

Effects of organic acids modified ITO anodes on luminescent properties and stability of OLED devices*

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In this paper, p-chlorophenylacetic acid and p-fluorophenylacetic acid were applied to modify the indium tin oxide (ITO) electrodes. The surface work functions of unmodified ITO, p-chlorophenylacetic acid modified ITO (Cl-ITO) and p-fluorophenylacetic acid modified ITO (F-ITO) are 5.0 eV, 5.26 eV and 5.14 eV, respectively, and the water contact angles are 7.3°, 59.1° and 46.5°, respectively. The increase of the work function makes the hole injection ability of the devices improved, which is proved by the hole transport devices. The self-assembly (SAM) layers transfer hydrophilic ITO to hydrophobic ITO, which makes ITO more compatible with the hydrophobic organic layers, making the organic film more stable during the operation. After modification, the organic light emitting diodes (OLEDs), SAM-modified ITO/NPB/Alq₃/LiF/Al, with better performance and stability were fabricated. Especially, the OLED with Cl-ITO (Cl-OLED) has a maximum luminance of 22 428 cd/m² (improved by 32.9%) and a half-lifetime of 46 h. Our results suggest that employing organic acids to modify ITO surface can enhance the stability and the luminescent properties of OLED devices.

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In recent years, research on organic light emitting diodes (OLEDs) has gradually become a hotspot, for its self-luminous, wide viewing angle and flexible characteristics^[1]. Indium tin oxide (ITO) sputtered on glass substrate is widely used in OLED devices as anode, because of its good electrical conductivity ($\sim 10^4$ S/cm), stable chemical structure and a high transmittance (more than 85% in the visible region)^[2].

But in practical applications, ITO as an inorganic electrode directly contacts with organic film layer, which causes a lot of problems. Firstly, there is a huge energy level difference between the ITO electrode and the hole transport layer (HTL), which makes the injection of hole carriers from anode terminal difficult, and the poor hole injection directly affects the device's light emission^[3,4]. Simultaneously, the surface of the inorganic ITO film is hydrophilic, and the HTL is a hydrophobic organic film. Therefore, the HTL has very poor wettability on the ITO surface. The poor contact between the ITO and the HTL severely affects the structural stability of the OLED device during operation, which affects the lifetime of the device.

In order to ameliorate the above problems, ITO electrodes are usually covered with self-assembly (SAM) layer through organic acids or organosilanes treatment^[5-7]. Hatton et al^[8,9] showed that SAM layer can increase the work function of ITO electrodes, lower the hole injection barrier between ITO and HTL, thereby significantly reducing the turn-on voltage of OLED devices and increasing the brightness of OLED devices. Leihua et al^[10] pointed out that the SAM treatment can improve the contact performance between the ITO electrode surface and the organic layer, so as to make the subsequent film more uniform and stable. Further research^[11] shows the organic layer on the SAM-modified ITO did not show de-wet even after annealing at high temperature for 1 h. Other research^[12,13] focused more on the impact of SAM modification on the work function of ITO electrode.

In this paper, p-chlorophenylacetic acid and p-fluorophenylacetic acid were used to modify the surface of ITO electrode, and molecular structures are shown in Fig.1. In order to study the influence of SAM modification on the hole injection capability and the lifetime of the

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OLED device, the hole only device and the OLED device were manufactured, respectively. The results suggest that through SAM modification of ITO surface, the luminescent properties and stability of OLED devices are improved.

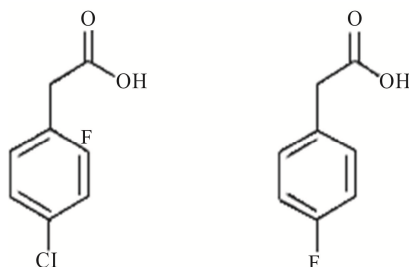


Fig.1 The molecular structures of (left) p-chlorophenylacetic acid and (right) p-fluorophenylacetic acid

Firstly, the ITO glass substrate was ultrasonic cleaned in the diluted cleansing detergent for 30 min at a temperature of 40 °C, and then was ultrasonic cleaned in deionized water for 10 min. After that, the ITO glass substrate was blown dry with ultrapure nitrogen gas, and then was placed on a heating stage at 120 °C for 10 min to remove the residual moisture from the surface of the ITO glass substrate. Finally, the dried ITO glass substrate was treated with an ultraviolet (UV) ozone cleaner for 15 min. The obtained ITO glass substrate after the above treatment is labeled as bare-ITO. The ITO glass substrate (185 nm ITO with a sheet resistance of 8 Ω/\square) was purchased from Huanan Xiangcheng Technology Co., Ltd. All the glassware should be soaked in alkaline solution for 2 h, and then thoroughly cleaned and dried at 60 °C in oven before use.

In order to form an SAM molecular layer on the surface of ITO, cleaned ITO glass was immersed in organic acid solution at room temperature. The concentration of organic acid solutions is 0.05 mol/L, where the organic acid is p-chlorophenylacetic acid and p-fluorophenylacetic acid, the solvent is analytical grade anhydrous ethanol. After modification, the SAM-modified ITO substrate was repeatedly washed with anhydrous ethanol, followed ultrasonic cleaning in anhydrous ethanol for 15 min, and finally dried by ultrapure nitrogen. The ITO glass substrates SAM modified by p-chlorophenylacetic acid and p-fluorophenylacetic acid are labeled as Cl-ITO and F-ITO, respectively.

In order to investigate the effect of SAM modification on the hole carrier injection between ITO and N, N'-diphenyl-N, N'-(1-naphthyl)-1,1'-biphenyl-4,4'-diamine (NPB), hole-only devices (SAM-modified ITO/NPB/Al) were fabricated. In hole-only device, the current is produced by hole injection from ITO electrode. Hole-only devices fabricated on bare-ITO, Cl-ITO, and F-ITO are labeled as bare-hole-only, Cl-hole-only and F-hole-only, respectively.

To explore the effect of SAM modification on the

performance of OLED devices, OLED devices with typical structure of SAM-modified ITO/NPB/Alq₃/LiF/Al were fabricated by evaporation. Firstly, 40-nm-thick NPB was evaporated on the ITO electrode as the hole transport layer. Then 60-nm-thick tris(8-quinolinolato) aluminum (Alq₃) was evaporated acting as a light emitting layer and an electron transport layer. Finally, LiF (1 nm)/Al (100 nm) was produced after the Alq₃ layer as cathode. OLEDs made on Cl-ITO, F-ITO and bare-ITO are labeled as Cl-OLED, F-OLED and bare-OLED, respectively. The structure of all devices is shown in Tab.1. All hole-only devices and OLEDs were encapsulated in a nitrogen filled glove box using UV adhesive and glass cover.

Tab.1 Structures of hole-only devices and OLED devices

Label	Device structure
Bare-hole-only	Bare-ITO/NPB(40 nm)/Al(100 nm)
Cl-hole-only	Cl-ITO/NPB(40 nm)/Al(100 nm)
F-hole-only	F-ITO/NPB(40 nm)/Al(100 nm)
Bare-OLED	Bare-ITO/NPB(40 nm)/Alq ₃ (60 nm)/LiF(1 nm)/Al(100 nm)
Cl-OLED	Cl-ITO/NPB(40 nm)/Alq ₃ (60 nm)/LiF(1 nm)/Al(100 nm)
F-OLED	F-ITO/NPB(40 nm)/Alq ₃ (60 nm)/LiF(1 nm)/Al(100 nm)

The voltage-current-brightness data of the devices were measured by a Keithley 2400 source measurement unit and a Spectroradiometer SR-UL1R (Topcon). All chemicals used in the experiment were analytical reagents. P-chlorophenylacetic acid, p-fluorophenylacetic acid, and analytical grade anhydrous ethanol were purchased from Aladdin Reagent Co., Ltd. NPB, Alq₃, LiF and Al were all purchased from Taiwan Machinery Technology Co., Ltd.

The carboxyl groups of the organic acids were dehydrated and condensed with the hydroxyl groups, arching organic acid molecules to the surface of ITO, thus spontaneously forming a self-assembled molecular layer, as shown in Fig.2. The number of organic carboxylic acid molecules self-assembled to the ITO surface is limited by the number of hydroxyl groups. The wettability of the ITO electrode surface is determined by the type, density and arrangement of functional groups of SAM layer^[14]. Considering the above situation, when the SAM reaction reaches the saturation, prolonging the duration of the SAM treatment has no significant effect on the wettability of the ITO electrode surface, which means that the water contact angle of the surface will have no longer significant changes. After the SAM modification, the water contact angle of the ITO surface was measured with an optical contact angle measuring instrument

(OCA50, Dataphysics), and the results are shown in Fig.3(a). During the first 8 h, the water contact angle of the ITO substrate shows an upward tendency, and then the water contact angle gradually stabilizes in the next 16 h. When the modification time is longer than 8 h, the SAM reaction on the ITO surface tends to be saturated. To ensure completed SAM modification, the ITO glass was SAM modified for 12 h each time.

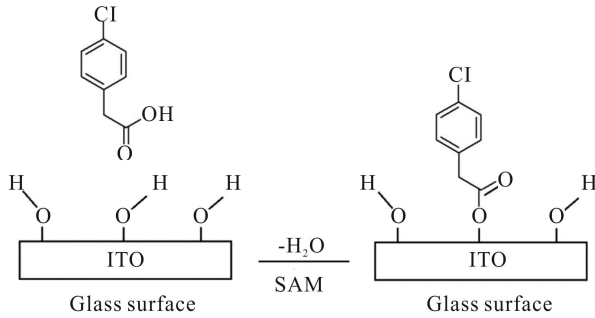


Fig.2 The p-chlorophenylacetic acid SAM-modified ITO, the carboxyl group of the organic carboxylic acid and the hydroxyl group on the ITO surface undergoing dehydration condensation reaction

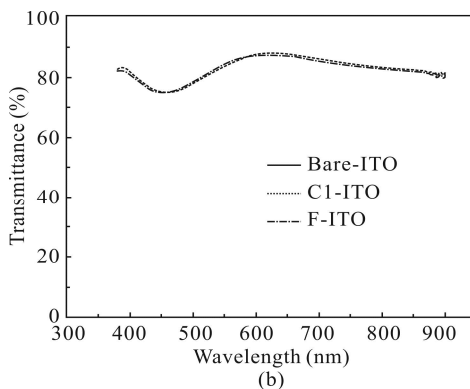
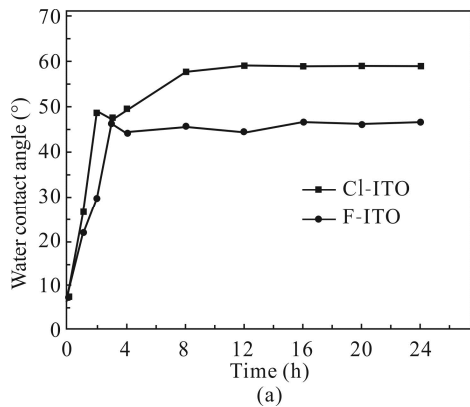


Fig.3 (a) The water contact angles of the surface of the ITO glasses modified with p-chlorophenylacetic acid and p-fluorophenylacetic acid measured at different treatment time; (b) The transmittance spectra of unmodified bare-ITO glass, Cl-ITO glass and F-ITO glass, where Cl-ITO and F-ITO were treated with p-chlorophenylacetic acid and p-fluorophenylacetic acid for 12 h, respectively

The transmittance spectra of ITO glass substrates in the visible region are shown in Fig.3(b). The data shows that modification treatment does not change the transparency of ITO glass significantly. The surface morphology of the surface of the ITO substrate was measured with an atomic force microscope (AFM). Fig.4 shows that Cl-ITO and F-ITO have similar surface morphology with bare-ITO, and their root mean square roughness (*RMS*) values are 2.43 nm, 2.44 nm and 2.39 nm respectively. The results suggest that SAM modification does not change the surface characteristics of ITO.

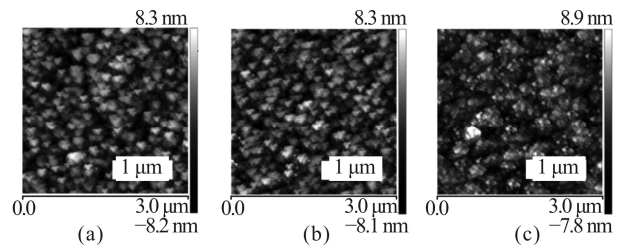


Fig.4 AFM images of (a) bare-ITO, (b) Cl-ITO and (c) F-ITO with the length of the scanned area of 3 μm

The work functions of bare-ITO, Cl-ITO and F-ITO are 5.0 eV, 5.24 eV and 5.15 eV, respectively, which are measured with AFM in KPFM mode as shown in Tab.2. As expected, self-assembled molecular layer with negative dipole can adjust the work function of ITO electrodes^[15,16]. The hole injection barriers are reduced as shown in Fig.5. It may improve the injection of hole carriers at the interface of the ITO electrode and the HTL layer and enhance the performance of the devices. To prove it, hole-only devices and OLED were fabricated.

Tab.2 Water contact angle, roughness and work function values of bare-ITO, Cl-ITO and F-ITO

	Bare-ITO	Cl-ITO	F-ITO
Water contact angle (°)	7.3	59.1	46.5
<i>RMS</i> (nm)	2.43	2.44	2.39
Work function (eV)	5.0	5.24	5.15

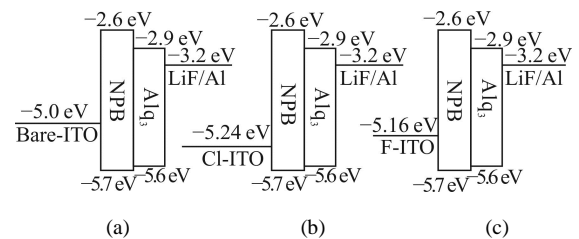


Fig.5 Level diagrams of OLED device with (a) bare-ITO, (b) Cl-ITO and (c) F-ITO

The current density-voltage curve of the hole-transporting device is shown in Fig.6. It can be seen that the current density values of Cl-hole-only and F-hole-only at the same voltage are obviously larger than

that of bare-hole-only. The results show that SAM modification can lower the hole injection barrier between ITO and NPB and increase the current density of the hole transport devices.

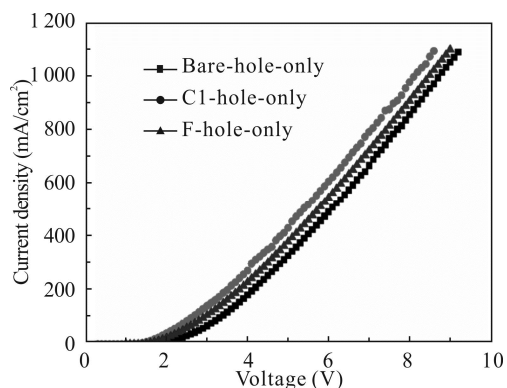


Fig.6 Current density-voltage curves of hole-only-devices

Fig.7(a) shows the luminance-voltage curves of OLEDs. The turn-on voltages of bare-OLED, C1-OLED and F-OLED are 3.2 V, 2.5 V and 2.9 V, respectively. As the SAM treatment reduces the hole injection barriers, the turn-on voltages of the OLED devices are also reduced, and the magnitudes of the decrease are positively correlated with the values of the work function of the ITO electrodes. Below 7 V, there is no significant difference in luminance among different devices. With the increase of voltage, the luminance of the bare-OLED is significantly lower than those of the other two devices. The maximum luminance values of bare-OLED, C1-OLED and F-OLED are 15 880 cd/m², 21 771 cd/m² and 22 428 cd/m², respectively. Compared with the basic device, after the SAM modification with p-chlorophenylacetic acid and p-fluorophenylacetic acid, the maximum luminance values of the OLED devices are obviously increased by 37.09% and 41.23%, respectively. The hole-only devices demonstrate that the hole carrier injection of the device is improved after the organic acids treatment, which is also the reason for improving the efficiency of OLED devices.

After the ITO is modified by organic acids, the current density of the OLED device is obviously dropped. As can be seen from Fig.7(b), the current density of bare-OLED is obviously larger than that of F-OLED, and the current density of F-OLED is slightly larger than that of C1-OLED, combined with luminance-voltage curves, the results suggest that after SAM modification of ITO surface, the device efficiency is obviously improved. The current efficiency-luminance curves of OLED devices are shown in Fig.8(a). At the same luminance value, the current efficiency of the OLED device fabricated on the SAM-treated ITO electrode is higher, which is corresponded to the conclusion of the previous discussion. The current efficiency of bare-OLED, C1-OLED and F-OLED at 200 cd/m² are 2.66 cd/A, 3.59 cd/A and 2.70 cd/A, respectively. After the ITO electrodes are treated with p-chlorophenylacetic acid and p-fluorophenylacetic acid, the maximum current efficiency of OLED is increased from 2.94 cd/A to 3.95 cd/A and 3.69 cd/A, and the efficiency roll-off is decreased from

31.97% to 17.72% and 18.69%, respectively.

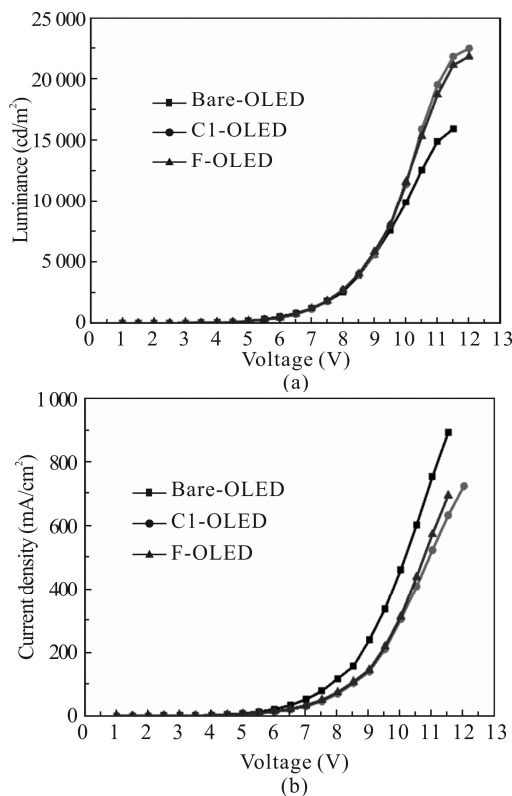


Fig.7 (a) Luminance-voltage curves and **(b)** current density-voltage curves of OLED devices

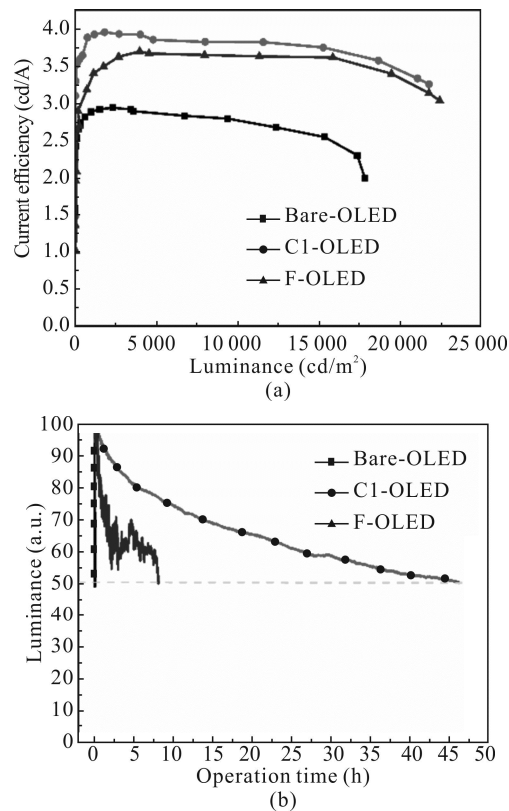


Fig.8 (a) Current efficiency-luminance curves and **(b)** half-lifetime performance of the OLED devices

The improvements of brightness and current efficiency are mainly due to the improvement of the hole injection and the contact performance at the interface of the ITO anode and the organic layer. The SAM treatment affects the wetting ability of the ITO electrode surface. Chong et al^[17] pointed out that the greater the contact angle of water, the greater the improvement on the contact performance, and the performance of device is positively correlated to the water contact angle value. Our experiment results also favor that conclusion.

Fig.8(b) shows the half-lifetime decay curves of OLED devices at initial luminance of 1 000 cd/m². The lifetime of CI-OLED, F-OLED and bare-OLED are 46.2 h, 8.1 h and 3.3 min, respectively. In general, the interface between inorganic ITO electrodes and the hydrophilic HTL is very unstable. NPB will detach and peel off from the surface of ITO after healing. The OLED devices will heat up during operation causing HTL degradation and low hole injection efficiency. Therefore, lifetime of the bare-OLED is only 3.3 min. After modification, the water contact angle is enhanced from 7.3° (bare-ITO) to 59.1° (CI-ITO) and 46.5° (F-ITO). The performance parameters of OLEDs are shown in Tab.3. In previous related reports, there is no mention of the effect of organic acid SAM treatment on device lifetime. As previously reported, the wettability of ITO surface is improved after modification, NPB deposited on the ITO surface can form closer contact with ITO which enhances the mechanical and thermal stability of the NPB films^[18,19]. The stability of the structure can directly affect the stability of the device during operation. As expected, after SAM modification with organic acids, the stability and lifetime of the OLED devices can be significantly improved.

Tab.3 The performance parameters of OLEDs, including turn-on voltage (V_{on}), maximum brightness (L_{max}), maximum current efficiency (CE_{max}), current efficiency at the current density of 200 mA/cm² (CE_{200}) and maximum current density (CD_{max})

Devices	V_{on} (V)	L_{max} (cd/m ²)	CE_{max} (cd/A)	CE_{200} (cd/A)	CD_{max} (mA/cm ²)
Bare-OLED	3.2	15 880	2.94	2.66	891
CI-OLED	2.5	22 428	3.95	3.59	723
F-OLED	2.9	21 777	3.69	2.70	693

In order to investigate the effects of SAM modified ITO on the properties of OLED devices, two organic acids are used. After the modification, the work functions of ITO are increased, reducing the hole injection barrier at the interface between ITO and NPB, resulting in the enhancement of the hole transport capability of OLED devices. Simultaneously, the improvement of wettability of ITO surface makes the HTL organic film layer flatter and more stable, significantly improving the stability of the devices. After modification, the performance of OLED devices is improved. The turn-on voltages of OLEDs are reduced, and the brightness and current efficiency are improved significantly. Especially, the maximum brightness of CI-OLED device is increased by

41.23%, and the maximum current efficiency is increased from 2.94 cd/A to 3.95 cd/A. The most important is that the half-lifetime decay of OLEDs is increased obviously. In conclusion, a simple, cost-effective and reproducible method of fabricating OLEDs with better performance and longer lifetime is provided.

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