Highly Sensitive UV–Vis-to-Near-Infrared Organic Photodetectors Employing ZnO: Polyethylenimine Ethoxylated Composite as Hole-Blocking Layer

Jingwen Li, Guanghong Liu, Wansheng Liu, Yichuan Si, Wanyuan Deng,* and Hongbin Wu*

Significantly suppressed leakage current and reduced shot noise in organic photodetectors (OPDs) are achieved by employing charge blocking layers, which have led to tremendous advances in highly sensitive devices with photoresponse covering from the ultraviolet to near-infrared regions. However, trap-assisted charge carrier injection through tunneling can significantly contribute to the sources of leakage current upon the use of charge blocking layers. Herein, it is shown that leakage current in organic photodetectors can be effectively reduced to an intrinsic lower limit by using a composite hole blocking layer (HBL) that consists of zinc oxide (ZnO) blended with different weight concentration of polymer polyethylenimine ethoxylated (PEIE). The best device shows an ultralow dark current density down to 0.18 nA cm$^{-2}$, which translates to high specific detectivity ($D^*$) over $1 \times 10^{12}$ Jones in broad response range from 340 to 1100 nm (with peak value of $4.2 \times 10^{13}$ Jones at 940 nm and $3.5 \times 10^{13}$ Jones at 1050 nm), approaching to the intrinsic dark current-limited detectivity value. It is found that the incorporated N atoms fill the defect site of oxygen in ZnO, thus giving rise to the reduced proportion of emission via defects.

1. Introduction

Nowadays, most photon detection techniques rely on photodetectors made with inorganic semiconductors, such as Si, InGaAs, and InSb. However, their broad applications are limited by the complicated fabrication, costly processing, mechanical inflexibility, and high-temperature and high-vacuum conditions toward large-size devices.$^{[1,2]}$ As a complementary alternative to inorganic photodetectors, organic photodetectors (OPDs) possess several advantages, such as low-cost fabrication, solution processability, and ease of tunable spectral sensitivity.$^{[3,4]}$ Benefiting from the rapid development of novel organic semiconductors, the device performance of OPDs has made tremendous progress in recent years, gaining considerable attention for their potential applications in various areas, such as image sensing, light communication, medical monitoring, and computer vision.$^{[5–7]}$

Apart from these progresses, the overall performance of OPDs is still limited by the low external quantum efficiency (EQE) owing to the undesired charge generation and collection,$^{[8,9]}$ large noise current owing to the poorly suppressed dark current as a result of charge injection under reverse bias, which is more severe in narrow bandgap materials as a result of reduced injection barrier height and the significantly increased intrinsic free carrier density.$^{[10–12]}$ More recently, Simone et al. showed that the dark current in OPDs can be modeled under the framework of charge injection from metal contacts into an energetically disordered semiconductor, in which material parameters including effective bandgap, charge disorder parameters, and mobility, and device parameters such as active layer thickness, applied voltage bias, and charge injection barrier play a role in the interpretation of the observed dark current.$^{[13]}$

In contrast, despite complicated factors that affect the dark current in OPDs due to the complex nature of organic materials, incorporation of the charge blocking layer between electrodes and semiconductors,$^{[14]}$ use of a thick active layer,$^{[10]}$ use of an inverted structure,$^{[15]}$ and employment of device structure with vertical organic composition$^{[16]}$ had been demonstrated as creative approaches to enhance the device performance so far.

Despite the successful implementation of the abovementioned strategies, however, there are still some key challenges that remain to further greatly boost the device performance of OPDs. For example, although minimized dark current under reverse bias is needed for high sensitivity, how to minimize tunneling injection of charge carriers triggered by interfacial trap states and the consequent dark current is a challenging aspect of the OPD research. It is known that trap states at metal electrode/active layer interface (also known as topological defects) can contribute to current through tunneling$^{[17]}$ and therefore

J. Li, G. Liu, W. Liu, Y. Si, W. Deng, H. Wu
Institute of Polymer Optoelectronic Materials and Devices
State Key Laboratory of Luminescent Materials and Devices
South China University of Technology
Guangzhou 510640, P. R. China
E-mail: wydeng@scut.edu.cn; hbwu@scut.edu.cn

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adpr.202100269.

© 2022 The Authors. Advanced Photonics Research published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

DOI: 10.1002/adpr.202100269
obstruct the realization of OPDs with high sensitivity. Furthermore, it has recently been demonstrated that tunneling injection in OPDs can take place via interfacial trap states regardless of the presence of charge blocking layer. Therefore, the ability to reduce dark current while maintaining high photoreponsiveness through proper use of charge blocking layer appears to play a decisive role in achieving high-performance OPDs.

In this study, we demonstrate highly sensitive OPDs with UV–Vis–near-infrared (NIR) photon detection capability based on the blend of a semiconducting polymer and a narrow bandgap small molecule acceptor. A composite layer consisting of zinc oxide (ZnO) and polyethyleneimine ethoxylated (PEIE) [19] is proposed to serve as an interlayer to reduce density of traps [20,21], suppress leakage current, and facilitate charge extraction. The composite layer architecture offers the benefits of (i) the work function of which is typically shallow (~4.0 eV) compared with that of the pure ZnO layer (~4.08 eV), corresponding to an increase of 0.08 eV in injection barrier height; (ii) reduced trap density (1.06 × 10^{-17} \text{cm}^{-3} \text{eV}^{-1}) compared with that of the pure ZnO layer (5.78 × 10^{-17} \text{cm}^{-3} \text{eV}^{-1}); and (iii) high thickness tolerance (thickness of the ZnO:PEIE layer in 30 nm) compared with that of the pure PEIE layer (restricted to ~10 nm). [22] The resultant OPDs with such composite layer give ultralow dark current density of 1.81 × 10^{-10} \text{A cm}^{-2} under a reverse bias of ~0.1 V, while EQE of 50% is to be preserved. These features ultimately translate into OPDs with state-of-the-art specific detectivity of 4.18 × 10^{15} Jones at 940 nm, and comparable detectivity covering the UV light to NIR region of the electromagnetic spectrum.

2. Results and Discussion

In this study, we use a classic conjugated polymer PTB7-Th [23] as an electron donor and a newly developed narrow bandgap small molecule COTIC-4F [24] as an electron acceptor. The chemical structures of the donor and acceptor are shown in Figure 1a alongside absorption spectra of thin film (Figure 1b). The absorption profile of pristine PTB7-Th film exhibits maxima at 640 and 700 nm, while the COTIC-4F thin film shows intense in the NIR region, with an absorption peak at 1000 nm and high absorption coefficient (α) of nearly 9 × 10^{4} \text{cm}^{-1} owing to the strong intramolecular charge transfer effect. As a result of the complementary absorption between the electron-acceptor materials, the blend exhibits strong optical absorption from 300 to 1150 nm, covering the UV–vis–NIR region. UV photoelectron spectroscopy (UPS) was used to determine the highest occupied molecular orbital (HOMO) value of PTB7-Th and COTIC-4F. From the measurement, we infer HOMO energy of ~4.91 eV for PTB7-Th film and ~5.07 eV for COTIC-4F film (Figure 1c and Figure S1, Supporting Information). Deducing from the optical bandgap, the energy level of the lowest unoccupied molecular orbital (LUMO) value was estimated to be ~3.36 and ~3.97 eV for PTB7-Th and COTIC-4F, respectively. Thus, the HOMO offset and LUMO offset in PTB7-Th:COTIC-4F blend are estimated to be 0.16 and 0.61 eV, respectively, which are the interfacial energetic driving force that allows efficient charge separation.

To evaluate the light signal detection performance, devices with an inverted structure of indium tin oxide (ITO)/hole-blocking layer (HBL) (30 nm)/active layer (100 or 280 nm)/MoO_x (10 nm)/Ag (100 nm) were fabricated. As displayed in Figure 2a, the OPD device exhibits a broad spectra response ranging from 300 to 1150 nm, suggesting that both PTB7-Th and COTIC-4F components simultaneously contributed to the photocurrent. The EQE for the OPDs with a thin active layer thickness (100 nm) is approaching 50% in the range of 600–1000 nm, with a maximum value approaching 56% at 650 nm, indicating efficient charge generation from both photoinduced hole transfer and photoinduced electron transfer pathways. The OPDs with a relatively thick active layer of 280 nm show decreased EQE in the long-wavelength region, while enhanced EQE is clearly seen in the short-wavelength region. The EQE spectra for a commercial silicon photodetector (HAMAMASTU S1787) are included for comparison. The responsivity (R) of the devices, defined as the ratio of photocurrent to the incident light intensity, is calculated from EQE(λ), according to the R(λ) = J_{ph} / hν, where J_{ph} is the photocurrent density, J_{light} is the incident light intensity, q is the elementary charge, h is the Planck constant, and ν is the frequency of light. The maximum responsivity of the 100 nm OPDs is 0.35 A W\(^{-1}\) at 950 nm (Figure 2b). We note that the responsivity of OPDs lags behind the commercial counterpart, mainly due to the undesirable carrier collection efficiency of ~70%, which is determined by the ratio of photocurrent and saturation photocurrent, as illustrated in Figure S2, Supporting Information. Nevertheless, the responsivity of both the OPDs in the range of 1000–1150 nm is among the best results of NIR OPDs reported so far, owing to the narrower bandgap and strong NIR absorption of COTIC-4F.

Current OPDs suffer from high dark (or noise) current typically due to the energetic disorder nature of organic semiconductor, as well as the interfacial trap-controlled charge injection, which greatly increased with a decreasing bandgap. As photodetectors are generally operated at reverse voltage, the dark current I_D, which is the output current that flows through an external load, can be described by the Shockley equation, following I_D = I_0[exp(q\nu/kT) - 1] + I_n, where the I_0 is the reverse saturation current, n is the ideal factor, k is the Boltzmann constant, T is the temperature, and R_sh is the shunt resistance. As shown in Figure 2c, the current density J_D for the OPD fabricated with a thin active layer of 100 nm under dark condition is up to 1.0 × 10^{-8} and 5.0 × 10^{-7} \text{A cm}^{-2} at ~0.1 and ~1.0 V, respectively. To suppress the dark current, we further use a thick-film strategy with a 280 nm thickness active layer to lower the probability of appearance of a pinhole and increase the shunt resistance, thereby leading to reduced leakage current. As a result, the dark current density is approximately reduced by two orders of magnitude, reaching a low value of 1.0 × 10^{-9} \text{A cm}^{-2} at a reverse bias of ~0.1 V, which is even lower as compared to that of a crystalline silicon photodetector (S1787). Owing to relatively high carrier mobility of ~4.4 × 10^{-4} cm\(^2\) V\(^{-1}\) s\(^{-1}\) for the hole and 5.2 × 10^{-4} cm\(^2\) V\(^{-1}\) s\(^{-1}\) for the electron (Figure S3, Supporting Information), the thick OPDs maintain a reasonably high EQE above 40% in the range of 600–1000 nm. The EQE values, combined with the fact that the dark current in the thick OPDs is of the same order of magnitude as the Si detector, enable a dramatically improved shot-noise-limited specific...
detectivity $D^* \ (\text{determined by } D(\lambda)^* = \frac{R(\lambda)}{\sqrt{2qJ}}) \text{ from } \approx 6.0 \times 10^{12}$ Jones to $\approx 2.3 \times 10^{13}$ Jones at 900–1000 nm, at a reverse bias of $-0.1 \text{ V}$, thereby achieving an optimal device performance comparable to a commercial silicon photodetector (Figure 2d).

The dark current in OPDs at reverse bias (also known as dark saturation current) has intrinsic and extrinsic origins. Intrinsic source originates from intrinsic recombination current induced by thermal radiation. Extrinsic contributions originate from topological defects, charge injection through the electrode governed by a thermionic emission model or tunneling model. To quantify the intrinsic and extrinsic sources of the reverse dark current in our devices, we first calculate the intrinsic recombination current induced by thermal radiation. The intrinsic saturation current of a photodiode comprises a radiative recombination current $I_{0,R}$ and a non-radiative recombination current $I_{0,NR}$. The radiative recombination current density $J_{0,R}$ originates from temperature-dependent background radiation, and can be written as $J_{0,R} = q \int \text{EQEPV}(E) \Phi_{BB}(E) dE$, where $\Phi_{BB}(E)$ is the blackbody spectrum at room temperature. To assess the $I_{0,R}$, we probe the photosresponse within the bandgap by applying Fourier transform photocurrent spectroscopy (FTPS). As illustrated in Figure S4, Supporting Information, the PTB7-Th: COTIC-4F device exhibits exponential response in low-energy regime with an ultralow Urbach energy of $\approx 22 \text{ meV}$, indicative of low energetic disorder and very narrow distribution of subbandgap states within the active layer. The results give rise to a low $I_{0,\text{Rad}}$ of $3.3 \times 10^{-17} \text{ A cm}^{-2}$, even lower than that of a silicon photodetector ($4.2 \times 10^{-17} \text{ A cm}^{-2}$). Following the reciprocity relationship between optical absorption and emission, which is given by $\Phi_{EL}(E) = \Phi_{BB}(E) \text{EQP}(E) \exp\left[\frac{qV}{kT} - 1\right]$, we further employ electroluminescence (EL) to calculate the non-radiative recombination current density $J_{0,NR}$, because the EQE of EL (EQEEL) is equal to the fraction of $J_{0,R}$ to the sum of $J_{0,R}$ and $J_{0,NR}$. As the OPDs exhibit an EQEEL of $1.0 \times 10^{-3}$%, a low value of $3.3 \times 10^{-12} \text{ A cm}^{-2}$ is obtained for $J_{0,NR}$, which is approximately two orders of magnitude lower than the measured dark current at $-0.1 \text{ V}$.

Figure 1. a) Chemical structure of polymer donor PTB7-Th and small molecule acceptor COTIC-4F. b) UV–vis–NIR absorbance spectra of PTB7-Th, COTIC-4F, and PTB7-Th:COTIC-4F films. c) HOMO energy level determined by UPS and LUMO energy level estimated from optical gap for the donor and acceptor.
Even with an optical bandgap as low as 1.1 eV, the contribution of the intrinsic recombination current to the total dark current can be negligible and therefore be excluded as a major source of the dark current in this OPD. Nevertheless, the recombination current calculated from FTPS/EL demonstrates an intrinsic lower limit of dark current. To approach this limit, it is of crucial importance to suppress the extrinsic source of dark current, such as charge carrier injection from the contact of semiconductor/metal, which is affected by the injection barrier height and the presence of trap in the interlayer. To further suppress the dark current originated from the injection, a hybrid ZnO:PEIE interlayer is incorporated as HBL. PEIE, an organic polymer containing simple aliphatic amine groups, was found to be an effective surface modifier for lowering the work function of the electrode. However, the limitation of insulation characteristics significantly restricts its thickness to ~10 nm in actual devices, under which situation it can be easily tunneled by charge carriers. Nevertheless, the intrinsic molecular dipole moments associated with the neutral amine groups in PEIE can lead to enhanced intermolecular interaction with other conductive materials, thus filling the defects, as well as smoothing out surface roughness.

Films of ZnO:PEIE were prepared by dissolving PEIE into ZnO precursor solution through spin-coating, followed by thermal annealing at 200 °C for an hour. As summarized in Table S1, Supporting Information, the work function of the hybrid HBL decreased from ~4.08 to ~4.00 eV upon increasing the concentration of PEIE to 0.15 wt%, which is determined by the Kelvin Probe technique. Benefiting from the reduced work function, the incorporation of the hybrid HBLs is expected to effectively block the hole injection from ITO cathode and result in reduced reverse saturation current, according to

$$J_s = \frac{A^* T^2 \exp\left(-\frac{\Phi_B}{k_B T}\right)}{\eta},$$

where $J_s$ is the reverse saturation current density, $A^*$ is the Richardson constant (with a vacuum value of 120 A cm$^{-2}$ K$^{-2}$), and $\Phi_B$ is the barrier height at the semiconductor/metal interface. As displayed in Figure 3a, the reverse dark current in the devices based on hybrid HBLs is substantially lower than that of devices with pure ZnO HBLs, suggesting that the addition of PEIE can suppress undesired charge injection. Especially, combined with thick-film strategy and application of ZnO:PEIE (0.10 wt%) layer, the $J_s$ is reduced to values of as low as 1.8 x 10$^{-10}$ A cm$^{-2}$ at ~0.1 V and 1.9 x 10$^{-9}$ A cm$^{-2}$ at ~1.0 V, respectively. The charge injection is dramatically suppressed by increasing the injection barrier height, which is in accordance with the abovementioned thermal emission equation. However, the quantitative relationship between the
saturation current and barrier height is not strictly held, where the $J_D$ only cut in half when the barrier height increased 0.06 eV. Hence, another source such as trap-assisted injection via the defects in the semiconductor/metal interface needs to be taken into account. Indeed, with an increasing energetic disorder, traps can induce more severe trap-assisted recombination, which in turn leads to an increase in injection current and a decrease in the amount of carrier extraction as photocurrent. As shown in Figure 3b,c, the photocurrent is slightly increased upon the use of hybrid HBLs, which can be ascribed to a suppressed trap-assisted recombination in the interlayer. However, the charge collection efficiency in the device with ZnO:PEIE (0.15 wt%) HBL is slightly reduced, mainly due to a decrease in conductivity of the hybrid films. Owing to its inherent insulating property, excessive addition of PEIE leads to poor conductivity, as illustrated in Figure S6, Supporting Information. As a result of reduced dark current density and slightly increased responsivity in the NIR region, the device with ZnO:PEIE (0.10 wt%) HBL exhibits very high detection of $4.2 \times 10^{13}$ Jones at 940 nm and $3.5 \times 10^{13}$ Jones at 1050 nm, surpassing the existing Si photodetector in a broad NIR spectrum (Figure 3d). Considering that dark current in OPDs is mainly dominated by non-radiative recombination current, the detectivity of OPDs shows a spectral dependence and strong dependence on intrinsic non-radiative recombination, as shown in Figure 3d. As can be clearly seen, apart from exceeding the state-of-the-art, the specific detectivity $D^*$ for the optimal device at around 1050 nm is only two orders of magnitude lower in comparison to the upper limit of intrinsic detectivity for photodetector, calculated from intrinsic non-radiative recombination and additional radiative recombination\(^{[11]}\) (with $\text{EQE}_{\text{EL}}=1 \times \times 10^{-3}$ and $E_U=22 \text{ meV}$, where $E_U$ is the Urbach energy of tail states within bandgap (Figure S4, Supporting Information).

The questions now are whether the addition of PEIE reduces the amounts of defects in ZnO and whether the reduced dark current is correlated to the distribution of defects. To verify our speculation, we first performed capacitance–frequency ($C–f$) measurement to determine the distribution of defects in the HBLs. This method is based on the frequency response of capacitance to an electric field, as trapping mobile charge

![Figure 3](image-url)

Figure 3. Device performance of the OPDs with different HBLs. a) Current density–voltage ($J–V$) characteristics in the dark. b) EQE and c) responsivity. d) Specific detectivity as a function of wavelength. The solid lines with symbols represent the best results of experimental $D^*$ studied in this work. The dashed lines represent the upper limit of $D^*$ for different contributions of non-radiative recombination currents and additional radiative recombination currents originated from the absorption of disorder-induced tail state (represented as Urbach energy $E_U$).
carriers by defects and their detrapping via thermal excitation under an applied alternating current signal can contribute to frequency dependence of capacitance.\cite{28,29} Hence, the characteristics of traps can be manifested through their response to the AC electric field. A trap with an energy level of \( E_t \) can respond to the electric field with a frequency lower than a certain frequency given by \( \omega_t = 2\pi f_t \exp\left(-\frac{E_t}{k_B T}\right) \), where \( \nu_0 \) is the attempt-to-escape frequency, which represents the rate of trapped charge carriers attempt to escape from the potential barrier of the trap. Above this frequency, the trapping and detrapping of charge carriers fail to follow the electric field and thus exclude contribution to the capacitance. This translates into a certain “demarcation energy” \( E_d \), defined by \( E_d = k_B T \ln\left(\frac{\omega}{\omega_0}\right) \), and only those traps above this demarcation energy can contribute to capacitance. Because it takes longer time to detrapping once captured by deeper traps, the response in lower-frequency capacitance spectra usually corresponds to the detrapping of deeper traps. Following the analysis presented in the previous study,\cite{23} the capacitance can be calculated by the integration of the contribution of traps in space from a certain position \( x \) to the boundary of the depletion region, or in terms of energy range between \( E_{d} \) and the Fermi level \( E_F \), given by \( C = \frac{q^2}{\mu_{ext}} \int_{E_{d}}^{E_F} \frac{N(E)}{\nu_0^d} dE \), where \( q \) is the elementary charge, \( \nu_0 \) is the local shift to the Fermi-level and the perturbation of the external applied signal, respectively. Assuming \( \mu_{ext} = \nu_0 \) constant, the density of trap states at the energy level can be derived from the derivative of capacitance with respect to angular frequency as \( N(E) = -\frac{q^2 \nu_0}{\mu_{ext} E^2} \frac{dC}{d\omega^2} \). It should be noted that characteristic features of negative capacitance is observed in low-frequency region for the devices with ZnO:PEIE HBL, which can be explained by the transient current originating from trap-assisted recombination in bipolar organic diodes.\cite{30,31}

To reveal the change in trap states upon the use of different HBLs, we compared the \( C-f \) characteristics of a series of stacks with the structure of ITO/different HBLs/MoO\textsubscript{3}/Ag, in which the active layer is absent. As shown in Figure 4a, the device with ZnO HBL exhibits the most dramatically changing capacitance in the high-frequency region between 1 and 5 MHz, indicative of the presence of a large trap DOS, while the stacks with ZnO:PEIE (0.10 wt%) HBL is about half of that of the device with ZnO HBL and is consistent with the experimental data. Therefore, our model provides a valid approach to correlate the reverse injection current to the distribution of traps in the blocking layer.

Further insight into the influence of PEIE addition can be inferred from steady-state photoluminescence (PL) measurement, as displayed in Figure 4e. The PL spectra of ZnO films exhibit two emission peaks, with one sharp peak centered at 390 nm, and a green emission peaked at \( \approx 580 \) nm. The UV emission originates from band-to-band exciton recombination, while the broad emission in the visible region is referred to as transitions from the oxygen vacancy (VO) as the defect to the valence band.\cite{32} Compared to the pure ZnO film, the PL emission of the hybrid film exhibits a significantly reduced proportion of emission in the visible region, suggesting a reduced trap density upon the addition of 0.10 wt% PEIE.\cite{33} Primarily, the non-radiative nature of trap-assisted recombination in an organic semiconductor fundamentally alters the nature of charge carrier recombination, thus leading to reduced radiative efficiency.\cite{25} As confirmed by results of photoluminescence quantum yield (PLQY) measurement, PLQY value in hybrid film (\( \approx 35\% \)) is about three times that in pure ZnO film (\( \approx 10\% \)), indicating that non-radiative recombination induced by defects is drastically suppressed. Furthermore, the time-resolved photoluminescence measurement was applied to investigate the decay kinetics of defects, and bi-exponential fitting is used to extract the lifetime, as summarized in Figure 4f. Under the frame of bi-exponential decay, the faster decay component is usually ascribed to non-radiative recombination processes that are related to defects introduced by VO complexes, while the slower decay is the result of radiative recombination of the free exciton. Here, we find that the fast decay constant is 0.24 ns for hybrid film, smaller than

\[ I_t \propto N_t \exp\left(-\frac{\Phi_{B, eff}}{k_B T}\right) \propto \exp\left(\frac{E_i}{k_B T}\right) \int N_0 \exp\left[-\frac{(E - E_t)^2}{\sigma^2}\right] dE \]

where \( I_t \) represents the trap-assisted injected current and the other parameters are the same as mentioned earlier. According to this model, charge carrier injection is more prone to occur in case of the deeper trap states and larger density of trap states, leading to higher dark current density. Figure 4d plots the calculated trap-assisted injected current \( I_t \) and the measured \( J_0 \) at \(-1.0 \) V against the change of PEIE concentration, also summarized in Table 1. The \( I_t \) exhibits a similar trend to the \( J_0 \), suggesting that the extrinsic dark current can mainly be attributed to charge injection via trap states in HBLs. Similar trends can be observed in the actual devices with the blend of PTB7-Th: COTIC as active layer (Figure S7 and Table S2, Supporting Information), suggesting that the detailed description by Equation (1) could be appropriate. Moreover, the calculated \( I_t \) for the device with ZnO:PEIE (0.10 wt%) HBL is about half of that of the device with ZnO HBL and is consistent with the experimental data. Therefore, our model provides a valid approach to correlate the reverse injection current to the distribution of traps in the blocking layer.
Figure 4. a) C-f spectra for the devices in stack of ITO/HBLs/MoO$_x$/Ag. b) The deduced trap DOS calculated from $N_t(E_\omega) = \frac{1}{C_0 V_{bi}} \frac{q}{w} k_B T \frac{dC}{d\omega}$ and the Gaussian fits to the trap DOS (solid lines). c) Schematic band diagram for the OPDs under operation mode. The defects in HBLs as injection sources are displayed as Gaussian-shape with narrow (red) and broaden (blue) distribution. d) Comparison of experimental $J_D$ at $-1.0 \text{ V}$ and calculated trap-assisted injected current $I_t$. The solid line corresponds to the calculated $I_t$ based on the resultant DOS listed in Table 1 (without active layers), while the dashed line denotes the result calculated using the parameter summarized in Table S1, Supporting Information. e) Steady and f) time-resolved PL spectra of the pure ZnO and ZnO:PEIE (0.10 wt%) films coated on quartz, excited by 360 nm femtosecond laser. XPS spectra of g) N$_{1s}$ core response and h) O$_{1s}$ core response of pure ZnO and ZnO:PEIE (0.10 wt%) films.
that of the ZnO film (0.30 ns). The observation may be mainly attributed to a decreased amount of trap states that require less time to populate and depopulate,\(^{34}\) and is consistent with the results of C–f measurement. It should also be noted that in addition to VO origin, these most commonly observed defect emission between 500 and 600 nm region can also be caused by zinc interstitials or Cu impurities, and other types of defects that have not been conclusively identified. Under this circumstance, excitons’ decay behaviors can be complicated and influenced by a number of factors, including sample preparation conditions and non-radiative recombination sites.

Several studies have demonstrated that inherent defects in ZnO film are produced during the growth process,\(^ {35}\) mainly due to the unexpected stoichiometric growth ratio of Zn and O atoms. The unbalanced growth leads to the formation of a large number of Zn interstitial atoms and O vacancies,\(^ {36}\) while the addition of N atoms is supposed to relieve oxygen deficiency.\(^ {37}\)

In this regard, X-ray photoelectron spectroscopy (XPS) was carried out to investigate the chemical composition of the pure ZnO and ZnO:PEIE (0.10 wt%) films, both were grown by sol–gel spin-coating. As shown in Figure 4g,h, N atom can be clearly observed in the composite HBL, while hardly observed in the ZnO film. In addition, upon the incorporation of PEIE, the O\(_{1s}\) peaks centered at around 530.2 eV, which corresponds to O\(^{2−}\) in the wurtzite structure of Zn\(_{2}\)O, together with the peak centered at 531.4 eV, which corresponds to the O–H bonds that are found to decrease slightly, consistent with previous studies.\(^ {21,38}\) The results indicate that the added N atom fills the deficient site of oxygen in the wurtzite structure of a hexagonal Zn\(_{2}\)O, and thus reduces the binding intensity of Zn–O and O–H bonds.

Other figures-of-merit for the optimal OPDs based on ZnO:PEIE (0.1 wt%) HBL are illustrated in Figure 5. Two critical parameters that evaluate the photodetector performance are the noise equivalent power (NEP) and the specific detectivity (D\(*\)). As NEP is usually specified for a bandwidth of 1 Hz, it can be given via NEP = \( \frac{S_n}{R(\lambda)} \), where \( S_n \) is the noise spectra density in the unit of A Hz\(^{1/2} \), and \( R(\lambda) \) is the photoresponse at a specific wavelength in the unit of A W\(^{-1/2} \). Here, fast Fourier transform signal analyzer equipped with a highly sensitive current preamplifier was employed to accurately determine the total noise current of OPDs. As shown in Figure 5a, in the region of low frequency (< 1 Hz), the total noise is approaching one order of magnitude higher than shot noise, which means flicker noise is the dominant source in this range. As the frequency increases, the total noise rapidly descends to the same level as shot noise around 4 × 10\(^{-15} \) A Hz\(^{-1/2} \), and the optimal NEP and D\(*\) are respectively calculated to be 1.27 × 10\(^{-14} \) W Hz\(^{1/2} \) and 3.15 × 10\(^{14} \) Jones, which is very close to the abovementioned shot-noise-limited D\(*\) shown in Figure 3.

Linear dynamic range (LDR), which represents the range within which photocurrent varies linearly with optical intensity as LDR = 20 lg \( \frac{I_{\text{in}}}{I_{\text{out}}} \), was figured out to be 128 dB for the optimal device (see Figure 5b). It should be noted that even under maximal irradiance of 5.79 mW cm\(^{-2} \), the photoresponse of the resultant device has not obviously deviated from linearity, indicating that the 128 dB LDR is not a saturated value. Response time, which is defined as the time that the response signal takes to go from 0% to 90% (rise time, \( T_r \)) and 100% to 10% (fall time, \( T_f \)) of a steady-state photocurrent is found to be 9 and 7 μs, respectively (Figure 5c). We note that the cut-off frequency at −3 dB and −6 dB is extracted to be 65 kHz and 80 kHz (Figure 5d), respectively, suggesting that our OPDs can satisfy many audio and video applications with a rate that is over 30 kHz. We further investigate the stability of these OPDs by characterizing their electrical properties before and after illumination. As illustrated in Figure S8, Supporting Information, the dark current density of ZnO-based devices drastically increases one order of magnitude after 5 min exposure under irradiation of solar simulator, while that is less sensitive to the illumination in hybrid HBL-based devices, indicating that the reliability of photosensing is enhanced after addition of 0.10 wt% PEIE.\(^ {39}\) Although good stability should be sought, the lifetime issue can also be influenced by the organic-electrode contact properties and encapsulation process, so careful control should also be taken to allow fair and rigorous assessment.

3. Conclusions

In summary, we reported high-performance UV–Vis–NIR OPDs based on the blend of PTB7-Th:COTIC-4F by using a composite HBL to suppress leakage current and facilitate charge extraction. The optimal OPD shows spectrally flat photoresponse in the range of 340–1110 nm and a maximal specific detectivity (D\(*\)) of above 4.2 × 10\(^{13} \) Jones at 940 nm, which is approaching twice as that of state-of-the-art commercial Si photodetector. As result of ultralow dark current density of 1.81 × 10\(^{-10} \) A cm\(^{-2} \), the D\(*\) at around 1050 nm is only two orders lower than the upper limit of detectivity for PTB7-Th: COTIC-4F photactive layer with intrinsic recombination current density of 3.3 × 10\(^{-12} \) A cm\(^{-2} \). Based on our model where traps as injection sources are included, the origin of reduced dark current density in the optimal device can be qualitatively ascribed to the reduced trap density in the composite HBL. The reduced trap distribution is confirmed by measurements of steady and time-resolved PL spectrum, as a result of occupation in the deficient site of oxygen in ZnO by the added N atom. The resultant OPDs exhibit a broad response bandwidth (cut-off frequency) of 65 kHz and a fast temporal response time around 7–9 μs, which can meet the requirement for lag-free imaging applications.

### Table 1. Parameters of defects distribution for the devices with different HBLs extracted from the Gaussian fitting in Figure 4b. The injection via traps is calculated according to Equation (1) by using the corresponding values of DOS.

| HBLs               | \( N_0 \) \( \times 10^{17} \text{ cm}^{-3} \) | \( E_i \) [eV] | \( \sigma \) [eV] | \( \lambda_i \) [μm] | \( J_{dc} \) [nA cm\(^{-2} \) at −1 V] |
|--------------------|-------------------------------------|--------------|--------------|----------------|----------------------|
| Pure ZnO           | 5.78                                | 0.29         | 28           | 1              | 4.81                 |
| ZnO:PEIE (0.05 wt%)| 1.96                                | 0.29         | 30           | 0.36           | 2.74                 |
| ZnO:PEIE (0.10 wt%)| 1.06                                | 0.28         | 29           | 0.13           | 1.91                 |
| ZnO:PEIE (0.15 wt%)| 1.79                                | 0.29         | 30           | 0.33           | 2.64                 |
Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

H.W. thanks the National Natural Science Foundation of China (No. 51521002) for financial support. W.D. acknowledges support from the National Natural Science Foundation of China (No. 62004069).

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

capacitance spectroscopy, dark current density, density of states, near-infrared organic photodetectors

Received: September 5, 2021
Revised: November 16, 2021
Published online: January 28, 2022

Figure 5. a) Comparison of measured total noise current and calculated shot noise limit from 0.1 to 12 Hz. b) Photocurrent versus irradiation intensity for the OPDs under illumination of 940 nm LED. c) Photoresponse of the OPDs to a 230 μs pulse LED with an incident power density of 5.79 mW cm\(^{-2}\). d) Device bandwidth measured under 940 nm LED illumination.

---

[1] X. Liu, Y. Lin, Y. Liao, J. Wu, Y. Zheng, J. Mater. Chem. C 2018, 6, 3499.
[2] Q. Lin, A. Armin, P. L. Burn, P. Meredith, Laser Photonics Rev. 2016, 10, 1047.
[3] W. Yao, Z. Wu, E. Huang, L. Huang, A. E. London, Z. Liu, J. D. Azoulay, T. N. Ng, ACS Appl. Electron. Mater. 2019, 1, 660.
[4] J. Huang, J. Lee, J. Vollbrecht, V. V. Brus, A. L. Dixon, D. X. Cao, Z. Zhu, Z. Du, H. Wang, K. Cho, G. C. Bazan, T. Q. Nguyen, Adv. Mater. 2019, 32, 1906027.
[5] X. Gong, M. Tong, Y. Xia, W. Cai, J. S. Moon, Y. Cao, G. Yu, C. L. Shieh, B. Nilsson, A. J. Heeger, Science 2009, 325, 1665.
