

Enhancement of optical and electrical performance of organic light emitting diodes fabricated by SAM modified ITO anodes

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Electrode modification in organic semiconductor devices has attracted much attention in last decade. Among these studies, ITO (Indium Tin Oxide) as an electrode is widely used in organic light emitting diode (OLED) due to its relatively low resistance and high transparency. On the other hand, it has rough surface and low work function compared to the organic molecules used in OLEDs. Since surface roughness limits the hole injection from anode into the hole transport layer (HTL), we have tuned OLED performance by means of a ferrocenecarboxylic acid (FCA) self-assembled mono layer (SAM) through adjusting the interface between ITO and the organic layer. The improvements in current, luminescence and device efficiency of OLED using SAM modified ITO were obtained comparing to OLED devices with bare ITO as anode. The electrical properties of the OLEDs are modeled by using the modified Shockley equation with Lambert W-function. This enhancement on device performance is attributed by better hole injection and smoothness of the layer between ITO and organic layers.

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1. Introduction

OLEDs have attracted much attention because of its applicability in commercial displays. Enhancement of display properties are mainly related to the efficiency and stability issues, therefore studies regarding the performance are great importance. One of the aims in OLED fabrication is reducing operating voltage, which is related to the increasing power efficiency and lifetime.

The interfacial problem of the deposited materials on different layers is crucial in terms of the performance and stability of an OLED device [1-3]. Poor adhesion between the organic and inorganic electrode layers may cause failure in crystallization of organic films and the device operation [2-5]. A various kind of treatment techniques have been used for both cathode/organic [6,7] and anode/organic [8] interfaces to improve the charge injection, and hence the performance of devices[9]. Alternatively, more attentions were paid on the anode side to the modification of indium tin oxide (ITO) anode/hole-transport layer (HTL) interface. ITO is one of the most used and famous anode layer in commercial OLED fabrication. Its surface resistivity ($\sim 30\Omega/\text{sq}$) is relatively low and it has high optical transparency ($\sim 90\%$) [5]. On the contrary, ITO layer suffers from lower work function ($\sim 4\text{eV}$) and rough surface properties when using in the sandwich OLED structures. Due to poor adhesion and stability problems between the ITO and organic layers of direct contact, performance and stability of OLED devices can be degraded [1-2].

In order to overcome this interfacial compatibility phenomena, various approaches have been proposed in the literature involving the ITO surface treatment by UV-ozone [10-12], acid /base solution [13-14], plasma [15-16] and self-assembled monolayers (SAMs) [17-21]. Although various mechanisms were proposed to explain the enhanced performance, the precise mechanism remains uncertainty due to the complexity of interactions at OLED interfaces.

More recently, SAM techniques have an extensive study area for OLED fabrication due to its low cost and easy processing properties [22-26]. Some researchers have showed that this technique has enhanced the adhesion, stability of HTL and have been used as a moisture blocking layer, as well [13, 21]. On the other hand, ITO has a rough surface and therefore the interface between ITO and organic layer should be improved by very thin SAM layer in order to increase the device efficiency. Nevertheless, the SAM layer plays an important role to increase work function of ITO and to modify the electrostatic conditions at the oxide surface of ITO [25-26].

In this study, we used ferrocenecarboxylic acid (FCA) based SAM (FCA: SAM) layer for modifying the ITO surface in terms of roughness and work function. OLED devices have been fabricated consist of the following consecutive layers of ITO/TPD/ALq3/LiF/Al for bare one and ITO/SAM/ALq3/LiF/Al for the modified one. The device with bare ITO is used for comparison. In order to evaluate the performance of OLED devices, current, luminescence and efficiency were analyzed.

2. Experimental section

Ferrocenecarboxylic acid (FCA), toluene, acetone, ethanol, 2-Propanol (Isopropanol), tris-(8-hydroxyquinoline) aluminum (Alq3), N,N'-Bis(3-methylphenyl)-N,N-diphenylbenzidine (TPD) were purchased from Sigma Aldrich and were used as received. ITO coated glass substrates were also purchased from Sigma Aldrich. Al metal with purity of 99.99% was used as a cathode material in OLED fabrication. ITO coated glass substrates ($15\Omega/\text{square}$) were cut into $1.5 \times 1.5 \text{ cm}^2$ pieces and were etched 5mm wide by using solution of nitric acid (HNO_3) and hydrochloric acid (HCL) for 10-15 minutes at room temperature. Each piece was cleaned with deionized water, 2-propanol, methanol and finally acetone in an ultrasonic bath. The cleaned substrates were dropped into solutions of SAM molecules prepared in 1mM toluene solution. After waiting 12 hours, SAM modified substrates were cleaned via toluene in ultrasonic bath for 3 minutes to remove the remaining molecules from the surface.

OLED devices were fabricated in glove box system made by MBraun company USA. Two OLED structures were fabricated according to the material used in anode: ITO/TPD (60 nm)/Alq3 (40 nm)/Al (125 nm) and ITO/SAM/TPD (60 nm)/Alq3 (40 nm)/Al (125 nm). Organic layers (TPD and Alq3) were deposited in high vacuum (10^{-6} torr) at a rate of $0.2 \text{ \AA}/\text{s}$. After the deposition of organic layers Al cathode (125nm) were deposited by using shadow mask. Surface morphologies of bare and FCA:SAM modified ITO were characterized using AFM system from NTMDT. Current-voltage and luminance-current characterizations were determined with Keithley 2400 sourcemeter and calibrated Si photodiode. Electroluminescence results were obtained from Admesy-Bronthes colorimeter and Ocean optics QE65000 fiber optic spectrometer. All the measurements were carried out in glove box system at room temperature.

3. Results and discussion

AFM images of bare and FCA:SAM modified ITO surfaces are shown in Figure 1 (a) and (b), respectively. Forming of SAM layer can contribute to enhance the adhesion between the inorganic ITO and the hole-transporting organic layers as well as to change ITO work function. RMS surface roughness values of bare and FCA:SAM modified ITO were measured as 0.463 nm and 0.387 nm, respectively. They show similar surface topologies indicating that no more than a single monolayer of SAM molecules was forming on the ITO surface. This result is an agreement with the literature [15]

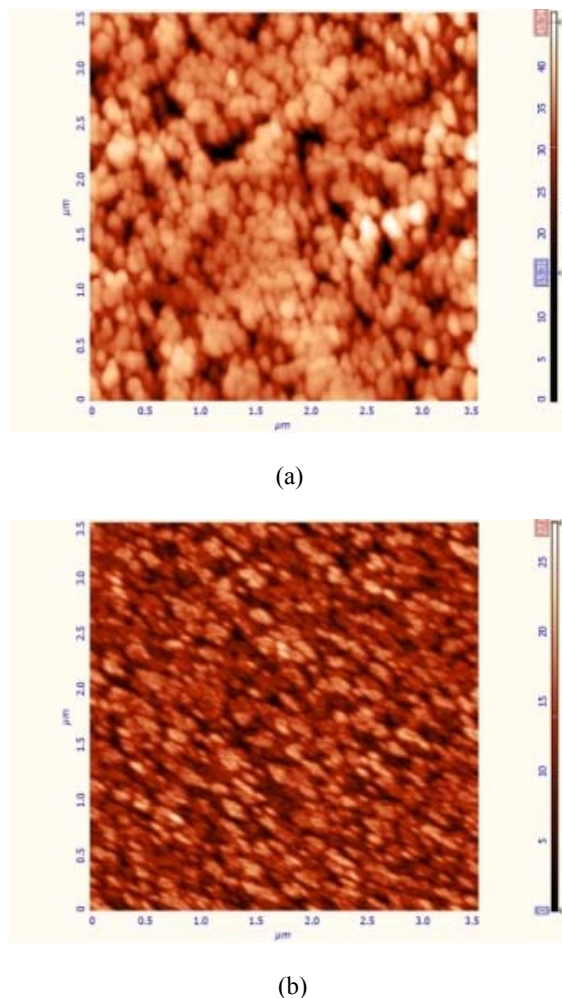
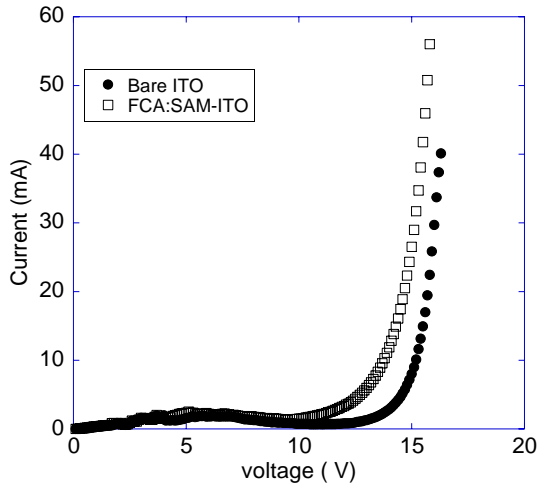
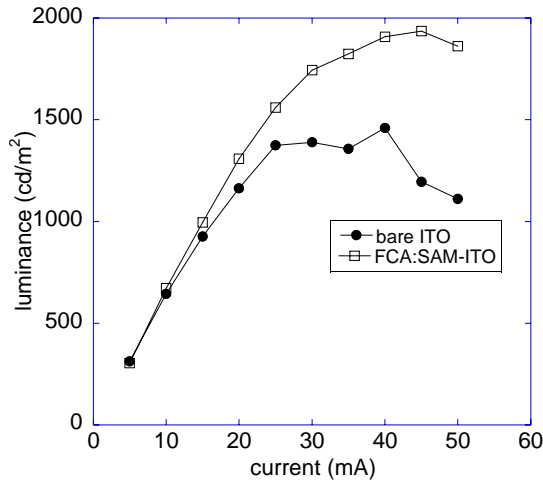


Fig. 1. AFM images for (a) bare ITO and (b) FCA:SAM modified ITO surfaces

Fig. 2 (a) and (b) show the current-voltage and luminance-current characteristics of the OLED devices fabricated on the bare ITO and FCA:SAM modified ITO anodes, respectively. It can be seen that SAM layer can affect the turn-on voltage value clearly. The turn-on voltages of these devices used bare and FCA:SAM modified ITO were measured as 15 V and 12 V, respectively. This results show that the improvement in the current and the turn-on voltage are related to better hole injection from anode to organic layer.



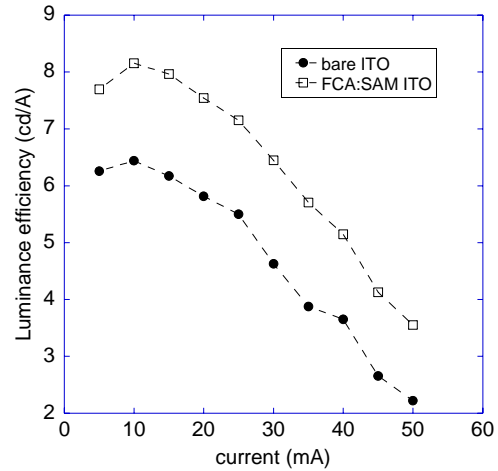
(a)



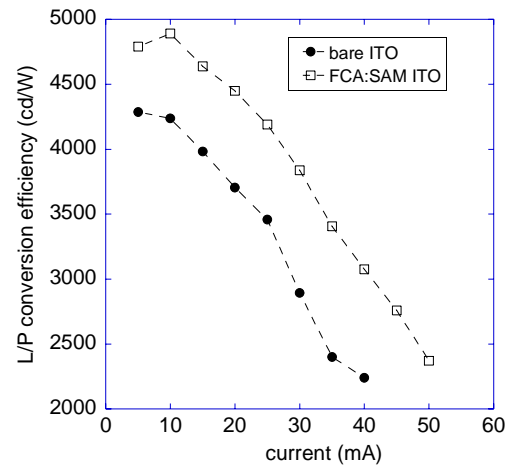
(b)

Fig.2. Current-voltage (a) and luminance-current (b) of bare and FCA:SAM modified ITO devices

Fig. 3 (a) and (b) represent the luminance and power efficiencies of these OLED devices, respectively. According to figure, the positive effect of the SAM layer on ITO surface on OLED performance was clearly observed. At low current values, the luminance and power efficiencies of the device with FCA:SAM modified ITO anode is higher than that of the bare ITO anode. This result points out that improvement the hole current density increases the balance of the charge carriers at low applied voltages. Nevertheless, the luminance and power efficiencies of the all the devices decrease at higher current.



(a)



(b)

Fig.3. Luminance (a) and power (b) efficiencies of bare and FCA:SAM modified ITO devices.

In order to model of I-V characteristic of OLED device Shockley equation is often used as follows [20]:

$$I = I_0 \times \left(e^{\frac{V - I \times R_s}{n k T}} - 1 \right) \quad (1)$$

where I_0 is the saturation current, n ideality factor, R_s series resistance, k Boltzmann coefficient and T temperature in Kelvin. At room temperature, kT is given by 0.025eV. This equation is well-defined but difficult to express explicitly because current appears on the both sides of equation. In order to overcome this complexity, it is convenient to use the Lambert W-function without making any approximation [27]. After some algebraic process, Equation (1) becomes as follows:

$$I = \frac{nkT}{R_s} \times \text{LambertW} \left(\frac{R_s I_0}{nkT} \times e^{\frac{V+R_s I_0}{nkT}} \right) \quad (2)$$

Matlab has been used to find the three fitting parameters (I_0 , n , R_s) corresponding the experimental data. Fitting parameters of both devices are also provided in Table 1.

Table1: The modified Shockley parameters for I-V curves of OLED devices

Device	Saturation current, I_0 (mA)	Ideality factor, n	Series resistance, R_s (ohm)
Bare ITO	2.3×10^{-7}	33	79.4
FCA:SAM ITO	2.3×10^{-4}	49	0.54

Fitting curves with the experimental data are shown in Figure 4. In generally, good agreement between the experimental data and the fitting equation has also been observed for OLED devices used bare and SAM modified ITO electrodes. Experimental data are off the fitting curve slightly at low voltage values. This is partly due to experimental errors. Besides the experimental errors, the equation (2) is not as accurate at very low current because the assumptions are not as valid. The series resistance (R_s) calculated from the model is observed to decrease incrementally with the incorporating SAM layer between ITO and organic layer. This result also indicates that SAM layer is an interfacial layer resulting better hole injection and turn-on voltages.

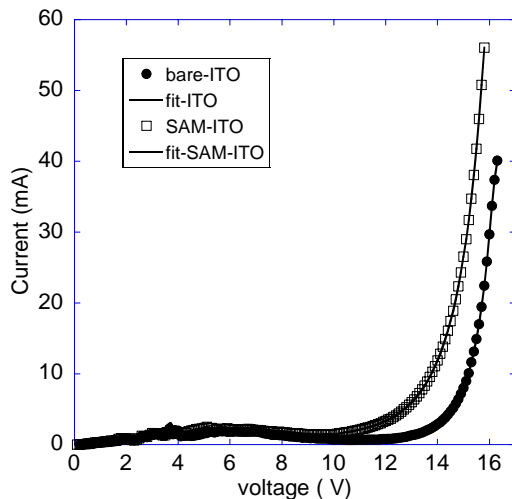


Fig.4. I-V curve fitting of bare and FCA:SAM modified ITO OLED devices (points are experimental data and line is calculated data)

4. Conclusions

We investigated the characteristics of the OLED devices with bare and FCA:SAM modified ITO anodes. The surface characterization of the modified ITO anode was performed using AFM technique. AFM results show that roughness is smoothed and SAM technique is applicable to improve the OLED performance. OLED devices were also fabricated and characterized by measuring current and luminescence. These results show that the OLED device with FCA:SAM modified ITO is more efficient and its turn on voltage is lower. In addition, it performed high current and displayed better luminescence compared to the bare one. The enhancements are attributed to increase hole injection and to balance charge carriers in emitting region. The model's I-V characteristics is found to be in good agreement with the experimental data.

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