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Hole-injection enhancement of top-emissive polymer light-emitting diodes by P3HT/FNAB modification of Ag anode

Lai-Wan Chong [a], Ying-Nien Chou [a], Yuh-Lang Lee [a,*], Ten-Chin Wen [a,*], Tzung-Fang Guo [b]

[a] *Department of Chemical Engineering, National Cheng Kung University, Tainan 701, Taiwan, Republic of China*
[b] *Institute of Electro-Optical Science and Engineering, National Cheng Kung University, Tainan 701, Taiwan, Republic of China*

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ABSTRACT

Based on the hole-transport characteristic of poly(3-hexylthiophene) (P3HT), self-assembled thin layer of P3HT was employed to modify the Ag anode of a top-emissive polymer light-emitting diodes (T-PLEDs) to enhance the hole-injection from the Ag anode. The experimental results show that introduction of a P3HT thin layer significantly decreases the threshold voltage of a T-PLED. However, only slightly increase of the work function was achieved due to this modification. To increase the work function of the P3HT modified Ag anode (Ag/P3HT), 1-fluoro-2-nitro-4-azidobenzene (FNAB) was introduced into the terminal tail ($-C_6H_{13}$) of P3HT thin layer, which leads to a work function increment of 0.23 eV and a further enhancement in the hole-injection. The luminous efficiency achieved by this modified anode (Ag/P3HT/FNAB) is about fourfold higher than the efficiency obtained from the base device.

1. Introduction

Top-emissive polymer light-emitting diodes (T-PLEDs) have attracted great attention recently due to the capability of fabrication the PLED displays directly on opaque substrates with pixel circuits of thin-film transistors, as well as other advantages including high aperture ratio, saturated color, low driving voltage, and high light intensity. To fabricate a T-PLED, an anode with high reflectivity and low electrical resistance is necessary and Ag was commonly used to fit this requirement. However, the work function of Ag is only about 4.3 eV, which always triggers a high barrier height for the hole-injection from Ag anode to the organic layer. To increase the work function of the Ag anode, surface modifications of the anode, by forming a thin oxide layer (Ag_2O) [1,2] or a self-assembled monolayer (SAM) [3–5], were employed in the literature. The efficiency enhancement by SAM was ascribed to the incorporation of a specific functional group which induces a dipole moment at the interface and thereby increases the work function of the electrode. The other functions of SAMs applied on organic light emission diodes (OLEDs) include increasing the compatibility between anode and HTL [6,7], enhancing the adhesion and stability of HTL [6,7], acting as a current blocking or moisture penetration blocking layer [8–11].

In the previous studies, SAMs were always prepared using thiols or silane derivatives which do not possess electronic or semi-conducting properties. In this work, a conjugated polymer with semi-conducting characteristic, poly(3-hexylthiophene) (P3HT), was employed to modify

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* Corresponding authors. Tel.: +886 6 2757575x62693; fax: +886 6 2344496.

E-mail addresses: yllee@mail.ncku.edu.tw (Y.-L. Lee), tcwen@mail.ncku.edu.tw (T.-C. Wen).

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the Ag anode. P3HT was known to be a hole-transport material and has been frequently applied in the devices of organic field-effect transistor [12,13] and photovoltaic [14–16]. The hole-transport property of P3HT is supposed to be advantageous to the hole-injection from an Ag anode. Furthermore, it had been shown that P3HT molecules bond chemically to Ag or Cu substrates through the linkage of S atom in the thiophene ring [17]. Therefore, it is possible to prepare a P3HT thin layer on Ag surface using a facile self-assembly process. This strategy was first examined in this work.

In a previous research [18], it was found that a SAM containing a terminal group of high electronegativity (e.g. fluorine) triggers a high work function of the modified surface. Based on this result, an electron-withdrawing function group, 1-fluoro-2-nitro-4-azidobenzene (FNAB), was introduced into the terminal tail ($-C_6H_{13}$) of the P3HT thin layer. This modified anode, Ag/P3HT/FNAB, was proved to have a higher work function and is more efficient to enhance the hole-injection. The importance of P3HT in the present strategy was confirmed by comparing the result with another device using 3-methylthiophene (CH_3TP)-modified Ag anode.

2. Experimental

Two T-PLEDs (ITO/Ag/HY-PPV/Ca/Ag and ITO/modified Ag/HY-PPV/Ca/Ag) were prepared in this study. Ag film of 150 nm thickness is deposited on the cleaned ITO glass substrate by thermal evaporation under a base pressure 10^{-6} torr and a deposited rate of 0.1 Å/s. After formation of Ag film, Ag anode was immersed in a chloroform solution containing 0.1 wt% P3HT for 30 min. After rinsing with chloroform and dried in a nitrogen steam, the P3HT modified anode, Ag/P3HT, was prepared. For the Ag/P3HT/FNAB anode, appropriate amount of FNAB solution was spread on Ag/P3HT substrate and air-dried in dark. FNAB was prepared by diazotization reaction of 4-fluoro-3-nitroaniline (FNA) as the procedure reported in the literature [19–21]. The FNAB-covered substrate was then exposed to a UV lamp (365 nm) for 20 min to carry out the nitrene reaction between azide (N_3) group of FNAB and methyl group ($-CH_3$) of P3HT. The substrate was then washed in succession by chloroform, and acetone, and dried in a nitrogen steam. The substrate was delivered to a vacuum chamber at 10^{-2} torr for 1 h and then transferred to the nitrogen-filled glove-box. The proposed structures for the prepared P3HT and P3HT/FNAB thin layers were schematically shown in Fig. 1. "High-yellow" phenyl-substituted poly(-para-phenylenevinylene) copolymer (HY-PPV) was used as the light-emissive layer and was spin-coated onto the Ag anodes. Finally, a semi-transparent top cathode, Ca (12 nm)/Ag (17 nm), was vapor deposited under 10^{-6} torr. The active pixel area of the device was 6 mm^2. The current–voltage (*I*–*V*) and brightness–voltage (*L*–*V*) characteristics were measured using a current/voltage source measurement unit (Keithley 2400) and a calibrated silicon photodiode driven by a Keithley source. The EL spectra are measured by a CCD array spectrum meter (Ocean optics USB2000). All the measurements are performed in a nitrogen-filled glove-box. XPS spectra were measured by JEOL, JAMP-9500F auger electron spectroscopy with a Mg Kα source (1253.6 eV). The work function of the anode electrodes were measured by a Riken Keiki AC-2 photoelectron spectroscopy in air.

3. Results and discussion

Table 1 shows the contact angle of water on base and modified Ag substrates. The contact angle of water on base Ag surface is 77.0°, ascribed to the absorption of hydrocarbon and carbonaceous impurities from the atmosphere [22]. After modification by P3HT, the contact angle increases slightly to about 107.1°, a value consistent to the contact angle measured for alkyl-chain terminated surfaces (90–110°) [23,24]. Therefore, the hydrophobic property of the P3HT modified Ag surface is attributed to the exposing of alkyl chains ($-C_6H_{13}$) contained in P3HT molecules.

After incorporation of FNAB by nitrene reaction, the contact angle of water on the Ag/P3HT/FNAB substrate was measured to be 92.6°. The effect of UV light illumination (required for nitrene reaction) on the P3HT properties was also examined by exposing the Ag/P3HT under UV lamp (365 nm) for 20 min. The contact angle measured for the UV-treated Ag/P3HT substrate was 106.5°, which is nearly identical to the result of non-UV-treated Ag/P3HT. This result suggests that the UV light illumination does not make significant change to the surface wettability of Ag/P3HT and, therefore, after the nitrene reaction, any variation in the contact angle should be resorted to the incorporation of FNAB [20]. For the ideal molecular model proposed in Fig. 1, the terminated ($-CH_3$) group was replaced by a less hydrophobic group FNAB. Therefore, it is

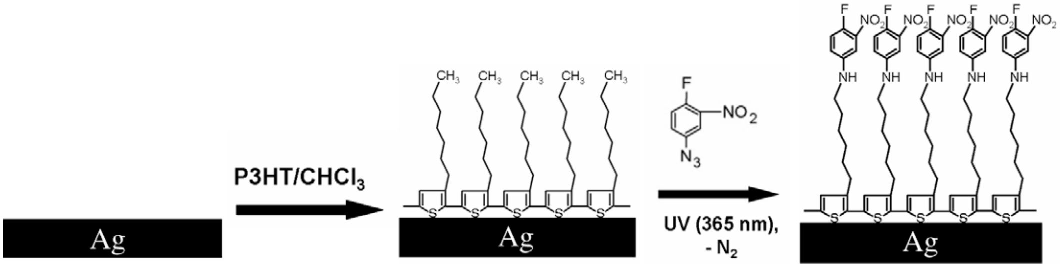

Fig. 1. The process for the deposition of P3HT and FNAB.