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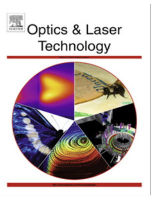

Full length article

Facile solution-processed aqueous MoO_x for feasible application in organic light-emitting diode

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ABSTRACT

Solution-processed techniques attract increasing attentions in organic electronics for their low-cost and scalable manufacturing. We demonstrate the favorite hole injection material of solution-processed aqueous MoO_x (s-MoO_x) with facile fabrication process and cast successful application to constructing efficient organic light-emitting diodes (OLEDs). Atomic force microscopy and X-ray photoelectron spectroscopy analysis show that s-MoO_x behaves superior film morphology and non-stoichiometry with slight oxygen deficiency. With tris(8-hydroxy-quinolinato)aluminium as emitting layer, s-MoO_x based OLED shows maximum luminous efficiency of 7.9 cd/A and power efficiency of 5.9 lm/W, which have been enhanced by 43.6% and 73.5%, respectively, in comparison with the counterpart using conventional vacuum thermal evaporation MoO_x. Current-voltage, impedance-voltage, phase-voltage and capacitance-voltage characteristics of hole-only devices indicate that s-MoO_x with two processes of "spin-coating/annealing" shows mostly enhanced hole injection capacity and thus promoting device performance. Our experiments provide an alternative approach for constructing efficient OLED with solution process.

1. Introduction

Organic light-emitting diodes (OLEDs) have been received numerous attentions in both academic researches and industrial applications because of their advantageous performance such as amazing color gamut, high efficiency and manufacturing convenience [1]. OLED is a typical carrier-injection dependent device that carrier balance governing luminous efficiency. Inserting carrier injection material between electrode and carrier transport layer is consequently proposed to fulfill such a function. Some extra metal oxides of MoO_x [2,3], V_2O_5 [4], NiO [5] and WO_3 [6] are widely-used hole injection layers (HILs) for their appropriate work function and superior film morphology. It is well established that MoO_x stands out as the favorite candidate for its non-toxicity, medium evaporation temperature, good transparence, tailored work function and improved device durability [3,7–11]. However, MoO_x is usually deposited using cost-intensive vacuum thermal evaporation. Recently, solution-processable techniques such as printing, roll-to-roll and doctor blading advance electronic devices with all solution process. Moreover, solution-processed techniques possess low-cost and scalable manufacturing. Solution processed HILs such as poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) [7,11], graphene oxide (GO) [12–14] and copper phthalocyanine-3,4′,4″,4‴-tetra-sulfonated acid tetra sodium salt (TS-CuPc) [15] are intensively investigated in OLEDs. PEDOT:PSS possesses strong hole injection ability, but its acidic nature and hygroscopicity are detrimental to device durability [7,11,16]. While GO behaves a work function of only ~5.0 eV [14], which limits its hole injection promotion especially in violet/blue emitters with deep highest occupied molecular orbital levels.

Solution-processed MoO_x is predominantly derived from sol-gel/precursor solution [17–23], ammonia-dissolved/dispersed solution [20,24,25], alcohol-dissolved/dispersed solution [1,11,18,26,27], nanoparticles suspension [8,28], or phosphomolybdic acid (PMA) [29]. It is also reported that MoO_3 powders show small amounts of solubility in water [7,20,25,30–32], which provides an easy-to-do and environment-friendly approach for preparing solution-processed aqueous MoO_x (s-MoO_x). In this study, we focus on s-MoO_x with facile fabrication process by directly dissolving MoO_3 powders into de-ionized water. Based on the MoO_x aqueous solution, superior film morphology is obtained by using conventional method of spin-coating/annealing process. Moreover, the MoO_x

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aqueous solution and subsequent annealing don’t involve ammonium molybdate ($(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$) precursor [33,34] and plasma treatment [9], which considerably simplifies device fabrication. In addition, in comparison with conventional one process of ‘‘spin-coating/annealing” [30], the hole injection capacity of s-MoO_x can be further enhanced by employing two processes of ‘‘spin-coating/annealing”, which contributes to extremely enhancement in device efficiency and decrease in driving voltage. Our results pave an alternative way for advancing OLEDs with solution process.

2. Experiment details

MoO_x solution (0.25% in weight ratio) was obtained by dissolving MoO_3 powders (>99.5%) into de-ionized water with continuously-prolonged stirring and heating at about 75 °C. The hydrolysis reaction of MoO_3 was occurred as Eq. (1).

$$MoO_3 + H_2O = MoO_4^{2-} + 2H^+ \qquad (1)$$

It is obvious that accumulation of H^+ ions significantly retards hydrolysis and weakens solubility of MoO_3 powders in de-ionized water. The maximum concentration of MoO_x aqueous solution was 0.25% in our experiments. ITO coated glass was chemically cleaned and served as substrate/anode for studied OLEDs. The HIL was formed by spin-coating MoO_x solution (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. The hole transport layer (55 nm) of N,N′-bis(naphthalen-1-yl)-N,N′-bis(phenyl)-benzidine (NPB), emitting layer (25 nm) of tris(8-hydroxy-quinolinato)aluminium (Alq_3), electron transport layer (15 nm) of 4,7-diphenyl-1,10-phenanthroline (BPhen) and bilayer cathode of LiF (0.8 nm)/Al (100 nm) were sequentially piled by thermal deposition under a vacuum of 4×10^{-4} Pa. The MoO_x HIL with one process of ‘‘spin-coating/annealing” refers as **s-MoO_x^{1}** (**Device A1**). While the MoO_x HIL with two or three processes of ‘‘spin-coating/annealing” refers as **s-MoO_x^{2}** (**Device A2**) or **s-MoO_x^{3}** (**Device A3**). The OLED without HIL (**Device B**) or using vacuum thermal evaporation MoO_x (e-MoO_x, 2 nm) as HIL (**Device C**) was also constructed for comparison. The active area of these devices was 5 × 5 mm^2. The layer thickness and deposition rate were monitored and controlled in situ with an oscillating quartz thickness monitor. Typical deposition rate for organics was ~2 Å/s. Fig. 1 shows the schematic structure of s-MoO_x based OLEDs. The molecular structures of organic materials used are shown in Fig. S1 in Supporting Information.

The current-voltage-luminance (*I-V-L*) characteristics were simultaneously measured with a computer controlled programmable Keithley 2636B Source Meter and Konica Minolta LS-150 Luminance Meter. The electroluminescent (EL) spectrum and 1931 Commission Internationale d’Eclairage (CIE) color coordinates were measured with an Ocean Optics Maya-2000-Pro Spectrum Scan. All measurements were carried out at room temperature under ambient conditions. An atomic force microscopy (AFM, Bruker Dimension Edge) was used for characterizing surface morphology. The X-ray photoelectron spectroscopy (XPS) was characterized with Thermo Scientific Escalab 250Xi System. A monochromatic Al Kα (1486.6 eV) was used in the XPS measurement. An Agilent 4294A Precision Impedance Analyzer was used for impedance spectroscopy analysis.

3. Results and discussions

Fig. 2 shows the AFM images of bare ITO and s-MoO_x^2 film coating onto ITO substrate. One sees that bare ITO shows distinct grains and grain boundaries embedded with a small amount of pin-holes on film surface. With MoO_x coating onto ITO, smooth surface with

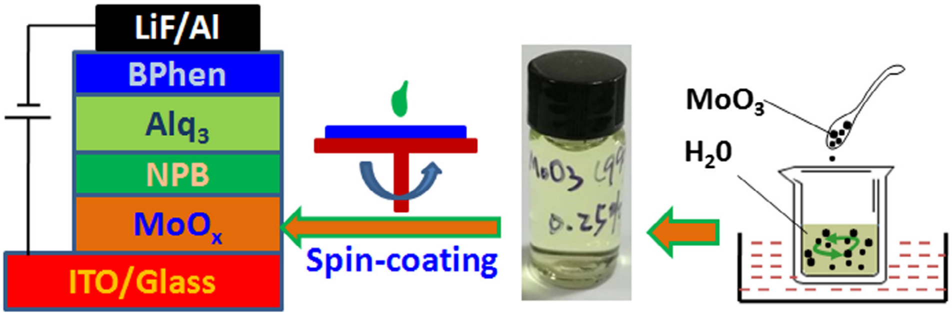

Fig. 1. Schematic structure of OLEDs with HIL of s-MoO_x formed by spin-coating MoO_x aqueous solution. The image of 0.25% MoO_x aqueous solution (faint yellow) is also incorporated in the figure. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

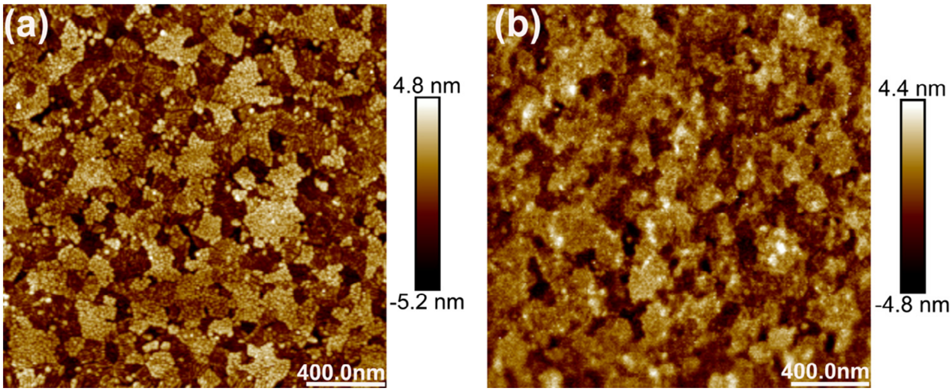

Fig. 2. The AFM images of (a) ITO and (b) ITO/s-MoO_x^2 with scanning area of 2 μm × 2 μm.