitting OLEDs fabricated by blade coating showed good performance [21–25].

In this paper, we present large-area top-emitting OLEDs fabricated via blade coating. The semitransparent cathode is composed of LiF/Al/Ag. Two main factors affecting the light-emitting efficiency are the transmittance and sheet resistance of the semitransparent cathode. Therefore, three different Ag thicknesses are evaporated to acquire their transmittances and sheet resistances. In order to demonstrate the potential of large-area fabrication, the light-emitting areas are set to 2 cm by 2.5 cm. The light emits uniformly from the 2 cm by 2.5 cm areas, with peak

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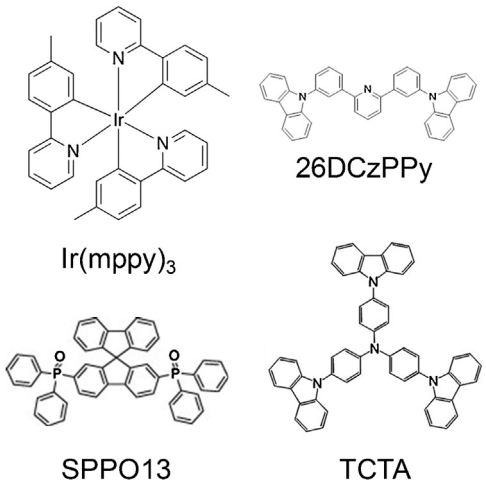

Fig. 1. The chemical structures of all the molecules.

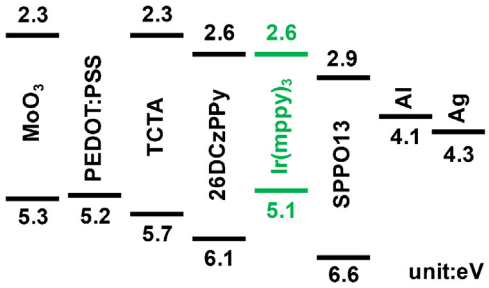

Fig. 2. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for the materials.

Table 1
The transmittance and sheet resistance of 5 nm, 10 nm, and 15 nm Ag with 3 nm Al, respectively.

	Transmittance (%)	Sheet resistance (Ω/□)
Al 3 nm/Ag 5 nm	66	59
Al 3 nm/Ag 10 nm	56	11
Al 3 nm/Ag 15 nm	42	5

current efficiency of 25.2 cd/A. Small-area devices (2 mm by 2 mm) of the same device structure are compared to the large-area ones and they showed comparable performances. With the same organic layer structure, the efficiencies of top-emitting devices are slightly higher than bottom-emitting ones. Therefore, large-area TEOLEDs have high efficiency, comparable to small-area TEOLEDs, and are able to replace bottom-emitting OLEDs with ITO. Cesium fluoride (CsF) gives a lower work function than lithium fluoride (LiF) [26,27]. Hence, the electron injection from semi-transparent cathodes into organic semiconductors is enhanced and the driving voltage is reduced. At 1000 cd/m^2 the voltage is reduced from 8 V for LiF device to 7 V for CsF device. Because of the thin thickness of salts like LiF and CsF, they may cause the uniformity challenges in large area evaporation. We further replace the evaporated salt by n-doping the electron transport layer by Cs_2CO_3 in solution. The large-area TEOLED with n-doping also show good efficiency of 25.6 cd/A and low driving voltage of 7 V at 1000 cd/m^2 using a salt-free Al/Ag cathode. Such cathode may also improve the lifetime by reducing the alkaline ion diffusion problem [28].

2. Experimental

The chemical structures of all the molecules used in this work are given in Fig. 1. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for the materials involved in this work are shown in Fig. 2 in eV. The Fermi level for the anode and cathode are also given. The 100 nm aluminum and 2 nm molybdenum trioxide are thermal-evaporated sequentially on a pre-cleaned glass substrate, which has an active area of 2 cm by 2.5 cm. Before coating the next layer, the molybdenum trioxide layer is treated by UV-ozone for 5 min to enhance surface affinity. Poly(3,4-ethylenedioxythiophene): poly (styrenesulfonate) (PEDOT:PSS, CLEVIOS™ P VP AI 4083) is spin-coated onto the molybdenum trioxide layer and annealed at 150°C for 15 min to form a 40 nm hole injection layer (HIL). 4,4′,4″-tris-(*N*-carbazolyl)-triphenylamine (TCTA) is dissolved in chloroform with 0.6 wt%, and then blade-coated onto the PEDOT:PSS layer. After annealing at 80°C for 10 min in nitrogen to remove the residual solvent, a 30 nm TCTA dry film forms as the hole transport

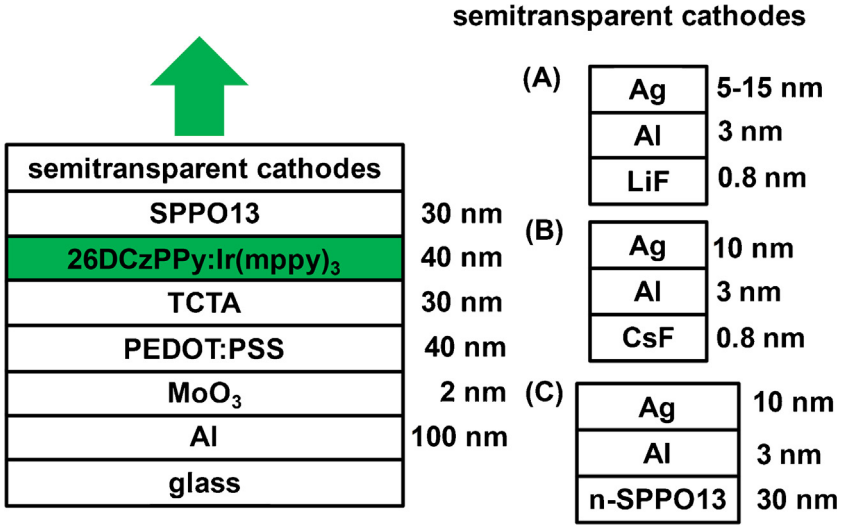

Fig. 3. The device structure of green phosphorescent OLED and semitransparent cathode (A) LiF (B) CsF and (C) n-doped ETL. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)