Organic Electronics 15 (2014) 1028–1034

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Color-stable, ITO-free white organic light-emitting diodes with enhanced efficiency using solution-processed transparent electrodes and optical outcoupling layers

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ARTICLE INFO

Article history:
Received 26 November 2013
Received in revised form 11 February 2014
Accepted 20 February 2014
Available online 5 March 2014

Keywords:
OLEDs
Transparent electrode
Conducting polymer
Optical outcoupling

ABSTRACT

In this work, we demonstrate color-stable, ITO-free white organic light-emitting diodes (WOLEDs) with enhanced efficiencies by combining the high-conductivity conducting polymer PEDOT:PSS as transparent electrode and a nanoparticle-based scattering layer (NPSL) as the effective optical out-coupling layer. In addition to efficiency enhancement, the NPSL is also beneficial to the stabilization of electroluminescent spectra/colors over viewing angles. Both the PEDOT:PSS and the NPSL can be fabricated by simple, low-temperature solution processing. The integration of both solution-processable transparent electrodes and light extraction structures into OLEDs is particularly attractive for applications since they simultaneously provide manufacturing, cost and efficiency advantages.

1. Introduction

Organic light emitting diodes (OLEDs) are typically realized with a transparent indium tin oxide (ITO) anode, which is brittle, expensive, thus limiting the low-cost manufacturing and mechanical flexibility of OLEDs. ITO electrodes generally require a high-temperature processing for crystallization of films, which also limits the use of flexible substrates. Furthermore, the energy level mismatch between the work function of ITO and the highest occupied molecular orbital (HOMO) of typical organic hole transport layers often hinders hole injection and formation of ohmic contacts [1–5]. Accordingly, alternative transparent electrodes for the replacement of ITO, such as carbon nanotubes [6], graphene [7], thin metals [8,9], metal grids [10], metal nanowires [11] and conducting polymers [12–14] have been widely investigated. Among them, the conducting polymer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) has attracted particular attention due to its excellent mechanical flexibility, chemical stability, good transmittance and conductivity, and low cost [15]. Various methods to improve the performance of PEDOT:PSS (particularly the conductivity) have been recently reported and these electrodes have been successfully used as transparent electrodes for OLEDs [16,17] as well as organic solar cells [18].

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http://dx.doi.org/10.1016/j.orgel.2014.02.017
1566-1199/

Similar to other solid-state lighting sources, typical OLEDs also suffer from a poor extraction efficiency of internally generated photons, resulting from a large mismatch of the refractive index between organic layers ($n\sim1.7$–1.9), ITO ($n\sim1.8$–2.0), glass ($n\sim1.5$), and air ($n\sim1.0$). The total internal reflection at the interfaces of devices strongly traps photons inside the device, which significantly limits the external quantum efficiency (EQE) of OLEDs. It is known that ~70–80% of the generated photons are trapped in conventional OLED structures due to total internal reflection or coupling to localized surface plasmon polaritons (SPPs) at the metallic surface [19–21], while internal quantum efficiencies of fully phosphorescent [22] and triplet-harvesting OLEDs [23] close to 100% have been reported. In order to overcome the limited optical outcoupling efficiency of OLEDs, various strategies of using internal or external light extraction layers/structures have been investigated [24–28]. External light extraction structures are typically constructed outside of the device (i.e. on the substrate side having no OLED devices). For instance, OLEDs can be combined with micro-lens arrays [24] or shaped substrates to extract the substrate modes [25].

Internal light extraction structures are typically fabricated between organic layers and substrates, which ideally provides access to efficient light extraction for both organic and substrate modes and thus should in principle yield higher extraction efficiencies than external extraction methods. Photonic crystals [26] and embedded low index grids [24] have been investigated as effective internal light extraction structures for OLEDs. However, these internal extraction architectures in general involve more complicated fabrication and thus are not cost-effective for real OLED applications. Recently, we have developed nanoparticle-based scattering layers (NPSLs) as effective internal extraction structures for OLEDs [29–31]. The strong light scattering effect prevents total internal reflection at internal interfaces, enabling extraction of more photons from devices. Such NPSLs can be readily prepared by mixing nanoparticles with polymer hosts and be coated by solution casting, which results in possessing cost and manufacturing advantages. In addition to enhancing optical out-coupling efficiencies of OLEDs, one also generally finds that the color stability of OLEDs over viewing angles is improved when NPSLs are incorporated, an effect we have attributed to re-mixing of emission over angles [29–31].

Here, by combining the high-conductivity polymer PEDOT:PSS as the transparent electrode and NPSLs as an effective optical out-coupling layer, we demonstrate color-stable, ITO-free white OLEDs (WOLEDs) with enhanced efficiency. Both the PEDOT:PSS and the NPSL can be fabricated by a simple, low-temperature solution processing method, making such structures and methods particularly attractive for applications.

2. Methods

2.1. Preparation and characterization of PEDOT:PSS electrodes

Thin films of high-conductivity PEDOT:PSS were prepared by spin-coating from a mixture solution of the aqueous PEDOT:PSS solution (Clevios PH1000, Heraeus) and 6 vol.% ethylene glycol (EG). Adding the co-solvent EG into the PEDOT:PSS has been reported to substantially increase the conductivity of PEDOT:PSS [18]. Spin-coated PEDOT:PSS films were subsequently annealed on a hot plate at 120 °C for 15 min under ambient conditions. The sheet resistance of the films was measured by the Van der Pauw method. The thicknesses of the PEDOT:PSS electrodes were measured by a surface profilometer (Veeco Dektak 150). The transmittance of PEDOT:PSS thin films was measured using a spectrophotometer (Shimadzu MPC 3100). The PEDOT:PSS films were laterally structured by laser ablation with a Nd:YAG laser (ACI Laser) for the use as bottom electrodes in OLEDs.

2.2. Preparation and characterization of NPSL

For preparation of the NPSL mixture solution, 600 mg of TiO_2 nanoparticles was added into a 4 cc solution of the organic host material. TiO_2 nanoparticles with an average diameter of ~240 nm were dispersed homogeneously in a solution of an organic host matrix by physical vibration/stirring in the presence of ~100 μm diameter ZrO_2 particles as a milling object. The nanoparticle size was chosen to give strong enough optical scattering and yet not to induce significant surface roughness of films. The host matrix consisted of a propylene glycol-monomethyl-ether acetate-based and methyl-isopropyl ketone-based transparent photoresist material (Everlight Chemical Industrial Corporation). The NPSL films were then prepared through spin-coating of the filtered mixture solution of photoresist/TiO_2 nanoparticles at 1000 rpm for 40 s, followed by heat curing at 130 °C for 10 min. The morphology of NPSL was analyzed by atomic force microscopy (AFM) and scanning electron microscopy (SEM), and the average root-mean-square (RMS) roughness of the films was determined by analyzing a scanning area of $5 \times 5\ \mu m^2$.

A UV–Vis spectrophotometer equipped with an integrating sphere (JASCO V570) was used to characterize the transmittance and optical scattering properties of the NPSL films. In this work, two different transmittance measures are used. The specular transmittance ($T_{specular}$), representing photons transmitted parallel to the incident beam, was measured by using a monochromatic light beam incident normal on the sample and then collecting transmitted light only in the normal direction (within a 5° collection angle). The total transmittance (T_{total}), representing both scattered or non-scattered photons, was measured by using a monochromatic light beam incident normal on sample and then using an integrating sphere to collect transmitted light over all angles. The diffuse transmittance ($T_{diffuse}$), representing photons scattered into all but the incident directions, could then be calculated as $T_{diffuse} = T_{total} - T_{specular}$. The *haze*, which is defined as the ratio of the diffusively transmitted light over the total transmitted light, was then calculated as $haze = T_{diffuse}/T_{total}$.

2.3. Fabrication and characterization of OLEDs

Four types of WOLEDs are investigated in this study, including an reference ITO-based device (*ITO device*), a