Organic Electronics 25 (2015) 156–164

Contents lists available at ScienceDirect

Organic Electronics

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

Hydroxyethyl cellulose filled with M^{2+} chelate complexes with ethylenediaminetetraacetic acid (EDTA) as an effective electron-injection layer for polymer light-emitting diodes

Cheng-Liang Wu, Yun Chen *

Department of Chemical Engineering, National Cheng Kung University, No. 1, University Road, Tainan 701, Taiwan, ROC

A R T I C L E I N F O

Article history:
Received 9 March 2015
Received in revised form 26 May 2015
Accepted 22 June 2015
Available online 29 June 2015

Keywords:
Electron-injection layer
Hydroxyethyl cellulose
Ethylenediaminetetraacetic acid
Chelate complex
Pseudo-metallic state

A B S T R A C T

An effective electron-injection layer (EIL) is crucial to the development of highly efficient polymer light-emitting diodes (PLEDs) using stable, high work-function aluminium as the cathode. This work presents the first investigation using hydroxyethyl cellulose (HEC), filled with chelate complexes [$(CH_3COO)_2$-M, EDTA-M; M: Ca^{2+}, Mg^{2+}], as an electron-injection layer (EIL) to fabricate multilayer polymer light-emitting diodes (ITO/PEDO:PSS/HY-PPV/EIL/Al) by spin-coating processes. Devices based on HEC doped with EDTA-M provided the best performance. The maximum luminance and maximum current efficiency of polymer light-emitting diodes with EDTA-Ca in an HEC layer were 7502 cd/m^2 and 2.85 cd/A, respectively, whereas those with EDTA-Mg were 8443 cd/m^2 and 3.12 cd/A, which was approximately seven- to eight-fold of that without EIL. This performance enhancement was attributed to electron donation from the chelator that reduces metal cations to a “pseudo-metallic state”, enabling it to act as an intermediate step to facilitate electron injection. The results demonstrate that chelates of bivalent cations with EDTA can potentially serve as electron-injection materials for optoelectronic applications.

1. Introduction

For more than two decades, polymer light-emitting diodes (PLEDs) [1–3] have attracted considerable attention for the fabrication of flexible, large-area displays because of their unique characteristics, such as self-emission, low cost, and easy processing by wet processes. Polymer light-emitting diodes are carrier injection devices, which basically require balanced hole and electron injection from the two electrodes, along with effective transport and recombination in the emissive layer [4,5]. Achieving high device efficiency requires the efficient injection of both electrons and holes [4,6]. Therefore, substantial improvements in device efficiency have been obtained upon modification of the anode [7–9], by the introduction of low work-function cathodes [10], and by using hole and electron injecting/transporting layers [11–15]. For most conjugated polymers, hole injection is more favorable than electron injection [12,16]. Thus, efficient injection of electrons from the cathode to emissive conjugated polymers plays a crucial role in improving device efficiency and stability.

Low-work-function metals such as Ca and Ba are used to enhance electron injection into organic materials; however, these metals are not stable in air and sometimes react with and diffuse into organic materials, thus deteriorating device performance. To overcome these problems, the cathode should be environmentally stable, and environmentally stable high work-function metals such as Al, Cu, Ag, and Au have recently been employed as cathodes. However, the high work-function of such materials results in a high energy barrier which markedly impedes electron injection from the cathode. Use of a water- or alcohol-soluble electron injection layers (EIL) based on a conjugated polymer grafted with amino groups, ammonium salt, or diethanolamino groups has been shown to allow the use of a high work-function metal as the cathode [17–27]. This is attributed to interfacial dipole enhancement or the formation of space charge fields between the emitting layer and the metal cathode thus reducing the electron injection barrier [17,23,28,29]. It has been suggested that interaction between the highly polar pendant groups of water- or alcohol-soluble conjugated polymer and the electrodes created an interface dipole [28–32]. Enhancement of this interfacial dipole has also been observed among non-conjugated polymer surfactant interface materials, such as poly(ethylene oxide) (PEO) [33–35], poly(ethylene glycol) dimethyl ether (PEGDE) [36,37], DNA [38,39], and insulating polymers containing simple aliphatic amine groups [40], Hydroxyethyl cellulose (HEC) derived from natural polymers may be expected to serve the same purpose. HEC is an

---

* Corresponding author.
E-mail address: yunchen@mail.ncku.edu.tw (Y. Chen).

http://dx.doi.org/10.1016/j.orgel.2015.06.035
1566-1199/

easily-obtained green material possessing polar groups, i.e., ether and hydroxyethyl groups on the main chain and side chain, respectively. The polar hydroxyl and ether groups are expected to create an interfacial dipole with the cathode to enhance the electron injection and hole-blocking ability of polymer light-emitting diodes [41]. Moreover, good solubility of HEC in water facilitates its mixing with salts and metal ions. These characteristics suggest its applicability as an electron-injection layer for polymer light-emitting diodes fabricated from water- or alcohol-soluble HEC blending with ions [20,21,42,43].

Chen et al. first reported the use of a water/methanol-soluble polymer grafted with 18-crown-6 chelating to K^+ as the electron-injection layer (EIL) [41]. Electron donation from the 18-crown-6 reduced cations to a stable "pseudo-metallic state" that allows the use of environmentally stable Al as the cathode. The chelation and binding of ions by appropriate chelating agents (chelators) increased the interfacial dipole to facilitate electron injection from the cathode [20,41]. Polar pendant groups in polymers, such as ether, amino, crown or azo-crown ether groups, also demonstrated this characteristic by binding with ions [20,41,44,45]. The application of a stable pseudo-metallic state as an intermediate step for effective electron injection opens an efficient way to enhance polymer light-emitting diodes performance.

This study proposes the use of an water-soluble natural polymer, hydroxyethyl cellulose (HEC), mixed with organic salts (EDTA-4Na or CH_3COONa) and alkaline earth metal cations (Ca^{2+} or Mg^{2+}), as the EIL in polymer light-emitting diodes using HY-PPV (PDY-132, Super Yellow, from Merck) as the emitting layer (EML) [37,46]. The water-solubility of the composite mixture, attributable to the polar ether and hydroxyethyl groups of HEC, will effectively avoid damaging the EML during the spin-coating of the EIL. In addition, the hole-blocking ether and hydroxyethyl groups of HEC can greatly decrease hole quenching in the cathode. Moreover, the Ca^{2+} or Mg^{2+} can be reduced to an intermediate "pseudo-metallic state" by forming complexes with organic chelators such as EDTA. This intermediate "pseudo-metallic state" is beneficial in decreasing the electron-injection barrier from a stable metal cathode (e.g., Al, Ag or Au) to facilitate electron injection. The device efficiency was efficiently enhanced when the HEC composite layer, with Ca^{2+} or Mg^{2+} chelated by EDTA, was inserted as an EIL [ITO/PEDOT:PSS/EML (HY-PPV)/EIL/Al]. The maximum luminance, maximum current efficiency, and maximum power efficiency were respectively 7505 cd/m^2, 2.85 cd/A, and 0.98 lm/W for Ca^{2+} ions, as opposed to 8443 cd/m^2, 3.12 cd/A, and 1.03 lm/W for Mg^{2+}. Resulting device performance was greatly superior to that without the electron-injection layer (1115 cd/m^2, 0.41 cd/A, and 0.29 lm/W). The results indicate that the natural polymer-derived HEC composite, doped with organic chelators coordinated with suitable bivalent metal cations, is a promising electron-injection material for high performance polymer light-emitting diodes using high work-function metal cathodes such as aluminum.

2. Experimental

2.1. Materials

Hydroxyethyl cellulose (HEC, average Mv ~90,000), tetrasodium ethylenediaminetetraacetate (EDTA-4Na or ethylenediaminetetraacetic acid tetrasodium salt hydrate, ⩾99.0%), sodium chloride (ACS degree, ⩾99.0%), and magnesium chloride hexahydrate (ACS degree, 99.0%) were purchased from Sigma-Aldrich Co. and used as received. Calcium chloride (dried powder, 97%) and sodium acetate (98%) were purchased from Alfa Chemicals and Showa Co., respectively. 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-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and the yellow-emitting material Livilux PDY-132 (Super Yellow; HY-PPV) were respectively acquired from Bayer and Merck.

2.2. Measurements

Cyclic voltammograms were recorded under a nitrogen environment at a scan rate of 50 mV/s using a voltammetric analyzer (CV-50W from Bioanalytical Systems, Inc.) at room temperature. The measuring cell was made up of a carbon rod as the working electrode, a platinum wire as the auxiliary electrode, and an $Ag/AgNO_3$ (0.08 V versus 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, which is defined as zero. Photovoltaic measurements of polymer light-emitting diodes were performed in a glove box under illumination from a Thermo Oriel 300 W solar simulator (AM 1.5G). The device structure was ITO/PEDOT:PSS/HY-PPV/EIL/Al using the composite HEC layer as EIL. X-ray photoelectron spectroscopy (XPS) measurements were carried out using an Axis Ultra DLD (Kratos) system, employing an MCP stack & delay-line photoelectron detector with scanned & snapshot spectroscopy modes. A Mg/Al achromatic X-ray source with a maximum power of 450 W was used along with a 500 mm Rowland circle Al monochromator with a base pressure of 1×10^{-9} Pa. The binding energies were calibrated to the C 1s peak at 284.6 eV. Thin film samples for the XPS measurements were obtained by casting HEC solutions onto a glass substrate using a spin-coater (Laurell WS-400-6NPP-LITE). An 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 thickness of PEDOT:PSS, HY-PPV, and the electron injection layers.

2.3. Fabrication of polymer light-emitting diodes

Multilayer polymer light-emitting diodes (PLEDs), with a structure of ITO/PEDOT:PSS/HY-PPV/EIL (composite HEC layer)/Al, were fabricated by spin-coating to investigate their optoelectronic characteristics. A glass substrate coated with an ITO conductive layer was used as the anode, with poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS, Bayer) as the hole-injection layer, Livilux PDY-132 (HY-PPV, Merck) as the light-emitting layer, composite HEC layer as the electron-injection layer, and aluminum as the metal cathode. The ITO-coated glass was washed in an ultrasonic bath successively using a neutral detergent with a de-ionized water mixture, de-ionized water, acetone and 2-propanol, followed by treatment in a UV-ozone chamber. A thick hole-injection layer of PEDOT:PSS (35 nm) was spin-coated on top of the cleaned ITO glass and annealed at 150 °C for 20 min in a dust-free atmosphere. The emitting layer (EML) (30 nm) was deposited by spin-coating the PDY-132 (HY-PPV) solution (5 mg/1 ml toluene) on top of the PEDOT:PSS layer at 3000 rpm and annealed at 65 °C for 20 min to remove the residual solvent. The electron-injection layer (15 nm) was cast on top of the EML by spin-coating of various solutions containing 4×10^{-3} M (the RU of HEC, EDTA-4Na, $CaCl_2$, $MgCl_2$), 8 or 16×10^{-3} M (CH_3COONa) and 16×10^{-3} M NaCl in different conditions of composite HEC water-mixture. Finally, aluminum (90 nm) was deposited as the cathode by thermal evaporation at about 2×10^{-6} Torr. The current–luminance–voltage (I–L–V) characteristics of the devices were recorded using a combination of a Keithley power source (model 2400) and an Ocean Optics