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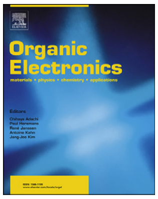

Solution-processed aqueous composite hole injection layer of PEDOT:PSS+MoO_x for efficient ultraviolet organic light-emitting diode

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ABSTRACT

Hole injection layer (HIL) plays a crucial role in governing external quantum efficiency (EQE) of ultraviolet organic light-emitting diodes (UV OLEDs). We develop a solution-processed aqueous composite HIL of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) incorporated MoO_x (PEDOT:PSS+MoO_x) and cast successful application to UV OLEDs. PEDOT:PSS+MoO_x is characterized in detail with scanning electron microscopy, atomic force microscopy, UV–visible absorption spectra, X-ray photoelectron spectroscopy, ultraviolet photoelectron spectroscopy and impedance spectroscopy measurements. The results show that PEDOT:PSS+MoO_x features superior film morphology and exceptional electronic properties such as enhanced surface work function and promoted hole injection capacity. With PEDOT:PSS+MoO_x as HIL, the UV OLED gives maximum EQE of 4.4% and radiance of 12.2 mW/cm^2 as well as improved durability. The electroluminescence peaks at 376 nm with full width at half maximum of 34 nm and stable voltage-dependent spectra. Our results pave a way for exploring efficient UV OLEDs with solution-processable techniques.

1. Introduction

Organic light-emitting diodes (OLEDs) have been investigated for almost three decades after Tang and VanSlyke documented efficient electroluminescence (EL) in 1987 [1]. OLED based consumer electronics are successfully applied in full-color displays and solid-state lightings. Ultraviolet (UV) OLED features short-wavelength emission and receives increasing attentions for its potential application to exciting lighting source [2,3], biological/chemical sensor [4] and high-density information storage [5–9]. However, UV OLED faces huge challenges such as low external quantum efficiency (EQE), inferior durability and intractable synthesis of emissive molecules [10]. Although numerous efforts have been made in enhancing device radiance and efficiency, most reported UV OLEDs give no more than 2% EQE [11–17]. Approaching 4% EQE is scarcely recorded. For instance, Mikami et al. reported UV OLED with EQE of 3.1% and EL peak of 380 nm by using 3-(4-biphenyl)-4-phenyl-5-*tert*-butylphenyl-1,2,4-triazole (TAZ) as emitting layer (EML) [3]. Lian et al. synthesized star-configurated carbazole derivatives (MTPC) and demonstrated 3.3% EQE with EL peak of 408 nm [18]. Ma et al. synthesized UV emissive molecule of diphenyl-[3'-(1-phenyl-1H-phenanthro[9,10-*d*]imidazol-2-yl)-biphenyl-4-yl]-amine (mTPA-PPI) and achieved device efficiency of 3.33% with EL peak of 404 nm [4]. Wu et al. demonstrated bi(9,9-diarylfluorene)s-based UV OLED with EQE of 3.6% and EL peak of 392 nm [19]. Exceeding 4% EQE is also demonstrated in TAZ-based device [20].

One of major factors restricting efficiency enhancement is the large hole injection barrier between indium-tin-oxide (ITO) anode and deep highest occupied molecular orbital (HOMO) level of intrinsic wide band-gap of UV emissive molecule. Developing effective hole injection/transport system is proposed as an easy-to-do approach for circumventing such a problem [21]. Conventional hole injection layers (HILs) of poly(3,4-ethylenedioxy-

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thiophene):poly(styrenesulfonate) (PEDOT:PSS) [3,6,22–24], MoO_x [4,16–18,25], ZnO [26], hexaazatriphenylenehexacabonitrile (HATCN) [27], copper-phthalocyanine (CuPc) [28,29], 4,4′,4″-tris[3-methylphenyl(phenyl)amino]triphenylamine (*m*-MTDATA) [30] and perfluorinated copper phthalocyanine ($F_{16}CuPc$) [15] are proven to be helpful in improving device performance. Dual HILs (e.g., Graphene oxide/MoO_x [13], PEDOT:PSS/PVK [31] and PEDOT:PSS/MoO_x [20]) and graded hole injection/transport system [14] are also tentatively investigated in UV OLEDs. Rather than using intensive vapor deposition techniques, solution-processed HIL may provide a trouble-shooting method for constructing efficient UV OLEDs [3,20,31]. A widely accepted solution-processed HIL in UV OLED application is PEDOT:PSS which usually features faintly acidic property [32,33]. MoO_x also shows well established application in OLEDs for its high work function, strong interfacial dipole and charge transfer [34–36]. However, MoO_x film is usually obtained by thermal deposition under high vacuum conditions. Fortunately, MoO_x behaves certain solubility in water [37,38] or other solutions [32,39,40], which facilitates to developing composite HIL (c-HIL) of PEDOT:PSS+MoO_x. Some applications to polymer LEDs [41], organic solar cells [39] and perovskite LEDs [42] are demonstrated. Here, we investigate efficient UV OLEDs by using solution-processed aqueous c-HIL of PEDOT:PSS+MoO_x with facile fabrication process, and achieve an attractive result of 4.4% EQE.

2. Experimental

2.1. Preparation of aqueous PEDOT:PSS+MoO_x blended solution

MoO_x water solutions with different concentrations (0.10 wt%, 0.15 wt% and 0.20 wt%) were prepared by directly dissolving MoO_3 powders (commercially purchased, 99.95%) into de-ionized (DI) water. The pristine MoO_3 features crystal orthorhombic phase, as shown in Fig.S1 in Supporting Information. Prolonged stirring and heating at about 70 °C were implemented (if necessary) till the MoO_3 powers were totally dissolved and the solution appeared faint yellow (Fig. 1). However, it is difficult to dissolve MoO_3 powders into DI water with increasing concentration to 0.25 wt%. The aqueous PEDOT:PSS+MoO_x blended solution for fabricating HIL was obtained by blending pristine PEDOT:PSS (commercially purchased, AI4083) with MoO_x water solution.

2.2. Device assembly

ITO coated glass was ultrasonically cleaned with acetone, ethanol and DI water, and served as substrate/anode for studied UV OLEDs. The c-HIL was obtained by spin-coating PEDOT:PSS+MoO_x blended solution after filtered through a 0.22 μm filter at 4000 rpm for 60 s and subsequently heat treated at 120 °C for 20 min in air conditions. Fig. 1 shows the schematic fabrication process of the c-HIL. Organic layers and cathode are thermally evaporated under a vacuum of 4×10^{-4} Pa. A series of UV OLEDs with structure of "ITO/HIL/4,4'-bis(carbazol-9-yl)biphenyl (CBP) (25 nm)/TAZ (20 nm)/4,7-diphenyl-1,10-phenanthroline (BPhen, 75 nm)/LiF (2 nm)/Al (100 nm)" were constructed. Firstly, we fabricate UV OLEDs with HILs of pristine PEDOT:PSS+0.20 wt% (**Device A20**), 0.15 wt% (**Device A15**), 0.10 wt% (**Device A10**) MoO_x solution in weight ratio of 1:1. The UV OLED (**Device A0**) with HIL of pristine PEDOT:PSS+H_2O (1:1 wt ratio, diluted PEDOT:PSS refers as *d*-PEDOT:PSS) is also constructed for comparison. Then, we fabricate UV OLEDs with HILs having different weight ratio of pristine PEDOT:PSS to 0.20 wt% MoO_x solution.

Device B31: PEDOT:PSS+0.20 wt%MoO_x solution (3:1).
Device B21: PEDOT:PSS+0.20 wt%MoO_x solution (2:1).
Device B12: PEDOT:PSS+0.20 wt%MoO_x solution (1:2).
Device B13: PEDOT:PSS+0.20 wt%MoO_x solution (1:3).
Device B14: PEDOT:PSS+0.20 wt%MoO_x solution (1:4).
Device B15: PEDOT:PSS+0.20 wt%MoO_x solution (1:5).

CBP and TAZ were served as hole transport layer and EML, respectively. BPhen, LiF and Al were served as electron transport layer, electron injection layer and reflective cathode, respectively. LiF and BPhen were carefully thickened with a purpose of slightly retarding electron injection and transporting for extremely optimizing carrier balance [12]. The deposition rate and thickness of each layer were monitored and controlled in situ using an oscillating quartz thickness monitor. Typical deposition rate was 1–2 Å/s for organics and 6–10 Å/s for Al. The schematic device structure and molecular structures of organic materials used were presented in Fig. 1.

2.3. Characterizations

The phase structure of pristine MoO_3 powders was characterized by X-ray diffraction (XRD, Bruker D8-ADVANCE).

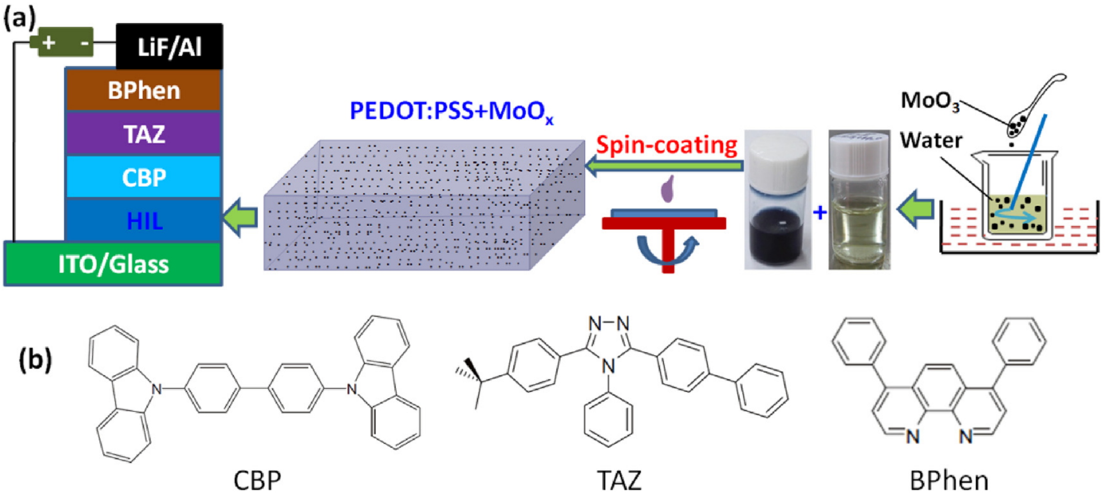

Fig. 1. (a) Schematic illustration of UV OLED with c-HIL of PEDOT:PSS+MoO_x and fabrication process. The images of 0.20 wt%MoO_x solution (faint yellow) and pristine PEDOT:PSS are also presented in the figure. (b) The molecular structures of CBP, TAZ and BPhen. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)