



Roles of electrode interface on the performance of organic photodetectors



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ABSTRACT

We report that the performance of organic photodetectors (OPDs) is significantly enhanced by tuning of electrode interface. Amino acids, PEO or LiF were deposited onto indium tin oxide (ITO) via a solution process (spin-coating or a hydrothermal process). These OPDs with the modified ITO as a cathode exhibit a large enhancement of the detectivity which is up to one order of magnitude higher than that of the counterpart OPDs with the pure ITO cathode. Meanwhile, the OPDs with the modification of ITO have the best response speed with a rise time of 3.9 μ s, which is half shorter than that (7.8 μ s) of the compared OPDs with pure ITO. The enhancement of the response speed was attributed to a better ohmic contact of the ITO electrode with the active layer due to the reduced work function of the ITO after modification. Impedance measurements show that the OPDs with the ITO modification have a largely decreased series resistance (R_s), which plays an important role in the increase of the performance.

1. Introduction

Organic photodetectors (OPDs) have been increasingly investigated in recent years due to their great potential in various important applications [1–4]. Compared with traditional photodetectors that utilize inorganic materials, OPDs possess inherent advantages of the wide material sources, high throughput solution processes, and the flexible, large-scale, and high resolution device fabrication. A generally worried issue for organic based devices is the fragility of organic materials which may lead to the weakness of device stability. However, this shouldn't be a crucial problem for OPDs since they actually need to undergo a very weak light illumination and a very small working current in their optoelectronic applications. Recent studies have shown that some OPDs have higher detectivity than inorganic silicon based photo detectors [5–8]. It will be crucial to roundly improve various properties, not only the detectivity, in future studies of OPDs.

Self-assembled monolayers (SAMs) have been widely used for surface modification in various fields because they only require a small amount of materials and they can realize a surface functionalization with little effects on the bulk properties. In the field of organic optoelectronic devices, the SAM can adjust the work function of electrodes by forming molecular dipoles on the interface of electrodes. Electrodes interface engineering with SAMs has been widely reported to improve the matching of electrodes work function to the energy level of organic active layer in both organic light-emitting diodes (OLEDs) and organic solar cells (OSCs) [9–14]. However, very few reports have

presented the investigation of SAMs on OPDs.

In this communication, we demonstrate that high performance OPDs can be achieved by the surface modification of ITO with self-assembled amino acids. The OPDs are developed with an inverted structure where the modified transparent ITO and a MoO_3/Al as the cathode and anode, respectively. The active layer is a blend of thieno [3,4-b]thiophene/benzodithiophene (PTB7) and [6,6]-phenyl C_{71} -butyric acid methyl ester (PC_{71}BM) with a wide band response from ultraviolet (UV) (about 350 nm) to near-infrared (about 800 nm). We roundly investigate various properties of the OPDs. The results prove that these OPDs have significantly high detectivity which results from low dark current and high photocurrent, very fast response speed, and excellent stability. Measurements such as X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectra (UPS) and AC impedance spectroscopy were carried out to investigate the mechanism of high performance.

2. Experiments

Arginine, alanine, histidine and PEDOT:PSS were purchased from Sigma-Aldrich[®]. P3HT, PTB7, PBDTT-DPP were purchased from Solarmer Energy, Inc., and PC_{71}BM was purchased from Sigma-Aldrich[®]. Indium-tin-oxide (ITO) glasses (7–10 Ω/Square) were purchased from CSG Holding Co., Ltd. An unfiltered He I (21.2 eV) gas discharge lamp and a total instrumental energy resolution of 0.1 eV was used to characterize the valence states and the vacuum level (VL) for

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the UPS measurement. A monochromatic Al K α source (1486.6 eV) was used for XPS measurements. All these measurements were performed at room temperature. ITO substrates were ultrasonically cleaned with acetone, detergent, deionized water, and isopropyl alcohol. The cleaned substrates were dried in a dry box and subsequently treated by UV-ozone for 15 min. For amino acids modification, these substrates were immersed in a 10 mM aqueous amino acid solution at 90 °C for 2 h. After this, the samples were rinsed with pure water and dried in a nitrogen glove box. For PEDOT:PSS modification, an aqueous solution of PEDOT:PSS was spin-coated onto these substrates at a speed of 1500 rpm for 40s, and then, they were heated at 110 °C for 40 min. For TiO₂ modification, TiO₂ was prepared by a sol-gel method, and the precursor gel was prepared according to our previous literature [6]. The precursor gel was spin-coated onto these substrates at a speed of 4000 rpm for 1 min. After that, they were sintered at 500 °C for 3 h in a sealed stove. A solution of 10 mg ml⁻¹ PTB7 and 15 mg ml⁻¹ PC₇₁BM in dichlorobenzene with the additive 1, 8-diiodooctane (DIO) (3% v/v), 10 mg ml⁻¹ P3HT and 10 mg ml⁻¹ PC₆₁BM in dichlorobenzene or 10 mg ml⁻¹ PBDTT-DPP and 20 mg ml⁻¹ PC₇₁BM in dichlorobenzene with the additive 1, 8-diiodooctane (DIO) (3% v/v), was spin-coated on top of the ITO at a slow speed of 500 rpm for 36 s. Then, the ITO was dried in nitrogen gas at room temperature for 12 h. Finally, an anode of 10 nm thick MoO₃ and 120 nm thick Al or a cathode of 10 nm thick Ca and 120 nm thick Al was deposited on top of the active layer by thermal evaporation. The typical active area of the devices was about 0.12 cm². A commercial laser diode (HLD690030N5J, ROHM) with a wavelength of 680 nm and an intensity of 0.25 mW cm⁻² was used as the light source. The dark current was recorded by Keithley 4200 source meter unit with samples placed in shielding metal box. A quantum efficiency (QE)/IPCE measurement system (SR830, Stanford Research Systems) was used to record the responsivity. Reverse bias on the device was provided by a constant output voltage from a 20 MHz Function/Arbitrary Waveform Generator (33220A, Agilent). For transient response measurement, the laser diode is powered by a square pulse from the Waveform Generator (33220A, Agilent). A 100 MHz digital oscilloscope (TDS 1012C-SC, Tektronix) was in series connected to the device under illumination of the laser diode to measure the photo-response voltage directly. For the linearity measurement, the photocurrent was recorded by the Keithley 2400 source measurement unit, and the light source was provided by the laser diode driven with different voltages and the light source of the quantum efficiency (QE)/IPCE measurement system added by light filters. The frequency response curves were acquired according to the change trend of frequency response of a Si photodetector and the equation:

$$F_{-3dB} = \frac{0.38}{T_r} \quad (1)$$

where T_r is the rise time. The noise current was measured with devices connected in series with the lock-in amplifier (SR830, Stanford Research Systems). Through choosing the integration time, lock-in amplifier reported a noise current in A Hz^{-1/2}. AC impedance spectroscopy was carried out by using the 5 Hz to 13 MHz LF impedance analyser. When the shot noise is the main source of the noise, the detectivity (D^*) can be calculated by the equation [5]:

$$D^* = \frac{R}{\sqrt{2q \cdot J_d}} \quad (2)$$

where D^* is the detectivity in cm Hz^{1/2} W⁻¹ or Jones, q is the elementary charge with the value of 1.6×10^{-19} C and J_d is the dark current density in A cm⁻², respectively.

3. Results and discussion

The chemical structures of the active materials and the device structure of the OPDs are shown in Fig. 1a. Amino acids were deposited on the surface of the ITO by a hydrothermal process. Amino acids used

here are arginine (Arg), lysine (Lys) and histidine (His) and the performance of these devices with amino acids were investigated (See Figs. S1–S2). Other than the amino acids, other materials such as polyethyleneoxide (PEO) and LiF, which are widely used as an interfacial material in organic electronic devices [15–17], are also employed to modify the ITO for comparison. Fig. 1b compares the current-voltage (I–V) characteristics of these devices in the dark with a cathode of blank ITO, PEO, LiF and Arg modified ITO. With the Arg modification, the device had approximately two order of magnitude in reduction in the dark current density at the bias voltage from –2 to 0 V. Inversely, as shown in Fig. 1c, the photocurrent responsivity (R_f) for the device with the Arg modification, had obvious enhancement at a wide arrange of wavelength from 350 to 780 nm. These results lead to the significantly high detectivity for the device with the modifications, which is shown in Fig. 1d. The plots of projected detectivity (D^*) of the device with Arg modified ITO was highest up to 1.25×10^{13} Jones at the wavelength of 775 nm and higher than 6.07×10^{12} Jones at the wavelength from 350 to 820 nm. The wide response of the device, which covers from UV to near infrared, will lead to more promising application in photoswitches, images and communications. With the PEO modification, the J_d at –0.1 V is 8.77×10^{-10} A/cm², R_f and D^* at 775 nm is 0.12 A/W and 7.36×10^{12} Jones. With the LiF modification, the J_d at –0.1 V is 1.33×10^{-9} A/cm², R_f and D^* at 775 nm is 0.13 A/W and 6.67×10^{12} Jones.

We attribute the increase of R_f and the decrease of dark current to the reduction of ITO work function. Fig. 2a shows the survey XPS profiles of the ITO and the ITO/Arg after a water rinse. The appearance of the N 1 s peak and the weakening of the In 3d indicate the success of the chemical modification of Arg on the surface of ITO substrates. Compared with that of ITO, an obvious N 1 s peak shown in the high-resolution XPS picture of ITO/Arg (Fig. 2b) further proves this chemical modification. UPS measurement shows that the surface work function of the ITO/Arg was significantly reduced to 3.6 eV from 4.7 eV of the surface work function of the original ITO (Fig. 2c). As shown in Fig. 2d, with the bare ITO as the cathode, it easily has schottky contact between ITO and the active layer due to the large barrier of electron between them. With ITO/Arg, it easily becomes ohmic contact because of the reduction of the barrier. The low work function enhanced the ohmic contact of the ITO electrode with the active layer for enhancing the ability of electron collection, resulting in the increase of photocurrent. This is similar to the process in widely reported OSCs [18–22]. As shown in Table 1, the surface modification of ITO with amino acids brought about an obvious decrease of series resistances (R_s). The low work function also decreased the dark current of the devices by avoiding parasitic injection of hole from the ITO electrode [23,24].

In addition to the detectivity, the response speed of OPDs is another key point in various applications. Fig. 3a shows the time-resolved photo response voltages (V_{rp}) of the device with or without Arg. The devices were illuminated under a red laser source driven by a rectangular wave voltage, and the voltage was measured by a 100 MHz digital oscilloscope. The response wave shape is clearly different from the original signal shape for the device without Arg compared with the device with Arg. With ON or OFF for the light irradiation switch, the device without Arg shows a rise time of 7.8 μ s and a decay time of 13.5 μ s, while the device with Arg are 0.8 and 1.4 μ s, respectively. The device with PEO shows a rise time of 3.9 μ s and a decay time of 7.2 μ s. The device with LiF shows a rise time of 1.2 μ s and a decay time of 1.5 μ s. The fast response speed allowed the devices to perform as a high-quality photosensitive switcher [25]. Fig. 3b shows the –3 dB bandwidth of these devices. The –3 dB bandwidth for the devices with ITO, PEO, LiF or Arg are 48.7 kHz, 97.4 kHz, 316.3 kHz and 475.1 kHz.

The bulk hetero junction OPDs in this study can be viewed as a similar p - n junction photodiode, where the total time of the response (T_r) is determined by the equation: [26]

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