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Solution-processed WO_x hole injection layer for efficient fluorescent blue organic light-emitting diode

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ABSTRACT

Solution-processed tungsten oxide (s-WO_x) interfacial layer for efficient hole injection in fluorescent blue organic light-emitting diode (OLED) is demonstrated. The OLED using 2-methyl-9,10-bis(naphthalen-2-yl)anthracene (MADN) as emitter shows luminous efficiency of 3.3 cd/A, power efficiency of 2.5 lm/W and external quantum efficiency of 4.6% with Commission Internationale d'Eclairage (CIE) color coordinates of (0.154, 0.102). Using MADN doped 1-4-di-[4-(N,N-diphenyl)amino]styryl-benzene as emitter, luminous efficiency of 10.8 cd/A, power efficiency of 6.4 lm/W and external quantum efficiency of 7.2% with CIE color coordinates of (0.167, 0.283) are achieved. Atomic force microscopy and X-ray photoelectron spectroscopy show that s-WO_x features superior film morphology and non-stoichiometry with slight oxygen deficiency. Current-voltage characteristics and impedance spectroscopy analysis indicate that s-WO_x behaves slightly enhanced hole injection and accordingly contributes to improved device performance in comparison with conventional vacuum thermal evaporation WO_x. Our results pave an alternative way for broadening WO_x application with solution process and advancing fluorescent blue OLEDs.

1. Introduction

Organic light-emitting diode (OLED) has developed to one of ideal candidates for next-generation displays due to its excellent image quality, high power conversion efficiency and mechanically flexible portability. The primary red, green and blue emitters are essentially required for constructing high-resolution full-color displays. Producing blue OLED with high efficiency and satisfactory chromaticity still remains challenging task, although superior red and green organic emitters are extensively documented [1,2]. It is well established that phosphorescent emission provides an irreplaceable approach for achieving high efficiency [3,4]. However, phosphorescent blue device features typical efficiency roll-off, poor device durability and unsatisfactory efficiency [4–6]. Conventional fluorescence and prevalent thermally activated delayed fluorescence blue OLEDs attract researchers' increasing interest [7–10]. 2-methyl-9,10-bis(naphthalen-2-yl)anthracene (MADN) is a widely-used fluorescent blue emitter as well as host matrix [11–14]. MADN itself gives attractive blue emission with 1931 Commission Internationale d'Eclairage (CIE) color coordinates of (~0.15, ~0.10) and luminous efficiency of ~3 cd/A [15,16]. Enhanced performance can be readily realized by using host matrix dispersed with highly fluorescent guest which produces high electroluminescence (EL) and desired hues [8,17]. 1-4-di-[4-(N,N-diphenyl)amino]styryl-benzene (DSA-Ph) stands out as a favorite blue guest dopant for its acceptable efficiency and sky blue emission [10,18].

On the other hand, chromaticity strongly depends on electron-hole recombination and emission zone as a result of excitons could be formed at the interface between hole transport layer (or electron transport layer) and emissive layer (EML) which extremely depends on carrier injection and transporting [11,19,20]. In comparison with tailoring electron injection characteristics, tuning hole

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injection capacity gains more feasibility for confining electron-hole recombination zone and thus governing EL characteristics. Organic hole injection layers (HILs) such as 4,4′,4″-tris[N,-(3-methylphenyl)-N-phenylamino]triphenylamine (*m*-MTDATA) [21], copper phthalocyanine (CuPc) [22], 1,4,5,8,9,11-Hexaazatriphenylene hexacarbonitrile (HAT-CN) [23] and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4-TCNQ) [24] are extensively investigated for their compatibility with OLED fabrication of vacuum thermal deposition. Recently, solution-processed techniques such as printing, roll to roll and doctor blading boost OLED towards low-cost and scalable manufacturing. In contrast to favorite solution-processed HIL of poly(ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) [25,26], solution-processed transition metal oxides of MoO_x [27], VO_x [28,29], NiO_x [30], La_2O_3 [31] and WO_x [32] receive numerous attentions for their high thermal and chemical stability. WO_x features high work function (~6.4 eV) [33], superior transmittance [34] and improved device durability [32,35], which accelerates its applications in organic electronic devices of OLEDs [36], polymer LEDs [35], quantum dot LEDs [32], organic solar cells [37,38], perovskite solar cells [39,40], thin film transistors [41] and photocatalysts [42,43]. In addition, the annealing process of solution-processed WO_x can be performed under ambient conditions without complicated O_2-plasma treatment, which extremely simplifies device fabrication process [32,44]. Here we demonstrate solution-processed WO_x (s-WO_x) interfacial layer for efficient hole injection in fluorescent blue OLEDs. With MADN as EML, s-WO_x based OLED shows luminous efficiency (LE) of 3.3 cd/A, power efficiency (PE) of 2.5 lm/W and external quantum efficiency (EQE) of 4.6% with CIE color coordinates of (0.154, 0.102). Using MADN doped DSA-Ph as EML, s-WO_x based OLED shows LE of 10.8 cd/A, PE of 6.4 lm/W and EQE of 7.2% with CIE color coordinates of (0.167, 0.283). The s-WO_x is slightly superior to conventional vacuum thermal evaporation WO_x (e-WO_x) in promoting device performance.

2. Experimental details

Tungsten oxide solution of nanoparticle ink was commercially purchased from Sigma-Aldrich with an initial weight ratio of 2.5% and viscosity of 8 cP. s-WO_x solution with different concentrations were diluted with ethanol for subsequent OLED fabrication. Indium tin oxide (ITO) coated glass was served as substrate and anode, and subjected to routine chemical cleaning. UV-ozone treatment for 15 min was performed before spin-coating s-WO_x at 4000 rpm for 60 s and annealing at 120 °C for 20 min under ambient conditions. The OLEDs were fabricated in a deposition chamber under 4×10^{-4} Pa vacuum. The schematic device structure of "ITO/HIL/N,N′-bis(naphthalen-1-yl)-N,N′-bis(phenyl)-benzidine (NPB, 55 nm)/EML/4,7-diphenyl-1,10-phenanthroline (BPhen, 30 nm)/LiF (0.7 nm)/Al" is shown in Fig. 1. NPB and BPhen served as hole transport layer and electron transport layer, respectively. LiF/Al served as typical bilayer cathode. For investigating the effect of HIL formed by spin-coating s-WO_x with different solution concentrations, a series of OLEDs (**Device M1~M3**) with MADN as EML were fabricated. The counterpart with e-WO_x as HIL (**Device EM**) was also constructed for comparison. It is difficult to accurately measure the thickness of s-WO_x due to the fact that the WO_x film is too thin and accordingly solution concentration is preferably used.

Device M1: ITO/s-WO_x (0.10%)/NPB/MADN (40 nm)/BPhen/LiF/Al.

Device M2: ITO/s-WO_x (0.15%)/NPB/MADN (40 nm)/.

Device M3: ITO/s-WO_x (0.20%)/NPB/MADN (40 nm)/.

Device EM: ITO/e-WO_x (1 nm)/NPB/MADN (40 nm)/.

Next, a series of OLEDs with host-guest doped EML of [MADN:3 wt% DSA-Ph] were fabricated for further investigating the effects of s-WO_x (**Device MD1~MD3**) and e-WO_x (**Device EMD**).

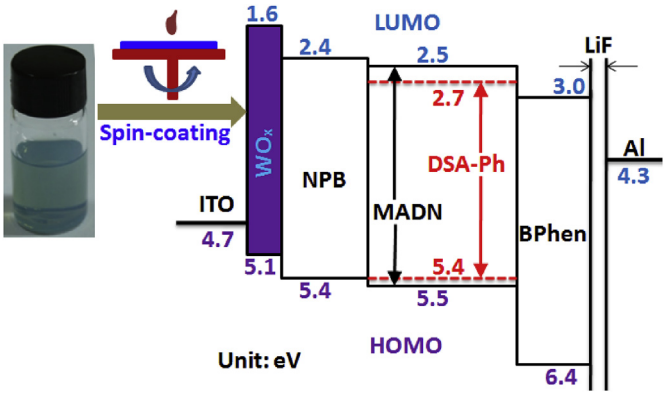

Fig. 1. Schematic device structure and energy level diagram of blue OLEDs with s-WO_x as HIL. The image of WO_x solution (0.5 wt.%) is also incorporated in the figure. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Device MD1: ITO/s-WO_x (0.15%)/NPB/[MADN:DSA-Ph] (40 nm)/.

Device MD2: ITO/s-WO_x (0.15%)/NPB/[MADN:DSA-Ph] (50 nm)/.

Device MD3: ITO/s-WO_x (0.15%)/NPB/[MADN:DSA-Ph] (55 nm)/.

Device EMD: ITO/e-WO_x (1 nm)/NPB/[MADN:DSA-Ph] (50 nm)/.

The deposition rate of organic materials was ~2 Å/s while that of LiF was ~0.1 Å/s. The chemical structures of some organic materials used are shown in Fig. S1 in Supporting Information. The luminance (*L*), current density (*J*) and voltage (*V*) characteristics were measured simultaneously using a Konica Minolta LS-150 Luminance Meter and a Keithley 2636B Source Meter. The EL spectrum and CIE color coordinates were measured with an Ocean Optics MAYA-2000-PRO Spectrum Scan. The atomic force microscopy (AFM) was mapped with a Bruker Dimension Edge. The X-ray photoelectron spectroscopy (XPS) pattern was recorded on an Escalab 250Xi System (Thermo Scientific). The UV−visible absorption spectra were analyzed by Shanghai Metash Instruments UV−visible Spectrophotometer (UV-6100). The photoluminescence (PL) emission and absorption spectra were characterized with a Fluorescence Spectrophotometer (RF-5301, SHIMADZU). The impedance spectroscopy was performed by an Agilent 4294A Precision Impedance Analyzer.

3. Results and discussions

3.1. MADN-based OLEDs

The electrical-optical features of OLEDs with MADN as EML are shown in Fig. S2 in Supporting Information. Some key parameters are displayed in Table 1. It can be seen that s-WO_x (Device M2) shows a maximum LE of 3.3 cd/A, PE of 2.5 lm/W and EQE of 4.6%, which are comparable to those (3.2 cd/A, 2.5 lm/W and 4.4%) of e-WO_x (Device EM). It indicates that s-WO_x just like e-WO_x, behaving robust hole injection and contributing to satisfactory device performance.

The typical EL spectrum of s-WO_x based OLED (Device M2) is illustrated in Fig. 2(f). One sees that the device gives attractive blue emission with EL peak of 436 nm which is reasonably ascribed to the MADN emission. Moreover, the EL spectra of Device M2 show negligible variation under different voltages (3V-9V). The corresponding CIE color coordinates are slightly altered from (0.157, 0.115) at 3 V to (0.154, 0.096) at 9 V, as shown in Fig. S3 in Supporting Information. These phenomena suggest superiority of stable voltage-dependent EL spectra and chromaticity of blue OLEDs with s-WO_x HIL.

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