

Indium Tin Oxide Modified by Au and Vanadium Pentoxide as an Efficient Anode for Organic Light-Emitting Devices

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Abstract—Au/vanadium pentoxide (V_2O_5) films on indium tin oxide (ITO) as composite anodes for hole injection in organic light-emitting devices (OLEDs) have been investigated. The device with ITO/Au (6 nm)/ V_2O_5 (6 nm) anode shows improved current density–voltage characteristics as compared with the device with ITO/Au as anode. Hole injection is significantly reduced when Au was added on ITO as an anode. However, while a thin V_2O_5 film is deposited on a Au anode, the barrier height is substantially reduced. The hole injection is facilitated, and the driving voltage of the device decreased by 10 V. In addition, the maximum current efficiency for the ITO/Au/ V_2O_5 OLED is ~ 3.5 cd/A, which is higher than that of the ITO/Au anode device (~ 1.1 cd/A) and ITO/ V_2O_5 OLED of ~ 2.8 cd/A.

Index Terms—Efficient anode, improved hole injection, organic light-emitting devices (OLEDs), reduced driving voltage.

CONVENTIONAL bottom emitting organic light-emitting devices (OLEDs) commonly use conductive indium tin oxide (ITO) as anode because of its high conductivity, transparency, and work function. However, the surface of ITO glass is chemically and physically ill defined, which will degrade the performance as the hole-injecting electrode in OLEDs. Over the past years, many methods were used to treat the surface of ITO [1]–[5], such as ultraviolet–ozone cleaning and oxygen plasma exposure, in order to enhance hole injection [1], [2]. These treatments were effective in removing residual surface contaminants and increasing oxygen content at ITO surface, resulting in the increase of work function to minimize interfacial charge injection barriers.

Moreover, the incorporation of injection enhancing interlayer at electrode–organic interfaces has been used as one alternative route to control carrier injection [6], [7]. Using metal oxides with high work function, such as AgO_x [8] and NiO_x [9], as an interfacial layer between ITO and organic material has

been proven to enhance hole-injection efficiencies. Vanadium pentoxide (V_2O_5) is a *p*-type semiconductor [10] with a high work function of ~ 5.4 eV [11]. It has also been used as an efficient modification layer of ITO and (*p*-Si) anode to enhance hole injection [12], [13]. In addition, many high work function metals such as Ag and Au [14], [15] have been studied as the anode materials. However, they are not suitable for the anode as the hole injection is virtually blocked when the metal anodes are used [16]–[18]. The reports generally concluded that the performance of OLEDs with metal anodes is poorer than those OLEDs with ITO anodes. However, the metals of Au and Pt with proper surface treatment on non-ITO electrodes, such as Si and Al, have been reported to improve the performance of top emission OLEDs [19], [20] but no obvious studies on ITO electrodes for bottom emission OLEDs.

In this brief, we use V_2O_5 coating on transparent thin Au film as a composite hole-injection layer on ITO anode for bottom emitting OLEDs. The characteristics of bottom emitting OLEDs with the composite anodes of ITO–Au– V_2O_5 are described. A thin oxide layer V_2O_5 is used to modify the surface of Au for enhancing the hole injection from Au by the increase of work function to 5.3 eV and thus sequentially improves emission efficiency. The effects of V_2O_5 layer on the enhancement of electrical properties of the bottom emitting OLEDs are discussed. Ultraviolet and X-ray photoelectron spectroscopy (UPS and XPS, respectively) analysis indicate that the higher work function of ITO/Au/ V_2O_5 (5.3 eV) than ITO/Au (5.0 eV) anode is due to Au surface band bending. Thus, the barrier for hole injection from ITO through Au/ V_2O_5 to the hole transport layer (HTL) is decreased. Our results show that the performance of OLEDs with V_2O_5 layer is greatly improved compared with the case of only Au layer on the ITO. Interestingly, it is also better than the ITO anode modified by V_2O_5 device.

All devices were fabricated on ITO coated glass with a sheet resistance of $10 \Omega/\square$, and thermally deposited LiF/Al was used as cathode. ITO substrate was cleaned and treated by O_2 plasma. The deposition was carried out at a pressure of less than 3×10^{-4} Pa without any vacuum break. The organics and metal oxide were evaporated at the rate in a range of 0.3–0.4 nm/s. The Au metals were evaporated at the rate of ~ 0.1 nm/s prior to the oxide and organic layer deposition. Al metal was evaporated at the rate of 0.3–0.5 nm/s. The devices have an emissive area of 3.57 mm². The organic layers consisted of 70-nm 4,4,6,6'-N,N'-bis[N-(1-naphthyl)-N-phenyl-amino]

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biphenyl (NPB) as the HTL, 50-nm tris(8-hydroxyquinoline) aluminum (Alq_3) as the electron transport layer, and emissive layer. The bilayer of LiF/Al was used as the efficient electron injection cathode. The structure of the device is ITO/Au(6 nm)/ V_2O_5 (5 nm)/NPB(70 nm)/ Alq_3 (50 nm)/LiF(1 nm)/Al(70 nm). For comparison, another three devices were fabricated. These three devices had the same organic and electron injection structure as the one just described, except that Au on the ITO without V_2O_5 coating, ITO coated with V_2O_5 , and bare ITO were used as the anodes.

The current–voltage–brightness characteristics were recorded using a computer controlled source meter (Keithley 2400) and photometer (IL1400A) with a calibrated silicon photodiode. The EL spectra were measured by Instaspec spectrometer. All measurements were carried out in ambient atmosphere at room temperature. The UPS of samples was measured with He discharge lamp (UV light of 21.2 V; Thermo Electron Corporation, ESCALAB 250). The XPS measurements were carried out with LargeAreaXL surface analysis system using a monochromatic Al K Alpha source.

The J – V characteristics of the four devices with ITO/Au/ V_2O_5 , ITO/Au, ITO/ V_2O_5 , and bare ITO anodes are shown in Fig. 1(a). The devices with the ITO/Au and bare ITO anodes show poor hole injection. However, by adding a layer of V_2O_5 with a thickness of 6 nm, the J – V characteristics of the device with ITO/ V_2O_5 and ITO/Au/ V_2O_5 anodes are dramatically improved as compared with the previous two OLED structures without V_2O_5 . For example, the current density of OLEDs with the ITO/Au and ITO/Au/ V_2O_5 anodes at 11 V are 0.065 and 69 mA/cm^2 , respectively. Fig. 1(b) shows that, at the same applied voltage, the luminance of the OLED with the ITO/Au/ V_2O_5 anode is much larger than that of the device with the ITO/Au anode. The driving voltage for a given current or a given luminance of the OLED with the ITO/Au/ V_2O_5 anode is significantly decreased by ~ 10 V as compared with that of the ITO/Au OLED due to V_2O_5 layer modification.

The current efficiency versus the current density of OLEDs is shown in Fig. 1(c). It can be seen that the maximum current efficiency of the ITO/Au/ V_2O_5 OLED (~ 3.5 cd/A) is three times more than that of the ITO/Au anode device (~ 1.1 cd/A). The results are attributed to the V_2O_5 modification layer. The existence of V_2O_5 increases the hole injection to HTL and thus increases the number of excitons at the interface of NPB/ Alq_3 . At the same time, the optical transmittance of ITO/Au/ V_2O_5 is higher than that of ITO/Au, as shown in Fig. 2, which is also one of the reasons for increasing the current efficiency. However, the optical transmittance of ITO/Au/ V_2O_5 is lower than that of ITO/ V_2O_5 , as shown in Fig. 2; the current efficiency of the ITO/Au/ V_2O_5 OLED (~ 3.5 cd/A) is still higher than ITO/ V_2O_5 OLED (~ 2.8 cd/A). Together with the J – V results of the ITO/Au/ V_2O_5 OLED, as discussed previously, the higher current efficiency of ITO/Au/ V_2O_5 OLED than ITO/ V_2O_5 OLED is attributed to the better charge balance [21]. Moreover, the improved current efficiency is not likely due to the microcavity effect [22] in the device with ITO/Au/ V_2O_5 anode because there is no change in electroluminescence spectrum (not shown in this brief).

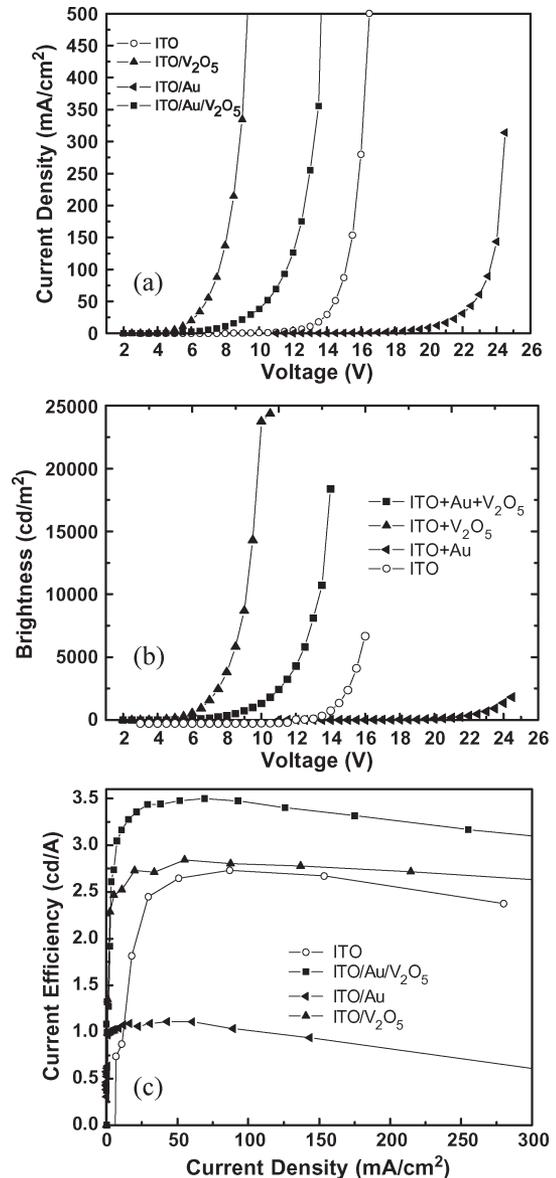


Fig. 1. (a) J – V , (b) L – V , and (c) current efficiency characteristics of OLEDs with ITO/Au/ V_2O_5 , ITO/Au, ITO/ V_2O_5 , and bare ITO anodes.

The reduction of operation voltage can be explained by lowering the barrier of hole injection from anode to HTL. The UPS was used to measure the work function. The UPS spectra of V_2O_5 , Au, and Au/ V_2O_5 on ITO, as well as bare ITO, are shown in Fig. 3. From the UPS spectra, the work function of ITO is determined to be 4.7 eV. This value is consistent with the commonly accepted values [23]. The measured work functions of the other ITO surfaces modified by V_2O_5 , Au, and Au/ V_2O_5 are 5.1, 5.0, and 5.3 eV, respectively. From these measured data, we observe that there are about 0.4- and 0.3-eV increases in the work functions of ITO and ITO/Au surfaces treated by V_2O_5 , respectively. The results indicate that the barrier for hole injection from ITO/ V_2O_5 and ITO/Au/ V_2O_5 anodes is decreased. Meanwhile, although the work function of Au is higher than that of bare ITO, the existence of an interface dipole at the Au–NPB interface results in a large hole-injection barrier of 1.35 eV, which virtually blocks the hole injection [18].

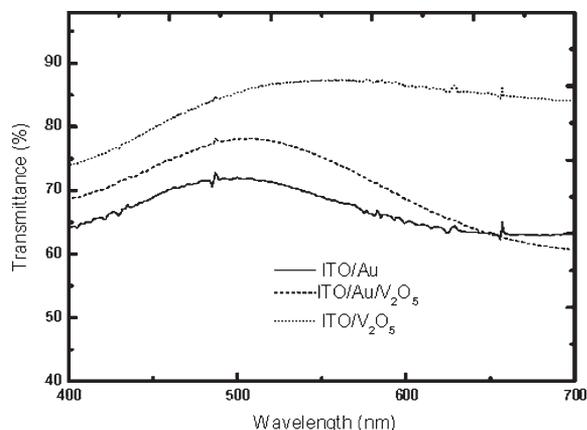


Fig. 2. Transmittance spectra of ITO/Au/V₂O₅, ITO/Au, and ITO/V₂O₅.

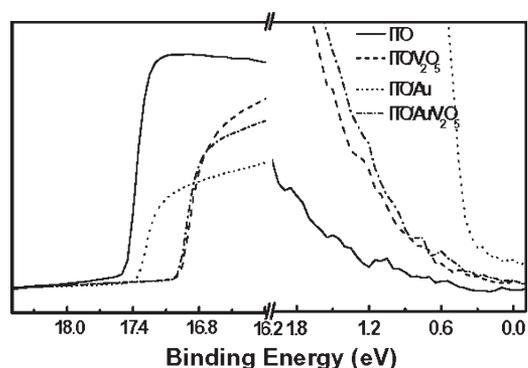


Fig. 3. UPS spectra of ITO (solid line), ITO/V₂O₅ (dash line), ITO/Au (dot line), and ITO/Au/V₂O₅ (dash dot line).

Fig. 4 shows the XPS wide scan data spectra of the bare ITO, ITO/V₂O₅, ITO/Au, and ITO/Au/V₂O₅ anodes. In Fig. 4(a), strong O 1s, In 3d, and Sn 3d peaks are obtained, which are attributed to the ITO anode layer. The fairly strong C 1s peak corresponded to the existence of organic contamination on the ITO anode. The results are similar to the reported ones [24]. By comparing the ITO/V₂O₅ case in Fig. 4(b) with the bare ITO case in Fig. 4(a), the additional V 2p peak and the stronger O 1s peak of the ITO/V₂O₅ case than that of the bare ITO are observed, apart from a slightly left shift of the peak position. It is also quite evident that the peak intensities of In 3d and Sn 3d (electron donor) are dramatically reduced on ITO surfaces treated by V₂O₅. These results are attributed to the modifications of V₂O₅ on ITO anode, which contributes to the enhancement of hole injection [1], [12]. The XPS of ITO/Au [Fig. 4(c)] is similar to that of bare ITO anode [Fig. 4(a)] except the additional peaks of Au 4d and Au 4f, i.e., no modification effect on the ITO surface. Therefore, Au on ITO cannot provide better hole injection, which is agreed with [18]. The XPS of ITO/Au/V₂O₅ [Fig. 4(d)] shows a similar spectrum to ITO/V₂O₅ [Fig. 4(b)] except the additional Au 4d and Au 4f peaks. This implies that V₂O₅ buffer layer offers modification effects on ITO/Au surface. Due to the composite anode of ITO and Au formed, the energy level difference exists between the ITO (4.7 eV) and Au (5.0 eV) interface; the device with ITO/V₂O₅ anode exhibited better *J-V* performance than the one with ITO/Au/V₂O₅ anode. It is also possible that Au as

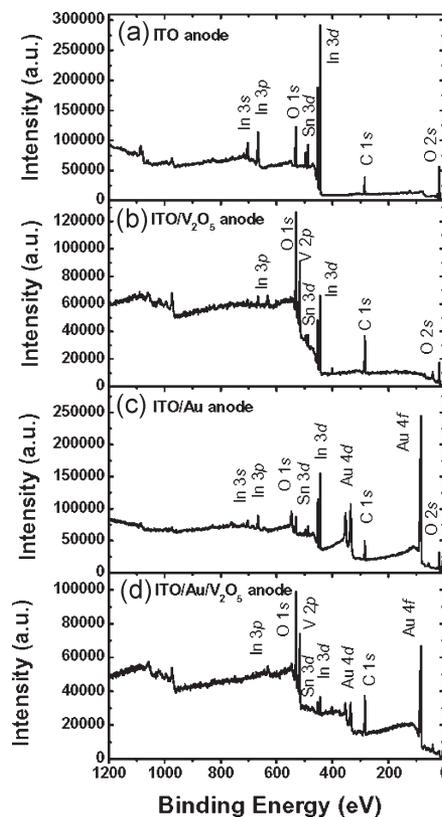


Fig. 4. XPS wide scan spectrum of (a) bare ITO anode film, (b) ITO/V₂O₅ anode film, (c) ITO/Au anode film, and (d) ITO/Au/V₂O₅ anode film.

a block layer that makes ITO/Au/V₂O₅ OLED has a better charge balance. Consequently, the current efficiency of the ITO/Au/V₂O₅ OLED (~ 3.5 cd/A) is higher than ITO/V₂O₅ OLED (~ 2.8 cd/A).

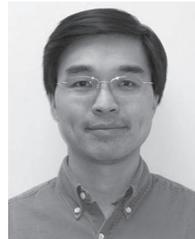
In summary, we show that ITO/Au/V₂O₅ composite electrode can be used as an effective anode for bottom emitting OLEDs. Hole injection is virtually blocked when Au is added on ITO as an anode. Interestingly, while an additional layer of V₂O₅ is introduced on Au surface, the hole injection is greatly enhanced. It is attributed to a lower energy level difference at the anode/organic interface. In addition, the device with ITO/Au/V₂O₅ as anode provides a better charge balance, which makes the current efficiency of the ITO/Au/V₂O₅ OLED (~ 3.5 cd/A) 1.25 times higher than that of the ITO/V₂O₅ OLED (~ 2.8 cd/A).

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