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Using an embedded nanocomposite layer to increase color-conversion efficiency of organic light-emitting diodes

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ABSTRACT

Down-conversion white organic light-emitting diodes (WOLEDs) have a significant advantage in generating stabilized white-light emissions, but still have room for further improvement in terms of color-conversion efficiency. We demonstrated that TiO_2 nanoparticles mixed with fluorescent dyes could be used to increase the absorption of dyes and thus boost the efficiency of color-conversion. WOLEDs with a nanocomposite color-conversion layer achieved high efficiencies of 12.3% (22.9 cd/A and 22.5 lm/W) and stable white-light emission. In addition, the EL spectra with different viewing angles are close to the ideal Lambertain curve. These outcomes indicate that the nanocomposite-based color-conversion possesses great potential for use in display and lighting applications.

1. Introduction

White organic light-emitting diodes (WOLEDs) have drawn significant interest due to several advantageous characteristics such as high efficiency, inherently diffusive lighting source, and high color rendering capability. In general, white light emissions could be simply obtained by vertically stacking organic emitting layers consisting of emitters with three primary colors or complementary colors [1,2]. Serious color shift can result from both carrier recombination zone (RZ) shift and energy transfer between emitters induced from the varying voltages [3]. Obviously, multiple emitters used in OLEDs inevitably complicate device architectures designed to produce stabilized white-light emission [4,5]. Consequently, although WOLEDs with multiple dopants exhibit great flexibility for color tuning, their practicality for display or lighting applications is limited by drawbacks including fabrication complexity, bias-dependent electroluminescence (EL) spectra, and time-dependent EL spectra along with different aging times of emitters.

These disadvantages could be remedied by using a single emitter in OLEDs. In 2008, Lee and Zhang developed a novel white-emitting material named 4,4′-di(9-(10-pyrenylanthracene))triphenylamine (DPAA) [6]. Using a simplified tri-layer architecture, DPAA-based WOLEDs achieved maximum efficiencies of 7.0 cd/A and 7.1 lm/W. However, single emitters with white-light emissions are still very rare, and their level of EL efficiency is much lower than those of WOLEDs employing multiple emitters. Color conversion is an alternative method to improve the color stability of WOLEDs [7–10]. In 2002, Duggal et al. demonstrated that white-light emissions could be obtained by combining blue polymer light-emitting diodes (PLEDs) with color-conversion layers (CCLs) [11]. Some photons originating from the blue PLEDs are absorbed in the CCLs and then converted to longer-wavelength photons. Thus, white-light emissions are generated by mixing unconverted blue photons and converted red photons. The

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monochromatic OLEDs avoid energy transfer from the wide-gap emitter to the lower-gap emitter. Furthermore, for OLEDs with a single blue emitter, extending and shifting the exciton formation zone does not alter the emission color. Moreover, modified electrical circuits could easily compensate for device degradation resulting from the aging of the single emitter. Hence, the design rules for CCLs-based WOLEDs must be concise, thus boosting the manufacturing yield and facilitating commercialization. Nevertheless, few studies have focused on CCLs due to limited progress in terms of color-conversion efficiency.

In 2006, Krummacher et al. employed a down-conversion scheme to construct a CCL on the reverse side of a glass substrate [12]. The orange phosphor in the CCLs absorbed the blue photons from the FIrpic-based OLEDs and then produced orange photons. Mixing the converted orange photons with the residually unconverted blue photons generates white light. The CCL-based WOLEDs achieved peak efficiencies of 25 lm/W and 39 cd/A. In 2011, Lee et al. demonstrated that the efficiency of color-conversion could be improved by using a microcavity structure in OLEDs [13]. The adopted microcavity structure could tune the spectrum of blue emissions to match the phosphor's excitation spectra, resulting in an improved down-conversion efficiency. In addition, the microcavity redistributes the optical modes in the device such that the substrate mode is enhanced [14,15], thus further improving color-conversion efficiency. However, the microcavity changes the viewing angle, thus limiting possible applications [16].

This study combines a nanocomposite diffuser with color conversion materials to improve color-conversion efficiency. We speculate that the scattering of nanoparticles (NPs) in CCLs could increase the light progression path and thus improve the absorption of emitters. Moreover, light-extraction efficiency could be simultaneously increased through employing a nanocomposite diffuser to reduce total internal reflection. Based on our previous study, the nanocomposite diffuser sandwiched between ITO and glass provides great improvement to efficiency. Experimental results indicate that blue phosphorescent OLEDs equipped with an internal nanocomposite color-conversion layer could generate a stable white light with high efficiency.

2. Experimental details

2.1. OLED fabrication and characterizations

The organic materials for the small molecules used were purchased from Nichem. All organic compounds utilized were subject to temperature-gradient sublimation under high vacuum before use. Additionally, the polymer material, poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (pedot:pss, Clevios PVP CH 8000), was purchased from Starck. The organic and metal layers were deposited by vacuum evaporation in a vacuum chamber with a base pressure of $<10^{-6}$ torr. The deposition system enabled the fabrication of the complete device structure without breaking vacuum. The deposition rate of the organic layers was kept at ~0.2 nm/s. The active area of the device was 2×2 mm^2, as defined by the shadow mask for cathode deposition. Current–voltage–luminance (*I–V–L*) characterization of the devices was performed using an Agilent 4156C semiconductor parameter analyzer and a Si photodiode calibrated with a Photo Research PR650. Electroluminescence spectra of the devices were recorded by using an Ocean Optics spectrometer.

Successful OLED design depends on the blue-emitter which produces the shortest wavelength emissions to equip with wide-gap host and wide-gap carrier transporting materials. The sky-blue phosphorescent emitter, iridium(III) bis[(4,6-di-fluorophenyl)-pyridinato-*N*,$C^{2'}$] picolinate (FIrpic) has been shown to possess a photoluminescence quantum yield that could reach nearly 100% in 3-bis(9-carbazolyl)benzene (mCP). In addition, devices with a bipolar host are better able to achieve carrier balance. We selected di-[4-(N,N-ditolyl-amino)-phenyl]cyclohexane (TAPC) and 1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB) as the hole-transport layer and electron-transport layer respectively due to their high carrier transport and exciton confinement capabilities [17]. In addition, the conductive polymer, pedot:pss, holds a distinct advantage in facilitating the planarization of the ITO substrate, especially in substrates with nanocomposite films [18].

A hybrid WOLED named as Devices HW was fabricated for comparison. Herein, three kinds of substrates were used to examine the performance of the OLEDs. Hybrid WOLEDs were constructed on top of a home-made ITO-coated glass substrate (i.e. Substrate I). The device architecture consisted of ITO (120 nm)/pedot:pss (~30 nm)/TAPC (10 nm)/mCP doped with 3 wt.% DCJTB (1 nm)/mCP doped with 8 wt.% FIrpic (18 nm)/mCP doped with 4 wt.% DCJTB (1 nm)/TmPyPB (50 nm)/LiF (0.8 nm)/Al (150 nm). The red/blue/red emitting layers were designed to stabilize the emission color with varying biases [19]. Fig. 1(a) shows a structural drawing of the materials employed in OLEDs.

2.2. Fabrication of the color-conversion layer with nanoparticles

We also tested color-conversion WOLEDs based on substrates both with and without NPs, and using a transparent negative photoresist as the host material. The efficient red-emitting fluorescent material, 4-(dicyanomethylene)-2-tert-butyl-6-(1,1,7,7-tetramethyljulolidin-4-yl-vinyl)-4H-pyran (DCJTB) seemed a good candidate because of its emission complementary to the sky-blue emission of FIrpic. However, the absorption spectrum of DCJTB exhibits less overlapping with the photoluminescence spectrum of FIrpic, which might result in poor energy transfer. This issue had been previously resolved by co-doping yellow-emitting 5,6,11,12-tetraphenylnaphthacene (Rubrene) with DCJTB, to create a stepwise energy transfer [20]. The high-energy exciton could be absorbed by the Rubrene and then cascade to the DCJTB. For determining the role of the assistant dopant (i.e. Rubrene), the corresponding PL and absorption spectra was performed and the concentration of each emitters were kept at about 10^{-4} M in CH_2Cl_2 solution. The PL spectra of emitters were measured using a charge-coupled device spectrograph and the 325