Inverted ternary OPD based on PEIE

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Abstract
In today’s rapid development of multiphase organic photodetectors (OPDs), research on inverted ternary OPDs is very necessary. Therefore, this paper innovatively proposes an inverted ternary organic photodetector (OPD) with a structure of ITO/PEIE/PC₆₁BM/P3HT:PCPDTBT/MoO₃/Al. And the PEIE electron transport layer (ETL), which is essential for the inverted structure, is used to study the effects of different thicknesses. Different thicknesses of PEIE have different effects on the photoelectric characteristics of the device. For the photodetector spin-coated with 0.15wt% PEIE solution, the photodetector shows resistance characteristics. For the photodetector spin-coated with 0.40wt% PEIE solution, the photodetector shows the characteristics of a photodiode. For the photodetector spin-coated with 0.45wt% PEIE solution, the photodetector shows the characteristics of a photomultiplier diode. The underlying mechanism is that different thicknesses of PEIE have different energy levels for ITO, and different cathode energy levels have huge differences in the working mechanism of the device.

Keywords OPD · Inverted · PEIE · Photomultiplier

1 Introduction
In recent years, OPD has gradually become a research hotspot, because it not only has the detection efficiency comparable to that of inorganic photodetectors, but also has the advantages of flexibility, variety of material choices, and simple manufacturing processes (Jansen-Van et al. 2016; Iftikhar et al. 2020; Zang et al. 2016; Liu et al. 2020; Wang et al. 2021; Shi et al. 2020; Li et al. 2020). In the ternary OPD, based on the principle of spectrum broadening, three organic materials with complementary absorption peaks are used as the active layer to achieve detection in the full spectrum from ultraviolet to near-infrared (Li et al. 2019; Wang et al. 2018; Liu et al. 2021; Valouch et al. 2012). However, in the ternary OPD, there are still problems such as low external quantum efficiency and large dark current, and these problems seriously affect the detection efficiency of the device (Li et al. 2015).
In order to solve the problem of the low external quantum efficiency of OPD, the researchers proposed that the device can be induced to produce a photoconductive effect by introducing traps (Gong et al. 2019). For example, Jonas Kublitski et al. used C$_{60}$ as an electron trap to induce hole tunneling injection, so that the EQE of the device reached 400% when the applied bias voltage was -5V (Jonas et al. 2021). Our research group has conducted a lot of research on this, mainly focusing on doping electron traps to induce holes tunneling to improve the external quantum efficiency of the device. For example, the active layer P3HT: PC$_{61}$BM is doped with C$_{60}$ as an electron trap, so that the device can achieve external quantum efficiency as high as 327.5% under -1V bias voltage and 460nm illumination (An et al. 2019). Doping C$_{60}$ into the active layer PBDT-TT-F: PC$_{61}$BM, the device achieves external quantum efficiency as high as 739.8% under a bias of -3V and 630nm illumination (An et al. 2020). In order to solve the problem of low trap utilization in the case of high concentration single doping, this research group also proposed the use of double doping C$_{60}$ and C$_{70}$ to improve the trap utilization, and achieve 8 times the external quantum efficiency from 1067.48% to 8510.17% growth (Shafian et al. 2015). Although the external quantum efficiency of the device can be significantly improved by doping traps in the active layer, there will be a phenomenon of doping gathered when doped with higher concentrations of doping, resulting in a reduction in the number of traps. It severely limits the practical application of trap-doped organic photomultiplier detectors.

Regarding the problem of large dark current in bulk heterojunction devices, the researchers proposed that devices with multiple active layer planar heterojunction structures can be fabricated. This approach can make the donor and the acceptor materials contact the anode and the cathode respectively, reducing the leakage current (Yang et al. 2013; Oliveira et al. 2019; Shen et al. 2016). However, due to the short diffusion distance of free carriers in organic materials, it is necessary to make the active layer of the device thinner, resulting in insufficient absorption of the active layer and the problem of poor photoelectric properties of the device.

In order to solve the above problems, this paper uses PEIE as the ETL to capture electrons at the cathode interface to induce hole tunneling injection to make the device work in the photoconductive mode to increase the external quantum efficiency. This paper adopts a composite structure of planar junction and heterojunction.

2 Experiment

2.1 Device preparation

An inverted ternary OPD was prepared in the experiment, and its structure was indium tin oxide (ITO) (20 mm×20 mm, 15Ωper square, Lumtec) /polyethoxyethyleneimine (PEIE) / PC$_{61}$BM(160nm) /P3HT: PCPDTBT(160 nm) /MoO$_3$ (10 nm) /Al(100nm). Figure 1 shows the structure diagram of the inverted ternary OPD and the energy level diagram of the material. The PEIE solution is obtained by diluting the PEIE (80% ethoxylation; 37wt% in H$_2$O) solution with deionized water to 0.15wt%, 0.4wt% and 0.45wt%, and stirring at room temperature with a magnetic stirrer for 12 hours. The PEIE ETL is prepared on the ITO cleaned with acetone and ethanol and dried with a nitrogen gun, spin-coated with a spin coater at a speed of 6000 rpm for 60 s, and then placed on a CNC hot plate for annealing for 30 minutes. The acceptor activity solution was prepared by weighing 10 mg of PC$_{61}$BM with an electronic balance and dissolving it in 1 mL of o-dichlorobenzene, and...
fully stirring it with a magnetic stirrer at room temperature for 12 hours. The acceptor layer was spin-coated on the PEIE ETL with a spin coater at a speed of 500 rpm for 60 seconds, and then annealed for 10 minutes. The donor active solution was prepared by weighing 7 mg P3HT and 3 mg PCPDTBT with an electronic balance, dissolving them in 1 mL o-dichlorobenzene, and fully stirring for 12 h at room temperature with a magnetic stirrer. The donor active layer was spin-coated on the acceptor active layer with a magnetic stirrer at 500 rpm for 60 seconds, and then annealed for 10 minutes. A high vacuum coater was used to vapor-deposit 15 nm MoO$_3$ electron barrier layer and 100 nm anode Al. Before spin-coating the PEIE ETL, a part of ITO (5 mm × 20 mm) needs to be etched away with concentrated hydrochloric acid to serve as the Al electrode area. And shield a part of ITO (5 mm × 20 mm) as a reserved cathode to avoid contact between positive and negative electrodes. The effective area of the final device is 1 cm$^2$.

2.2 Testing and characterization

The Keithley 2636B Semiconducting System is used to test the J-V image to characterize the electrical characteristics of the device. The specific method is to connect the ITO cathode of the device to a high voltage, and the anode Al to a low voltage, and pass a direct current of -3V to 3V. Test the J-V of the device under different voltage driving and different wavelengths of light to the OPD. According to the electrical characteristics of the device, the external quantum efficiency (EQE), responsivity (R) and the specific rate ($D^*$) of the device can be obtained by calculation, and the performance of OPDs can be measured by these parameters. In order to directly understand the absorption of the OPD active layer film to different wavelengths of light, the UV-Vis spectrophotometer (PerkinElmer, Lambda 950) can be used to measure the absorbance of the active layer film of the device in the visible-infrared spectrum range.

2.3 Feature parameter calculation

The responsivity ($R$), external quantum efficiency ($EQE$) and the specific detection rate ($D^*$) can be a good measure of the photoelectric characteristics of the device. The calculation formula is as follows:
\[ R = \frac{J_{ph}}{P_{in}} = \frac{J_{light} - J_{dark}}{P_{in}} \]  

(1)

\[ EQE = \frac{J_{ph}h\nu}{P_{in}q} = \frac{R\nu}{q} = 1240 \cdot \frac{R}{\lambda} \]  

(2)

\[ D^* = \frac{R}{\sqrt{2qJ_{dark}}} \]  

(3)

Among them, \( J_{ph} \) is the photogenerated current, which is equal to the difference between the photocurrent and the dark current, \( J_{light} \) is the current generated by the device under illumination, \( J_{dark} \) is the dark current, \( P_{in} \) is the incident light power and \( \lambda \) is the wavelength of the incident light.

3 Results and discussion

The test results of ternary OPDs with different PEIE thicknesses prepared in the experiment were analyzed. Through the test results of Abs spectrum, J-V, C-V and parameter calculation, the influence of different thickness of PEIE on the optical properties of the film and the electrical properties of OPDs is analyzed. By measuring the absorption spectra of P3HT, PC_{61}BM and PCPDTBT single material and mixed material films, as shown in Fig. 2. As show by Fig. 2, according to the principle of complementary absorption spectra, the ternary OPD proposed in this paper can achieve full-spectrum detection from visible light to near-infrared light (Wang et al. 2017). And it is found that suitable thickness of the PEIE film can increase the absorption intensity of the device in the full spectrum range. Too thick or too thin PEIE thickness will affect the absorption performance of the device, but these effects are very weak and can be ignored.

In this paper, the film morphologies of spin-coated PEIE solutions of 0.15wt%, 0.4wt% and 0.45wt% were observed with an atomic force microscopy (AFM) as shown in Fig. 3a, b and c. It is found that the roughness of the three films are very similar, so it shows that
Fig. 3  AFM image of spin-coated a 0.15wt%, b 0.4wt% and c 0.45wt% PEIE solution on ITO substrate
changing the mass ratio of the PEIE solution has no obvious effect on the roughness of the film.

In order to explore the influence of different thicknesses of PEIE ETL films on the electrical characteristics of OPDs, the J-V characteristics of OPDs were tested under different optical powers of blue (460nm), green (530nm) and red (800nm).

Figure 4a shows the J-V curve of OPD spin-coated with 0.15wt% PEIE solution under the condition of red light (800nm) with different optical powers. 4(b) shows the J-V curve of OPD spin-coated with 0.4wt% PEIE solution under the condition of red light (800nm) with different optical powers. It can be concluded that under the irradiation of 800nm red light, its J-V characteristics tend to be the same regardless of its optical power. And its diode characteristics are not obvious compared with the ETL of OPDs spin-coated with 0.4wt% PEIE solution, and it is similar to a resistor with a fixed value. This is because the concentration of the spin-coated PEIE solution is too low and the thickness of the PEIE on the device is too thin to improve the energy level of the cathode ITO.

Figure 4c shows J-V characteristic curve of the OPDs spin-coated 0.4wt% PEIE solution as ETL under green light (530nm) with optical power of 0.9, 1.45 and 3.3mW/cm2. As shown in Fig. 4, the photocurrent of OPDs spin-coated with 0.4wt% PEIE solution as a ETL under red light is an order of magnitude higher than that under green light. And no matter it is under the red light condition or the green light condition, the photocurrent will increase with the increase of the optical power under the bias voltage of 0-1v. This is because the incident light power increases, the photogenerated excitons generated also increase, and the photocurrent by dissociation of the device will reach the reverse saturation current faster. Figure 4d, e and f are J-V plot of three-phase inverted OPDs spin-coated with 0.45wt% PEIE solution under dark conditions and 430nm, 550nm, 750nm light.

EQE, R and D* of OPDs can be calculated according to formula (1),(2),(3) and the value of J-V curve. Under a bias of 2.5V, the EQE, R and D* of the three-phase inverted OPDs spin-coated 0.45wt% PEIE solution under different illumination and different optical power are shown in Table 1.
It is obvious from Table 1 that the R and EQE of the device are highly dependent on the light intensity. In the case of the same wavelength, R and EQE increase with the increase of the light intensity, but in the case of different wavelengths, the light intensity is not the main factor affecting the R and EQE of the device. For example, the external quantum efficiency under blue light conditions of 430nm and 1.32mW/cm$^2$ is much higher than that under red light conditions of 750nm and 2.51mW/cm$^2$. This phenomenon can be explained as a decrease in the trapping efficiency of additional excitons generated by the increase in optical power due to the saturation of electron traps and the decrease in induced hole mobility.

It can be seen from Table 1 that the EQE of the device is greater than 100%, which indicates that the device has a photoconductivity effect (Anefnaf et al. 2021). This is because the spin-coated PEIE ETL increases the energy level of ITO (Kublitski et al. 2021). The higher energy barrier will cause the accumulation of photogenerated electrons at the interface between electrode and the active layer, thereby greatly increasing the photocurrent gain, making EQE>100%.

Table 1 R and EQE of OPDs at a bias voltage of 2.5V and placed under different light conditions

| Lighting conditions   | R (A/W) | EQE (%) | D$^*$ (Jones) |
|-----------------------|--------|---------|---------------|
| 430nm+1.05m W/cm$^2$  | 0.71   | 203     | 2.798×10$^{11}$ |
| 430nm+1.32m W/cm$^2$  | 0.98   | 281     | 3.862×10$^{11}$ |
| 550nm+3.01m W/cm$^2$  | 1.04   | 233     | 4.099×10$^{11}$ |
| 550nm+4.02m W/cm$^2$  | 1.64   | 370     | 6.463×10$^{11}$ |
| 750nm+2.51m W/cm$^2$  | 1.00   | 225     | 3.941×10$^{11}$ |
| 750nm+3.42m W/cm$^2$  | 1.23   | 278     | 4.847×10$^{11}$ |

Figure 5 shows the working principle diagram of inverted OPDs. The energy level of ITO itself is -4.8eV, and the energy level of ITO is increased to -3.95eV by spin coating with a suitable thickness of PEIE (Klab et al. 2020)(Li et al. 2021). If the PEIE spin-coated is too thin, ITO will be closer to the HOMO energy level of PC$_{61}$BM, and it will tend to be an anode that collects holes rather than a cathode that collects electrons. However, due to the presence of the MoO$_3$ electron blocking layer in the inverted device (Liu et al. 2021), the device cannot be an conventional OPDs. Therefore, the J-V curve of the OPDs device that spin-coated 0.15wt% PEIE solution as a ETL does not show obvious diode characteristics, as shown in Fig. 4a.

The multiplication mechanism of the PEIE modified OPD is shown in Fig. 5(c). When the device is exposed to light, the excitons generated by the absorption of photons by the active layer PC$_{61}$BM and P3HT:PCPDTBT film will dissociate at the interface of the PC$_{61}$BM and P3HT:PCPDTBT film. The holes generated by dissociation move to the HOMO energy level of P3HT:PCPDTBT and the electrons move to the LOMO energy level of PC$_{61}$BM. In the inverted device, the PEIE-modified ITO improves the potential barrier between the ITO electrode and the optical functional layer, allowing photo-generated carriers to accumulate in the electron transport layer. This high-strength bound electrons will thin the barrier for hole injection from the ITO electrode, and at the same time further lead to hole injection from ITO to P3HT. When a reverse bias is applied to the device, even under light power of a few mW/cm$^2$, the accumulation of electrons at the interface between the active layer and the electrode will induce tunneling and injection of holes on the electrode, resulting in a higher photocurrent.

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Because the charge density between the electrodes can determine the capacitance of the device, the C-V characteristic curves of the device spin-coated 0.3wt% and 0.45wt% PEIE are drawn, as shown in Fig. 6. It can be seen from the figure that only changing the weight ratio of the spin-coated PEIE solution changes the capacitance of the device, which shows that the charge at the electrode interface does accumulate. Under zero voltage, the capacitance difference of the device with 0.3wt% PEIE spin-coated under light and dark

**Fig. 5**  a Working principle diagram of inverted OPDs b Energy level diagram of devices spin-coated 0.15wt%PEIE c The working mechanism of OPDs photomultiplier caused by PEIE ETL

**Fig. 6**  C-V characteristic curves of spin-coated 0.3wt% and 0.45wt% PEIE in the light and dark state
conditions is 7.06nF, while the capacitance difference of the device with 0.45wt% PEIE under light and dark conditions is 16.74nF. This indicates that the device with 0.45wt% PEIE spin-coated has accumulated more photogenerated carriers due to the enhanced injection barrier.

It is analyzed and concluded that the appropriate thickness of PEIE can effectively realize the high detection performance of the inverted ternary OPD in the visible light to near-infrared wavelength range.

4 Conclusion

In a word, this paper innovatively designed an inverted ternary OPD whose structure adopts a composite structure of planar junction and bulk heterojunction. In this innovative structure, the influence of the thickness of the PEIE on the working mode of the OPD is studied. The results show that for the photodetector spin-coated with 0.15wt% PEIE solution, the photodetector shows resistance characteristics. For the photodetector spin-coated with 0.40wt% PEIE solution, the photodetector shows the characteristics of the photodiode. For the photodetector spin-coated with 0.45wt% PEIE solution, the photodetector shows the characteristics of a photomultiplier diode. Among them, when 0.45wt% PEIE solution is spin-coated, under 550nm light and the optical power is 4.02mW/cm², the device achieves a responsivity of up to 1.64A/W and an external quantum efficiency of 370% under 2.5V bias.

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