



## Solution-processed phosphorus-tungsten oxide film as hole injection layer for application in efficient organic light-emitting diode



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### ABSTRACT

The research on new functional layer materials and optimization of fabrication in organic light-emitting diode (OLED) has been continuously concerned. In this work, phosphotungstic acid solution used as a precursor is spin-coated onto ITO anode, and then a phosphorus-tungsten oxide ( $\text{WO}_3\text{-P}_2\text{O}_5$ ) film is obtained after annealing treatment. Various parameters which include film composition, surface morphology, work function and optical property are measured. It suggests that the film has the composition of 24  $\text{WO}_3\text{-P}_2\text{O}_5$  annealed at 200 °C, which exhibits work function of 5.55 eV, surface root mean square (RMS) roughness value of 1.525 nm and optical transmittance of over 92%. The  $\text{WO}_3\text{-P}_2\text{O}_5$  film is used as hole injection layer (HIL), and the OLED with the structure of [ITO/  $\text{WO}_3\text{-P}_2\text{O}_5$ / TPD/ Alq<sub>3</sub>/ LiF/ Al] is fabricated. The performance of device shows turn-on voltage of 2.6 V, maximum luminance of 13553 cd/m<sup>2</sup>, maximum current efficiency of 5.87 cd/A and maximum power efficiency of 3.44 lm/W, respectively. The results provide a new way to deposit HIL based on solution-processed metal oxide in efficient OLED.

### 1. Introduction

Organic light-emitting diode (OLED) has gained more attention in panel displays and solid-state lighting for its distinguished advantage in efficiency [1], color rendering index [2] and flexibility [3]. In general, the structure of OLED basically contains [anode/ hole injection layer (HIL)/ hole transport layer (HTL)/ emitting layer (EML)/ electron transport layer (ETL)/ electron injection layer (EIL)/ cathode]. In detail, indium tin oxide (ITO) anode used in OLED has a work function of about 4.8 eV [4] and the highest occupied molecular orbital (HOMO) energy level of typical HTL material is about 5.4 – 6.1 eV [5,6]. The large energy barrier (between ITO anode and HTL) is adverse for hole injection from ITO to HTL. Hence, the interface modification of anode become one of the research hotspots in OLED, which can reduce the injection barrier to improve the device performance [7,8].

There are mainly two ways to modify the ITO interface which can adjust work function of the ITO or improve the contact between ITO and HTL. The plasma treatment is verified to be effective way because it can increase the work function and wettability of the ITO surface. It usually includes oxygen plasma treatment [9], polymerized fluorocarbon (CF<sub>x</sub>) plasma [10] and chlorine (Cl<sub>2</sub>) plasma [11,12]. However, the ITO treated by plasma should be used as soon as possible because it cannot be conserved for long. The other way is adopting HIL. HIL is

usually prepared by the deposition of transition metal oxides (TMOs) or organic compounds. Poly(3,4-ethylenedioxy-thiophene): poly(styrenesulfonate) (PEDOT:PSS) is known as one of the most widely used HIMs for its excellent mechanical flexibility, appropriate HOMO energy level and high transmittance [13]. However, because of insulating PSS, solvent post treatment is usually used for increasing conductivity of PEDOT:PSS [14,15]. TMOs such as MoO<sub>3</sub> [16,17], NiO [18] and WO<sub>3</sub> [19,20] have been investigated to be used as HIL materials, because they possess high work function, favorable semiconducting properties and good transparency [21]. Among TMO used in OLED, WO<sub>3</sub> gained more attention due to its high work function and highly transparent in visible region [22]. The deposition of WO<sub>3</sub> usually adopts thermally evaporate or magnetron sputtering process.

Unlike the vacuum deposition methods, solution processes such as roll-to-roll, spin-coating and ink-jet print are low-cost, simple methods to form thin film. Therefore, solution processed WO<sub>3</sub> used as HIL material get more popular. Yang's group reported a solution-processed WO<sub>3</sub> HIL for polymer light-emitting diodes (PLEDs), which exhibited the maximum luminance of 27560 cd/m<sup>2</sup> at 10 V. The device showed higher current density and luminance compared to the PLEDs fabricated with only ITO [23]. Colmann's group demonstrated a solution processed blue OLED comprising WO<sub>3</sub> HIL. The device current efficiency increases from 8 cd/A when using PEDOT:PSS to 14 cd/A upon

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the incorporation of  $\text{WO}_3$  [24]. However, the employment of solution process to deposit  $\text{WO}_3$  film becomes difficult due to the harsh dissolution conditions and complex synthesis process [25]. Therefore, efforts have been made to develop a precursor for  $\text{WO}_3$  HIL. It has been reported that phosphoric acid ( $\text{H}_3\text{PO}_4$ ) can increase the ITO work function [26]. Unfortunately, the work function of acid-treated ITO dramatically decreases after deposition of HTL. In this contribution, inorganic acid has the potential to be precursor for HIL.

Herein, this work intends to prepare precursor using the excellent solubility of phosphotungstic acid ( $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot x\text{H}_2\text{O}$ ) which contains transition metal (tungsten), and to obtain the coating solution which is suitable for various solution processing. Then HIL film is obtained by annealing the phosphotungstic acid film. Afterward, the film composition, surface morphology and work function are studied. At last, high-performance OLED is fabricated due to the hole injection property.

## 2. Experiment

The ITO glass substrate (sheet resistance of about  $8\ \Omega/\text{sq}$ ) was purchased from Advanced Election Tech which was used as anode in OLEDs. Methanol, 2-propanol, acetone, acetonitrile, tetrahydrofuran, toluene, chlorobenzene and dimethyl sulfoxide (DMSO) were purchased from Tianjin Concord Technology. Phosphotungstic acid ( $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot x\text{H}_2\text{O}$ ), tungsten trioxide ( $\text{WO}_3$ ),  $N,N'$ -bis(3-methylphenyl)- $N,N'$ -bis(phenyl)-benzidine (TPD), Tris-(8-hydroxyquinoline) aluminum(III) ( $\text{Alq}_3$ ), LiF and aluminum (Al) were purchased from Shanghai Energy Chemical. PEDOT:PSS (BAYTRON®P VP CH 8000) was purchased from Xi'an Polymer Light Technology Corp.

OLED was designed with the structures of [ITO/HIL/TPD (25 nm)/ $\text{Alq}_3$  (60 nm)/LiF (1 nm)/Al (100 nm)]. Firstly, ITO glass substrates were successively cleaned with DI water, 2-propanol, acetone and methanol in an ultrasonic bath for 20 min. Then they were boiled in 2-propanol and dried with nitrogen gas flow, followed by the oxygen plasma treatment (3 min, 80 W and 1 mbar).  $\text{WO}_3$ - $\text{P}_2\text{O}_5$  and PEDOT:PSS, which were used as HIL materials, were spin-coated onto the ITO glass substrates in air at a spinning speed of 2000 rpm for 30 s.  $\text{WO}_3$  layer and other functional layers were prepared by the method of vacuum thermal evaporation under a pressure of  $5 \times 10^{-4}$  Pa. In detail, the thermal evaporation rates of  $\text{WO}_3$ , TPD,  $\text{Alq}_3$ , LiF and Al were 0.3, 1.7, 1.7, 0.3 and  $10\ \text{\AA}/\text{s}$  with the thickness of 3 nm, 25 nm, 60 nm, 1 nm and 100 nm, respectively.

The measurement conditions of HIL film and device performance were as follows: thermal property of phosphotungstic acid was measured by TGA-Q500. Optical property, surface morphology, chemical analysis and work function of  $\text{WO}_3$ - $\text{P}_2\text{O}_5$  films were investigated by UV-Vis spectrometer, atomic force microscope (AFM), X-ray photoelectron spectroscopy (XPS) and photoelectron spectrometer (Riken Keiki AC-2). The current density–voltage–luminescence ( $J$ - $V$ - $L$ ) characteristics of OLEDs were investigated using a chroma meter CS-2000 (Konica Minolta) and a source measure unit (Keithley 2400). All the devices characterizations were performed at room temperature without any encapsulation.

## 3. Results and discussion

### 3.1. Solubility of phosphotungstic acid

In order to choose appropriate solvent, phosphotungstic acid powders are put into eight kinds of solutions which are water, methanol, 2-propanol, acetone, acetonitrile, tetrahydrofuran, toluene and chlorobenzene. The conditions of dissolving are shown in Tab. S1. As can be seen from the results, phosphotungstic acid dissolves easily into all of solvents but toluene and chlorobenzene. As known to all, most of the hole transport materials (HTM) have high solubility in chlorobenzene or toluene. From the structure of OLED, HIL is contact with HTL, therefore the two layers inevitably corrode one another to depress

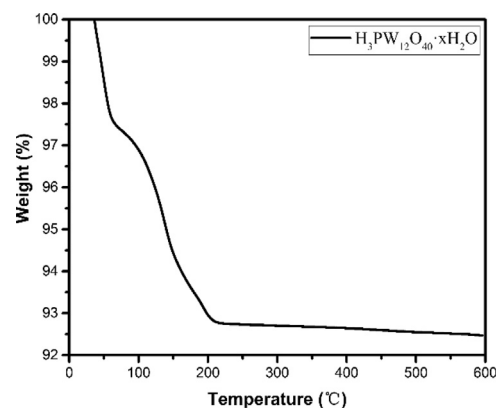


Fig. 1. TGA curve of phosphotungstic acid powder.

heavily the performance of device especially solution process fabrication [27,28]. It should be possible that phosphotungstic acid solution can avoid the corrosion phenomenon because of its insoluble characteristics in chlorobenzene and toluene when it is used as a HIL precursor. Further film formation experiment suggests that it can form stable film when using methanol and acetonitrile as solvent. Considering methanol has the lower boiling point, the acetonitrile is a good candidate for dissolving phosphotungstic acid powders, and the concentration of phosphotungstic acid is 10 mg/mL.

### 3.2. The composition of phosphotungstic acid and thin film

As phosphotungstic acid ( $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot x\text{H}_2\text{O}$ ) contains the combined water, the annealing condition of the film can be determined according to its thermal behavior. TGA curve of phosphotungstic acid is shown in Fig. 1. From the curve, phosphotungstic acid powder has rapid weightless when the temperature increases, and then it becomes very gentle near 200 °C. It indicates that the combined water of phosphotungstic acid can easily lose. Furthermore, the weightlessness rate is 7.2% at 200 °C. Hence, phosphotungstic acid can be calculated with composition of  $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 11\text{H}_2\text{O}$ .

To confirm the composition of thin film, the atomic ratio on the surface has been analyzed by XPS (Tab.S2). It can be concluded that W/P atomic ratio of the film without annealing treatment is 11.4:1. Furthermore, with the increase of processing temperature, W/P ratio increases gradually. When the annealing temperature is 200 °C, W/P ratio is 12.3:1. It means that the film has composition of 24  $\text{WO}_3$ - $\text{P}_2\text{O}_5$ , which accords with Keggin heteropolyacids structure of phosphotungstic acid ( $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ) [29]. When the annealing temperature increased up to 300 °C, W/P ratio increases as the phosphorus oxide has a little weightlessness visibly.

### 3.3. Valence state of W and work function of thin film

The valence states of metal elements such as Mo and W in TMO thin films can result in different work function [30]. Fig. 2 indicates the W 4f signals of the XPS spectra in samples which contained  $\text{WO}_3$  and  $\text{WO}_3$ - $\text{P}_2\text{O}_5$  (treated at different conditions). The W 4f<sub>7/2</sub> and W 4f<sub>5/2</sub> peaks are carried out through using the C 1s peak position with binding energy (BE). The position and shape of photoemission peaks are helpful to confirm the valence state of W atom. It has been proved that the position and the shape of W 4f photoemission peak represent W atoms with a valence state of VI, when W 4f<sub>7/2</sub> situates at BE of  $36.0 \pm 0.1$  eV and W 4f<sub>5/2</sub> centers at  $38.2 \pm 0.1$  eV (with a peak ratio of 4:3). Besides, another lower BEs (BE of W 4f<sub>7/2</sub> is 31.3 eV, and of W 4f<sub>5/2</sub> is 33.5 eV with a peak ratio 4:3) are attributed to W atoms with zero valence [29,31]. For the  $\text{WO}_3$  thin film, it completely confirms to the character peak of W (VI) (BE of W 4f<sub>7/2</sub> is 36.0 eV, and of W 4f<sub>5/2</sub> is 38.0 eV). And for the  $\text{WO}_3$ - $\text{P}_2\text{O}_5$  films (unannealed), the character peaks

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