



Letter

Modifying organic/metal interface via solvent treatment to improve electron injection in organic light emitting diodes

Qing Wang^a, Yan Zhou^b, Hua Zheng^a, Jian Shi^c, Chunzeng Li^c, Chanmin Q. Su^c, Lei Wang^a, Chan Luo^a, Diangang Hu^a, Jian Pei^b, Jian Wang^{a,*}, Junbiao Peng^{a,*}, Yong Cao^a

^a Institute of Polymer Optoelectronic Materials and Devices, South China University of Technology, State Key Laboratory of Physics and Chemistry of Luminescence, Guangzhou 510640, PR China

^b Key Laboratories of Bioorganic Chemistry and Molecular Engineering, Ministry of Education, College of Chemistry, Peking University, Beijing 100871, PR China

^c Nano Surfaces Division, Bruker Corporation, 112 Robin Hill Road, Santa Barbara, CA 93117, USA

ARTICLE INFO

Article history:

Received 3 June 2011

Received in revised form 22 July 2011

Accepted 28 July 2011

Available online 11 August 2011

Keywords:

Organic light emitting diodes

Organic/metal interface

Surface engineering

Solvent treatment

Electron injection barrier

Interface dipole

ABSTRACT

By simply spin-coating the solvents, such as ethanol and methanol, on top of the organic active layer, the performance of polymer organic light-emitting diodes is significantly enhanced. The quantum efficiency is increased by as large as 58% for low work function Ba/Al cathode devices after solvent treatment. An interface dipole between the organic layer and the metal layer induced by the solvent, either from the intrinsic dipole or the interaction between the solvent and the cathode metal, is responsible for the device performance improvement. The interface dipole layer, which is confirmed by the Kelvin Probe Force Microscopy and the photovoltaic measurements, lifts the vacuum level on the metal side, thereby reducing the electron injection barrier at the organic/metal interface, and leading to better device performance.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Organic light emitting diodes (OLEDs) are “dual-injection” devices in which electrons and holes are injected from the opposite electrodes into an electroluminescent (EL) layer to produce light [1–3]. It is essential for the electrons and holes to be balanced inside the EL layer to achieve high efficiency. However, since most organic light-emitting materials have high LUMO (lowest unoccupied molecular orbital) level, the injection of electrons from the cathode is extremely critical to balance the charges. Modifying the organic/metal interface becomes an efficient way to reduce the electron injection barrier between the organic active layer and the cathode metal layer. Various organic/metal interface modification approaches have been successfully

realized, including the deposition of low work function metals [4,5], alkaline halides and alkali-earth halides [6,7], metallic compound [8–10], as well as surfactants [11–13].

Recently, water/alcohol-soluble conjugated polyelectrolytes (CPEs) or their neutral precursor [14–17], and self-assembled monolayers (SAMs) [18–20] emerged as promising materials for organic/metal surface engineering. For CPEs to improve the electron injection, two operation mechanisms have been proposed, based on the results of photovoltaic measurements and electroabsorption spectroscopy. One is that an interface dipole was formed to lower the injection barrier because of the strong interactions between the amino, ammonium, or hydroxyl group of the CPE, and the cathode metal [21–23]. The other is that the charge accumulation due to the considerable hole-blocking at the organic/metal interface, along with ion migration within the CPE layer, redistributes the internal field to reduce electron injection barrier [24,25]. About SAM's interface modification, it has been demonstrated

* Corresponding authors. Tel.: +86(20)8711 4525; fax: +86(20)8711 0606.

E-mail addresses: jianwang@scut.edu.cn (J. Wang), psjbpeng@scut.edu.cn (J. Peng).

that the work function of the cathode metals could be tuned on a large scale by the individual molecular dipoles and the interface dipole formed upon chemisorption of the SAM organic molecules [19,20,26,27], leading to the improvement of device performances.

In our contribution, we discovered that by spin-casting the solvents commonly used to dissolve CPEs and SAMs on top of the organic layer before the deposition of the metal layer, the device performance was significantly enhanced. The quantum efficiency is increased by as large as 58% for low work function Ba/Al cathode. An interface dipole between the cathode and the EL layer induced by the solvent (either from the solvent's intrinsic dipole or the interaction between the solvent and the cathode metal), is identified by the Kelvin Probe Force Microscopy (KPFM) to be responsible for the reduction of the electron injection barrier, and further verified by the photovoltaic measurements. The process of solvent treatment to modify the organic/metal interface is simple, efficient, cost-effective and easy to be adopted in industrial manufacturing.

2. Experiments

Three conjugated polymers PFO ADS 329 (from American Dye Sources, Inc.), P-PPV, and MEH-PPV (both from Canton Oledking Optoelectric Materials Co. Ltd.), were used for device fabrication. While the solvent treatments work for all the polymer devices, we select P-PPV as the representative to demonstrate our work.

Before making the light emitting devices, the ITO substrates were thoroughly cleaned in sequence in ultrasonic bath of acetone, isopropyl alcohol, detergent, de-ionized water, isopropyl alcohol, and went through O₂ plasma for 20 min. A thin layer of PEDOT:PSS was spin-casted in air followed by 10 min' baking at 200 °C in nitrogen. After PEDOT:PSS annealing, a 75 nm thick poly[2-(4-(3',7'-dimethyloctyloxy)-phenyl)-*p*-phenylenevinylene] (P-PPV) layer was spin-casted from *p*-xylene solution. To treat the organic/metal interface by solvent, 60 μL of the selected solvent were spin-coated on top of the P-PPV layer with the spinning speed of 2000 rpm for 1 min. The device was completed by thermally evaporating the metal cathode consisting of either 4 nm Ba covered by a 120 nm Al in vacuum under a pressure of 3×10^{-4} Pa.

Samples for KPFM measurements were prepared by spin-coating P-PPV on stainless steel pucks 12 mm in diameter, and spin-coating respective solvent on top of the P-PPV film. The KPFM measurements were performed with both single-pass mode and lift-mode on Bruker's Multimode® 8 scanning probe microscope in a customized glove-box (MBraun). SCM-PIT probes (platinum-iridium coating, Bruker) were used throughout the measurements. All the sample preparations and KPFM measurements were carried out inside a nitrogen filled glove-box with both O₂ and H₂O below 0.1 ppm to minimize surface contamination. The CPD images were obtained on a 1×1 μm area, over which the averaged CPD values are used.

For other experiments' details, please refer to the Supplementary data.

3. Results and discussions

To demonstrate the effect of solvent treatment on OLEDs, the green light-emitting conjugated polymer P-PPV, was selected, and two solvents most widely used to dissolve CPEs and SAMs: methanol and ethanol, were chosen with the device structure of ITO/PEDOT (45 nm)/P-PPV (75 nm)/Ba (4 nm)/Al (120 nm). The current density (*J*)-bias (*V*)-luminescence (*L*) characteristics, and the luminous efficiency's (LE) dependence on the current density are illustrated in Fig. 1a and b, respectively. Compared with the device without solvent treatment, which has the maximum quantum efficiency (QE) of 6%, LE of 17.0 cd A⁻¹ and brightness of 57,291 cd m⁻², the device treated with ethanol has the maximum QE of 9.5%, LE of 26.9 cd A⁻¹ and brightness of 83,575 cd m⁻². The device with methanol treatment exhibits similar performance improvement with the highest brightness of 74,663 cd m⁻², LE of 25.3 cd A⁻¹ and QE of 9.0%. After modifying the organic/metal interface by ethanol, the maximum quantum efficiency was increased by 58%. Even at high working brightness (3000 cd m⁻²), the devices treated with ethanol and methanol show a quantum efficiency of 8.5% and 6.6%, respectively.

In order to understand the functions of the organic/metal interface after solvent treatment, electron-only devices were fabricated with structure of ITO/Sn (130 nm)/P-PPV (75 nm)/Ba (4 nm)/Al (120 nm). The *J*-*V* characteristics are depicted in Fig. 1c. With methanol or ethanol treatment, the devices exhibits higher electron current than the device without solvent treatment at the same operation voltage after turn-on. The results indicate that using solvent can greatly improve the electron injection, leading to balanced charge density inside the active layer.

The electron injection improvement is due to the reduction of the electron injection barrier. Photovoltaic measurement is a direct measurement of the built-in potential which scales with the electron injection barrier height on the cathode side, when the anode and the organic layers are identical for all the devices [28]. Fig. 2 shows the *J*-*V* characteristics of the devices under white-light illumination (100 mW cm⁻²). The open-circuit voltage (*V*_{oc}) increased from 1.85 V for the untreated Ba/Al device, to 2.10 and 2.20 V for ethanol and methanol treated devices, respectively. The significant enhancement of *V*_{oc} (0.25 V from ethanol and 0.35 V from methanol) clearly confirms that the electron injection barrier is substantially lowered at the organic/metal interface after interface modification. Reducing electron injection barrier helps electron injection and makes electron and hole density balanced inside the EL layer, improving the device performance as evidenced in Fig. 1b.

Some groups have reported that a change in molecular orientation can affect the work function/ionization energy [29]. In our studies, the polymers are PPV and PFO based which are nonpolar or low polar materials. They form stable and smooth films by spin-coating their solutions in the non-polar solvents such as *p*-xylene. Moreover, those polymers are not soluble in either ethanol or methanol. Therefore, it is highly unlikely that spin-coating a small amount of ethanol/methanol on a dense solid film could change the

Download English Version:

<https://daneshyari.com/en/article/1264734>

Download Persian Version:

<https://daneshyari.com/article/1264734>

[Daneshyari.com](https://daneshyari.com)