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Hydroxyethyl cellulose doped with copper(II) phthalocyanine-tetrasulfonic acid tetrasodium salt as an effective dual functional hole-blocking layer for polymer light-emitting diodes

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ABSTRACT

We report a doping method to improve the performance of solution-processed polymer light-emitting diodes (PLEDs). Doping 12 wt% copper(II) phthalocyanine-tetrasulfonated acid tetrasodium salt (TS-CuPc) into hydroxyethyl cellulose (HEC) as a dual functional hole-blocking layer (df-HBL) of multilayer PLED (glass/ITO/PEDOT:PSS/HY-PPV/TS-CuPc-doped HEC/LiF/Al) significantly enhanced maximum luminance, maximum current and power efficiency over that without the df-HBL (10,319 cd/m^2, 2.98 cd/A and 1.24 lm/W) to (29,205 cd/m^2, 13.27 cd/A and 9.56 lm/W). CV measurements reveal that HEC possesses a powerful hole-blocking capability. Topography and conductivity AFM images show that doping TS-CuPc increases the interfacial contact area and interfacial conductivity, which can overcome the insulating nature of HEC and thus further facilitate electron injection. Enhancements in device performance are attributed to the improved carrier balance and recombination in the presence of df-HBL, confirmed in electron-only and hole-only devices. Moreover, apparently raised open-circuit voltages provide further evidence that enhanced electron injection is indeed realized by the df-HBL. This study demonstrates an effective approach to develop highly efficient PLEDs.

1. Introduction

For more than two decades, polymer light-emitting diodes (PLEDs) have attracted considerable attention for the potential of their intriguing optoelectronic properties for use in fabricating large area, flexible electronic devices. PLEDs are carrier-injection devices, which basically require balance of hole- and electron-injection from the two electrodes, along with effective transport and recombination in the emitting layer [1,2].

Generally, effective and balanced charge carrier injection is crucial to achieve efficient PLEDs. However, for most conjugated polymers, hole injection is easier than electron injection [3,4]. In addition, holes are usually more readily transported than electrons in conjugated materials [5,6]. Therefore, a hole-blocking layer (HBL) was practically introduced into PLEDs to balance the injection/transport of charge carrier. Furthermore, by moving the recombination zone away from the metallic cathode to avoid exciton quenching [7,8], a powerful HBL can substantially improve devices performances. The hole-blocking layer is typically made of conjugated small-molecular materials by vacuum thermal deposition, which is both complex and energy-intensive. Therefore, some efforts have been made to develop solution-processed hole-blocking materials, such as solution-processed conjugated small molecules; 2,7-bis(diphenylphosphoryl)-9,9’-spirobi(fluorine) (SPPO13) [9,10], non-conjugated polymers; poly(ethylene oxide) (PEO), poly(ethylenimine) (PEI) [11–13] and some n-type metal oxides; zinc oxide (ZnO) [14,15]. Among these hole-blocking materials, non-conjugated polymers can effectively block and confine the holes in the emitting layer, due to their low-lying highest occupied molecular orbital (HOMO) levels [12,13,16]. In addition, because these non-conjugated polymers are polar or hydrophilic, when fabricated as HBLs they usually chose high polar solvents (e.g., water, alcohol or acetonitrile) which exhibit orthogonal solubility for commonly used emitting layer materials. This can prevent the HBL solvent from damaging the previous emitting layer. Moreover, thanks to the polymer's good film-forming property, the non-conjugated polymer HBL can be prepared more smoothly and uniformly than small molecules. However, the lower melting temperatures of non-conjugated polymer, PEO (65 °C) or linear PEI (76 °C) [17,18],

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degrade device structure stability. Because the fabrication of metallic cathodes (or electron-injection layers) requires thermal deposition, vacuum evaporator exceeding the polymer melting point can easily cause melting or dewetting, thus damaging the device structure [19,20].

On the other hand, non-conjugated polymers can also be used as an electron-injection layer [21–24]. An effective interfacial dipole is readily formed between such polar polymers and a metallic cathode due to interfacial interactions. Although carrier recombination in the emitting layer occurs due to the dual role of the electron-injection/hole-blocking layer, the insulating nature of the non-conjugated polymer still degrades electron injection and transport. Aside from directly fabricating an electron-injecting layer (alkali salts or low-work function metal) on top of the non-conjugated polymer layer, there are two modified strategies to overcome this issue: (I) Controlling polymer thickness to nanoscale (<10 nm) to produce an electron-tunneling effect to reduce the electron-injection barrier [19,24,25] and (II) doping with helpful electron injection/transport materials such as conjugated small materials, alkali salts and n-type metal oxides, blended with non-conjugated polar polymer to improve the conductivity, operational voltage, and interfacial dipole [11,12,26,27]. In addition, we noticed that the chelation or binding of metal ions can successfully improve electron injection. Metal cations, reduced by appropriate chelating agents (chelators) or polar pendant groups of molecules, effectively act as an intermediate step to facilitate electron injection [28–32]. This metal chelated complex could potentially be used as a cathode interface or electron collecting layer in optoelectronic applications [30–33]. Recently, a water-soluble metal chelated complex, copper(II) phthalocyanine-tetrasulfonated acid tetrasodium salt (TS-CuPc), had been used as a hole-interfacial and hole-injection layer in organic solar cells and organic light-emitting diodes (OLEDs), respectively [34–37]. In particular, different from copper(II) phthalocyanine (CuPc), the water-soluble TS-CuPc can increase conductivity of inorganic materials and reduce carrier barrier height in organic electronics through a solution process [37,38]. However, its HOMO energy level (about −5.3 eV) is too low for use as hole-blocking material. Therefore, to overcome this limitation, TS-CuPc could combine with appropriate water-soluble, non-conjugated polymeric binders to achieve hole-blocking properties.

This study used a water-soluble, non-conjugated hydroxyethyl cellulose (HEC), doped with copper(II) phthalocyanine-tetrasulfonated acid tetrasodium salt (TS-CuPc), as a dual functional hole-blocking layer (df-HBL) in a multilayer polymer light-emitting diode (glass/ITO/PEDOT:PSS/HY-PPV/TS-CuPc-doped HEC/LiF/Al). The polar HEC polymer not only possesses good film-forming properties, but also effectively prevents corrosion of the EML during spin-coating. After fabrication as HBL, the non-conjugated HEC significantly obstructs the hole transport from the EML to decrease hole quenching in the cathode. In addition, the high thermal stability of HEC can prevent device damage due to HBL melting, particularly following thermal deposition of LiF/Al. Meanwhile, doping of TS-CuPc successfully improves the electron-injection capability of HEC, providing an electron-injection jumping step from the matched lowest unoccupied molecular orbital (LUMO) level, and forming a spike-like structure on top of the df-HBL layer to increase interfacial contact area and interfacial conductivity, thus further facilitating electron injection. Thus, this df-HBL simultaneously possesses effective electron-injection and hole-blocking capability. When the 12 wt% TS-CuPc-doped HEC was inserted as the df-HBL, the maximum luminance (L_{max}), maximum current and power efficiency (CE_{max}, PE_{max}) were respectively enhanced to 29,205 cd/m^2, 13.27 cd/A and 9.56 lm/W, while that without a df-HBL was respectively 10,319 cd/m^2, 2.98 cd/A and 1.24 lm/W. This result indicates that the TS-CuPc-doped HEC layer greatly improves the carrier balance and recombination in PLEDs and results in enhanced device performance.

2. Experimental

2.1. Materials

Hydroxyethyl cellulose (HEC, average Mv ~90,000) and copper(II) phthalocyanine-tetrasulfonic acid tetrasodium salt (TS-CuPc) (50.0%) were purchased from Sigma-Aldrich Co. and used as received. Complementary metal oxide semiconductor (CMOS) grade isopropanol (99.5%, J. T. Baker) and acetone (99.5%, J. T. Baker) were obtained from commercial sources and used without further purification. Hole-injection material poly(3,4-ethylene dioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, P VP AI 4083) and the yellow-emitting material Livilux PDY-132 (Super Yellow; HY-PPV) were respectively acquired from Clevios and Merck.

2.2. Measurements

Cyclic voltammograms (CV) were recorded under a nitrogen environment using a voltammetric analyzer (CV-50W from Bioanalytical Systems, Inc.) at a scan rate of 50 mV/s. The measuring cell was made up of a glassy carbon rod as the working electrode, a platinum wire as the auxiliary electrode, and an $Ag/AgNO_3$ (0.08 V vs. FOC) electrode as the reference electrode. The electrodes were immersed in 0.1 M acetonitrile solution of tetrabutylammonium perchlorate [$(n\text{-}Bu)_4NClO_4$]. The energy levels were calculated using the ferrocene (FOC) value of 4.8 eV with respect to the vacuum level defined as zero. The thermogravimetric analysis (TGA) of HEC was investigated with a PerkinElmer TGA-7 thermal analyzer, under a nitrogen atmosphere and at a heating rate of 10 °C/min. The thermal decomposition temperature (T_d) was determined at 5% weight loss of the HEC. Thermal transitional behavior of the HEC from 30 to 220 °C was investigated with a differential scanning calorimeter Mettler Toledo DSC 1, under a nitrogen atmosphere at a heating rate of 10 °C/min. Photovoltaic measurements of PLED were performed in a glove-box under illumination from a Thermo Oriel 300W solar simulator (AM 1.5G). The device structure was glass/ITO/PEDOT:PSS/HY-PPV/TS-CuPc-doped HEC/LiF/Al. Thin layers of PEDOT:PSS, HY-PPV and TS-CuPc-doped HEC were deposited by solution-coating process using a spin-coater (Laurell WS-400-6NPP-LITE). A conventional atomic force microscope (AFM), equipped with a Veeco/Digital Instrument Scanning Probe Microscope (tapping mode) and a Nanoscope III controller was used to examine the surface topography and thickness of the layers. Conductive atomic force microscope (C-AFM) measurements were obtained from a Bruker Dimension Icon system with a PeakForce Tunneling AFM (PF-TUNA) module. Using a PF-TUNA probe with a spring constant of 0.4 N/m and a tip coating of 25 nm Platinum/Iridium, this module was built on PeakForce tapping to show local current mapping. This C-AFM measurement was taken under a bias voltage of 1.0 V applied to the sample, and analyzed with NanoScope Analysis v1.40 from Bruker.

2.3. Fabrication of polymer light-emitting diodes

A multilayer PLED, with a structure of glass/ITO/PEDOT:PSS (35 nm)/HY-PPV (45 nm)/TS-CuPc-doped HEC layer (11 nm)/LiF (1 nm)/Al (90 nm), was fabricated by subsequent procedures to investigate its optoelectronic characteristics. A glass substrate coated with an ITO conductive layer (anode) was successively deposited with PEDOT:PSS as the hole-injection layer, HY-PPV as