Organic Electronics 20 (2015) 158–163

Contents lists available at ScienceDirect

Organic Electronics

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

Single layer deep blue polymer light emitting diodes with chlorinated Indium Tin Oxide after surface modification for high performance

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ARTICLE INFO

Article history:
Received 15 July 2014
Received in revised form 9 February 2015
Accepted 10 February 2015
Available online 20 February 2015

Keywords:
Chlorine free radicals quench
Poly(9,9-di-n-octylfluorene)
PLED
Chlorinated-ITO

ABSTRACT

Chlorinated-Indium Tin Oxide (Cl-ITO) has been found to have higher work function than the pristine ITO. When used as anode for polymer light-emitting diodes (PLEDs) with deep blue emitting β-phase poly(9,9-di-n-octylfluorene) (β-PFO) as the emitting layer, it allows hole injection without barrier. However, the presence of chlorine free radical on the surface of Cl-ITO leads to an exciton quenching effect. The surface modification on anode by dipping into 1% ammonium (NH_4OH) aqueous solution to remove free chlorine radicals on surface can enhance device performance significantly. The single layer device Cl-ITO (treated)/β-PFO/CsF/Al gives the maximum brightness 16773 cd/m^2 and maximum luminance efficiency 2.40 cd/A, which are higher than those with untreated Cl-ITO, (2519; 0.27) and CFx treated ITO, (7800; 1.8) and PEDOT:PSS coated ITO, (12884; 1.43). The ease of the present anode treatment allows the one-layer-only device to be a promising candidate for practical application.

1. Introduction

Polymer light-emitting diode (PLED) [1,2] has drawn great attention due to its potentiality for fabrication of large-area, light-weight and flexible displays by solution process. Owing to the high electrical conductivity and excellent visible light transmitting property, Indium Tin Oxide (ITO) is widely used as the anode in optical devices. However, its work function (~4.7 eV) [3] is low relative to the highest occupied molecular orbitals (HOMOs) (>5.5 eV) of fluorene-and phenylene-based emitting polymer, which results in a large hole injection barrier. Thus, further surface treatment is required to lower the barrier, such as (i) introducing thin organic interlayer like poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS) [4,5] or inorganic interlayer like molybdenum oxides (MoO_3) [6] as hole injection layer (HIL), (ii) utilizing O_2 plasma [7,8], ultraviolet (UV)-ozone [9,10] or CFx plasma [11] treatment to adjust surface atomic composition and meanwhile remove the contamination on ITO, or (iii) inserting self-assemble monolayer (SAM) [12–15] to increase the work function by interfacial dipole effect.

Recently, Lu and coworkers reported that the work function of ITO can be raised dramatically from 4.7 to 6.13 eV via exposing ITO to *o*-dichlorobenzene (ODCB) under UV irradiation at 254 nm [16]. With the chlorination, the hole injection barrier between Cl-ITO (work function 6.13 eV) and the hole transport layer, 4,4′-N′,N′-dicarbazole-biphenyl (CBP) (HOMO 6.1 eV), was eliminated completely and the resulting green phosphorescence organic light-emitting diodes achieved the outstanding performance, 97 lm/W at 100 cd/m^2.

In deep blue PLED, poly(9,9-dioctylfluorene) (PFO) is widely studied because of its quite high photoluminescence quantum efficiency (PLQE) 59% as thin film [17],

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http://dx.doi.org/10.1016/j.orgel.2015.02.013
1566-1199/

good thermal and color stability and excellent film-forming quality [18]. However, the device suffers from low hole current due to the high hole injection barrier since it possesses much higher HOMO level (~5.8 eV). In order to overcome this problem, Poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,4′-(N-(4-s-butylphenyl))diphenylamine)] (TFB) was inserted in between ITO and buffer layer to lower the hole barrier [19], and the resulting device exhibited the promoted maximum brightness (the maximum luminance efficiency) 3205 cd/m^2 (1.6 cd/A) from 2967 cd/m^2 (1.0 cd/A). Another way for anode modification via introducing a CFx thin film on top of ITO for enhancement in the hole injection was proposed [11], giving the promoted performance 7800 cd/m^2 (1.80 cd/A) relative to that with PEDOT:PSS 1800 cd/m^2 (1.3 cd/A). In this work, we introduce chlorinated-ITO (Cl-ITO) for β-PFO-based PLED and demonstrate that the exciton quenching effect can be reduced with the surface modification. After ammonium aqueous solution treatment to remove residual chlorine radicals, the device achieves the maximum brightness 16,773 cd/m^2 and maximum luminance efficiency 2.4 cd/A, which are higher than those of the device with untreated Cl-ITO by factors of about 7 and 9, respectively. This method is not only simple in device fabrication but also provides a dramatic enhancement in the hole injection.

2. Experimental procedure

2.1. Materials

The synthesis of polymers (poly(9,9-dioctylfluorene) (PFO) using for device fabrication was carried out according to our previous report [20].

2.2. Device fabrication and instrumentation

In the preparation of Cl-ITO, patterned ITO glass substrate was exposed to UV-generated ozone atmosphere

Table 1
The work functions of anodes with different treatments.

Treatment	E_{cutoff}	E_{onset}	Work function[a]
0 min	16.90	0.70	5.00
2 min	17.02	1.29	5.47
5 min	16.96	1.23	5.58
5 min with NH_4OH	17.26	1.58	5.52

[a] The work function is determined by the formula $E\phi = h\nu - (E_{cutoff} - E_{onset})$, where $h\nu$ is incident photon energy [26] (21.22 eV) of He I, the high binding energy cutoff (E_{cutoff}) and HOMO region (E_{onset}) are the turning points.

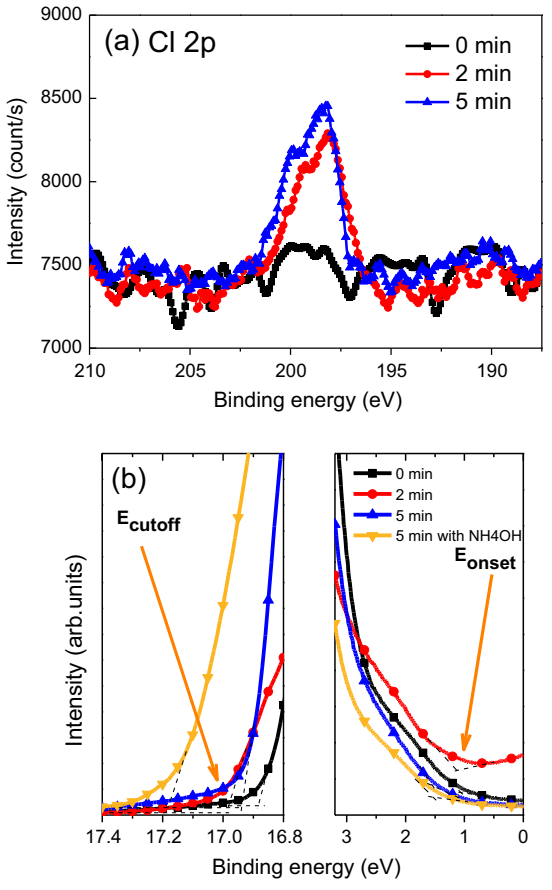

Fig. 1. (a) XPS spectra of Cl 2*p* with different ODCB treating time. (b) UPS spectra with different ODCB treating time and 5 min ODCB treating time with further 1% 3 min NH_4OH treatment.

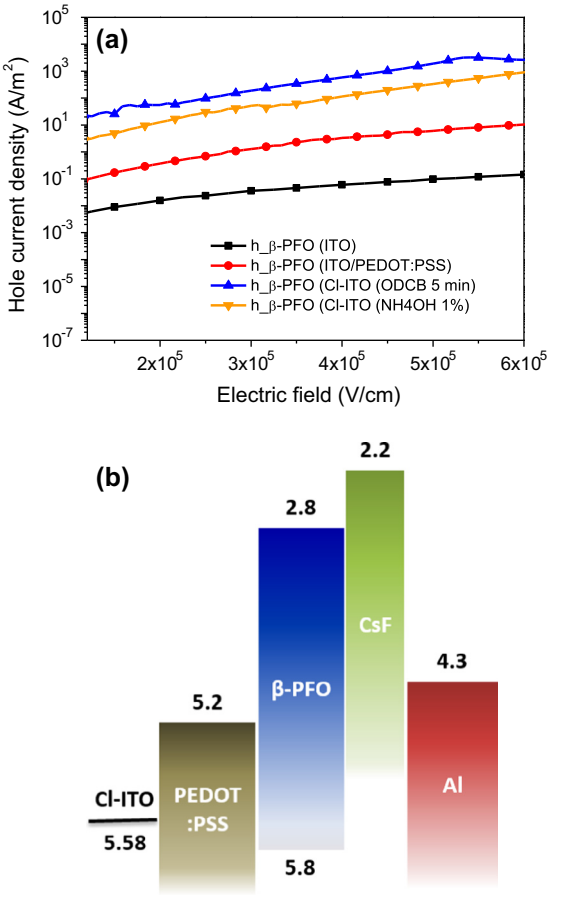

Fig. 2. (a) Current densities from hole-only devices based on the anodes, ITO, ITO/PEDOT:PSS, Cl-ITO (ODCB 5 min) and Cl-ITO (NH_4OH 1%), respectively. (b) The energy level diagram of the materials in the device.