Organic Photodetectors

Subjects: Nanoscience & Nanotechnology
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Organic photodetectors (OPDs) have gained increasing interest as they offer cost-effective fabrication methods using solution processes and a tunable spectral response range, making them particularly attractive for large area image sensors on lightweight flexible substrates. Carrier blocking layers engineering is very important to the high performance of OPDs that can select a certain charge carriers (holes or electrons) to be collected and suppress another carrier. Carrier blocking layers of OPDs play a critical role in reducing dark current, boosting their efficiency and long-time stability.

Keywords: organic photodetector ; carrier blocking layer ; energy alignment ; dark current ; efficiency

1. Introduction

Photodetectors can convert optical signals to electronic signals, which are widely applied in optical communication, environmental monitoring, cameras, smart phones, image sensing, and so on [1][2][3][4][5]. Compared to commercial photodetectors such as silicon (Si)- and indium gallium arsenide (InGaAs)-based photodetectors, OPDs are increasingly attractive for light sensing applications as they combine detection wavelength tenability, solution processability, and high photogeneration yield with low fabrication costs, lightweight, and flexibility [6][7]. The basic structure of OPDs generally includes two essentials parts: an active layer for light absorption and electrodes for the collection of charge carriers (electrons and holes). The working mechanism of OPDs is similar to that of organic photovoltaics (OPVs), which can be summarized as (i) the organic semiconductors absorb photons to generate excitons (electron−hole pair) and then the excitons diffuse to donor/acceptor interfaces; (ii) the excitons separate into electrons and holes driven by electric field force formed by extra applied bias; (iii) holes are transferred to the anode through the channels formed by the highest occupied molecular orbital (HOMO) of the donor, and electrons are transported to the cathode via the channels formed by the lowest unoccupied molecular orbital (LUMO) of the acceptor; (iv) the holes and electrons are collected by the corresponding electrode to generate photocurrent.

Continuously improving the high gain property, OPDs have achieved significant breakthroughs and rapid evolution in the last several decades, thanks to the developments of novel donor/acceptor materials, the innovations of the device structure, and interface engineering. Kang et al., reported high-detectivity green-selective all-polymer p-n junction photodetectors by engineering the π-conjugation networks and insulating properties of p- and n-type polymers [8]. Zhang et al., achieved planar heterojunction (PHJ) OPDs based on the medium-band gap fullerene C^{60} and a new low-band gap fused-ring non-fullerene acceptor bilayer structure for a tunable spectral response [9]. Nie reported that aligned nanofibers (ANs) prepared by electrostatic spinning technology as an interfacial layer can significantly enhance the performance of inverted OPDs [10]. Due to the lower relative permittivity ($\varepsilon_r \approx 3$–4) of organic in comparison with inorganic materials [11], excitons with a relatively high binding energy of ≈ 0.35–0.5 eV are generated after light absorption, rather than free electrons and holes. Thus, the active layer of OPDs is often based on a bulk heterojunction (BHJ) architecture that comprises finely bicontinuous and interpenetrative networks of electron donor and acceptor phases, in which this structure facilitates exciton dissociation and charge transport to the relevant electrodes [12].

2. Carrier Blocking Layer Materials and Application in Organic Photodetectors

Different types of blocking layer materials have been demonstrated to play a critical role in OPDs. At present, the interface layer materials in organic solar cells and OPDs have great similarities. However, due to the different working mechanisms of devices, not all materials can be used in OPDs. Therefore, more research and optimization of these materials should be carried out for OPDs. From Table 1 and Table 2, we can ascertain the development of OPDs in hole and electron blocking layer materials in recent years, respectively. However, more efforts are needed to promote their applications and to propose new materials for OPDs.

Table 1. Survey of the main characteristics of OPD employing materials such as HBLs.

Materials	Device Structure	J_d (A cm^{-2})	*EQE* (%)	*D** (Jones)	*R* (A W^{-1})	Measurement Conditions	Ref
BCP	ITO/PEDOT:PSS/active layer/BCP/Al	1.1×10^{-9}	-	1.4×10^{12}	0.068	−2 V, @ 800 nm	[13]
	ITO/TPBi/MoO_3/C70/active layer/BCP/Al	2.2×10^{-2}	68,927 1	2.2×10^{12}	188	−6 V, @ 345 nm	[14]
	ITO/PEDOT:PSS/active layer/BCP/Al	1.3×10^{-5}	2170	8.3×10^{11}	6.39	−15 V, @ 360 nm	[15]
Bphen	ITO/TAPC:MoO_3/active layer/Bphen/Ag	1.11×10^{-9}	41.8	6.43×10^{12}	0.121	−3 V, @ 360 nm	[16]
	ITO/PEDOT:PSS/active layer/BCP/Ag	4.82×10^{-4}	-	3.7×10^{11}	-	−1.5 V, @ 350 nm, 0.5 mW cm^{-2}	[17]
	ITO/MoO_3/CuI/active layer/Bphen/Al	$\sim 10^{-2}$	400	10^{12}	-	−8 V, @ 870 nm	[18]
	ITO/PEDOT:PSS/active layer/BCP/Ag	$\sim 10^{-5}$	43.78	2.67×10^{12}	0.25	@ 710 nm	[19]
	ITO/TAPC/active layer/BCP/Ag	1.15×10^{-9}	74.6	4.14×10^{13}	0.439	−2 V, @ 730 nm	[20]
PEIE	ITO/PEIE/active layer/MoO_3/Ag	7.7×10^{-9}	60	4.8×10^{12}	0.24	−1.5 V, @ 546 nm	[21]
	ITO/PEIE/active layer/Al	4×10^{-5}	12,000	2.27×10^{12}	54	−0.8 V, @ 530 nm	[22]
	ITO/PEIE/active layer/Au	7.7×10^{-10}	-	2.2×10^{13}	0.32	−2 V, @ 629 nm	[23]
	ITO/PEIE/active layer/Al	2.77×10^{-6}	3200	1.04×10^{12}	14.25	−1 V, @ 550 nm	[24]
	PEDOT:PSS/PEIE/active layer/PEDOT:PSS	1.5×10^{-10}	55	3.45×10^{13}	-	−5 V, @ 530 nm	[25]
PFN	ITO/PFN/active layer/Ag	5.10×10^{-4}	67.09	2.47×10^{12}	0.37	−0.5 V, @ 680 nm	[26]
	ITO/PFN/active layer/Al	$\sim 10^{-3}$	650	1.76×10^{12}	8.7	−15 V, @ 520 nm	[27]
	ITO/PFN/active layer/Al	1.92×10^{-8}	208.11	9.1×10^{12}	0.921	−0.5 V, @ 550 nm	[28]
	ITO/PEDOT:PSS/active layer/PFN-Br/Ag	$\sim 10^{-8}$	65	10^{13}	-	−10 V, @ 860 nm	[29]
	ITO/PEDOT:PSS/active layer/PFN-Br/Al	4.85×10^{-10}	56	2.61×10^{13}	0.33	−0.1 V, 720 nm	[6]
PEI	PEDOT:PSS/PEI/active layer/PEDOT:PSS/PEDOT:PSS	$\sim 10^{-7}$	65	-	-	−4 V	[30]
	PEDOT:PSS/PEI/active layer/Poly-PT/PEDOT:PSS	$\sim 10^{-7}$	65	2.2×10^{12}	-	−1 V, @ 505 nm	[31]
	PEDOT:PSS/PEI/active layer/PEDOT:PSS	5.7×10^{-8}	46	3.35×10^{12}	-	−1 V, @ 525 nm	[32]

Materials	Device Structure	J_d (A cm^{-2})	*EQE* (%)	*D** (Jones)	*R* (A W^{-1})	Measurement Conditions	Ref
C_{60}	ITO/PEDOT:PSS/active layer/C_{60}/Al	8×10^{-10}	60	~10^{13}	-	−1 V, @ 532 nm	[33]
	ITO/PEDOT:PSS/active layer/C_{60}/Al	1.1×10^{-10}	67.1	9.2×10^{12}	0.38	−1 V, @ 700 nm	[34]
	ITO/ZnO/active layer/MoO_3/Ag	6.51×10^{-8}	~70	2.58×10^{11}	0.48	−0.1 V, @ 700 nm	[35]
	Ag/ZnO/active layer/PEDOT:PSS	~10^{-10}	-	2×10^{12}	0.3	−1 V, @ 532 nm	[36]
	ITO/ZnO/active layer/MoO_3/Al	3.9×10^{-9}	140,000	6.3×10^{12}	-	−0.5 V, @ 680 nm	[37]
	ITO/ZnO/PEIE/active layer/MoO_3/Ag	8.075×10^{-6}	62	3.749×10^{12}	0.281	2 V, @ 680 nm	[38]
	PEDOT:PSS/ZnO/PEIE/active layer/PEDOT:PSS	2.11×10^{-8}	~40	~10^{11}	~0.17	0 V, @ 700 nm	[39]
TiO_2	ITO/TiO_2/active layer/MoO_3/Ag	~10^{-7}	-	~10^{12}	0.022	0 V, @ 350 nm	[40]
	ITO/TiO_2/active layer/Al	1.09×10^{-7}	113	1.9×10^{12}	0.5	−1 V, @ 550 nm	[41]
	ITO/TiO_2/active layer/MoO_3/Al	~10^{-9}	94.22	2.93×10^{13}	-	0 V, @ 690 nm	[10]
SnO_2	ITO/SnO_2/active layer/Al	2.89×10^{-4}	1430	2.29×10^{13}	6.97	−1 V, @ 625 nm	[42]
	ITO/SnO_2/active layer/MoO_3/Ag	~10^{-9}	~70	5.82×10^{12}	-	−1 V, @ 900 nm	[43]
Cs_2CO_3	ITO/PEDOT:PSS/active layer/Cs_2CO_3/Al	2.1×10^{-8}	>100	3×10^{12}	-	−3 V, @ 450 nm	[44]
LiF	ITO/PEDOT:PSS/active layer/LiF/Al	1.7×10^{-8}	-	-	0.004	−3 V, @ solar simulator	[45]
	ITO/PEDOT:PSS/active layer/LiF/Al	2.7×10^{-7} (−1 V)	5600	-	15.9	−40 V, @ 360 nm	[46]

[1] Graphene oxide functionalized with cysteine.

Table 2. Survey of the main characteristics of OPD-employing materials such as EBLs.

Materials	Device Structure	J_d (A cm^{-2})	*EQE* (%)	*D** (Jones)	*R* (A W^{-1})	Measurement Conditions	Ref
TFB	ITO/TFB/active layer/Al	2×10^{-8}	35	3.34×10^{12}	-	−5 V, @ 900 nm	[47]
	PEDOT:PSS/TFB/active layer/F8TBT/Al	4×10^{-9}	20	-	-	−0.5 V, @ 650 nm	[48]
	ITO/PEDOT:PSS/TFB/active layer/Al	8×10^{-9}	9	-	-	−0.5 V, @ 530 nm	[49]
	ITO/TFB/active layer/Al	3.4×10^{-11}	82	2.19×10^{13}	0.44	−5 V, @ 660 nm	[50]
TIPS pentacene	ITO/TIPS pentacene/active layer/Al	1×10^{-9}	52	1.44×10^{13}	-	−5 V, @ 610 nm	[51]
	ITO/TIPS pentacene/active layer/Al	9×10^{-10}	80	1.63×10^{13}	-	−5 V, @ 530 nm	[52]

Materials	Device Structure	J_d (A cm^{-2})	*EQE* (%)	*D** (Jones)	*R* (A W^{-1})	Measurement Conditions	Ref
PEDOT:PSS	ITO/PEDOT:PSS/active layer/Al	~10^{-3}	~250	~6×10^{11}	0.93	−10 V, @ 400 nm	[53]
	ITO/PEDOT:PSS/active layer/Al	2.68×10^{-6}	3.92×10^{5}	1.4×10^{11}	46.1	−25 V, @ 510 nm	[54]
	ITO/PEDOT:PSS/active layer/Al	~10^{-7}	2000	~10^{11}	~0.4	−50 V, @ 510 nm	[55]
	ITO/PEDOT:PSS+ GO–Cys [1]/active layer/Al	~10^{-10}	-	5.7×10^{12}	~0.15	−0.1 V, @ 620 nm	[56]
P3HT	ITO/PEIE/active layer/P3HT/MoO_3/Al	~1.5×10^{-9}	-	4.15×10^{12}	0.19	−0.1 V, @ 525 nm	[57]
	ITO/ZnO/active layer/P3HT/MoO_3/Al	1.1×10^{-8}	70	3.0×10^{12}	0.34	−3 V, @ 630 nm	[58]
	ITO/ZnO/active layer/P3HT/Ag	9×10^{-5}	-	6.59×10^{10}	0.214	−2 V, @ 630 nm	[59]
NiO_x	ITO/NiO_x/active layer/Yb/Ag	~10^{-8}	53.39	2.15×10^{12}	0.253	−1 V, @ 525 nm	[60]
	ITO/NiO_x/active layer/ZnO/Ag	3.4×10^{-8}	~52	1.2×10^{12}	0.25	−1 V, @ 600 nm	[61]
	ITO/ZnO:Al/active layer/NiO_x/Ag	1.13×10^{-7}	-	3.86×10^{12}	0.74	−5 V, @ 525 nm	[62]
	ITO/ZnO:Al/active layer/NiO_x/Ag	8.09×10^{-8}	81.93	2.15×10^{12}	0.35	−5 V, @ 525 nm	[63]
MoO_3	ITO/ZnO/active layer/MoO_3/Ag	5.9×10^{-9}	-	3.04×10^{12}	-	−3 V, @ 650 nm	[64]
	Al/ZnO/active layer/MoO_3/Ag/MoO_3	2.95×10^{-7}	31	4.49×10^{11}	0.14	−1.5 V, @ 650 nm	[65]
	Al/PCBM/active layer/MoO_3/Ag/MoO_3	1×10^{-9}	30	6×10^{12}	-	−1 V, @ 500 nm	[66]
V_2O_5	ITO/PEDOT:PSS + V_2O_5/active layer/V_2O_5/Al	5.53×10^{-3}	-	-	-	−1 V, @ (AM 1.5 G) solar simulator	[67]
CuSCN	ITO/CuSCN/active layer/LiF/Al	2.7×10^{-10}	57.2	4.4×10^{13}	0.4	−0.1 V, @ 870 nm	[68]
	ITO/CuSCN/active layer/BCP/Mg:Ag	1×10^{-8}	-	-	-	−1 V	[69]

(1) Organic interface materials in OPDs are expected to be used in future flexible wearable electronic devices, and further research is needed. However, it is necessary to develop new strategies to solve the problem that they are orthogonal to the solvent of the organic active layer according to the device structure.

(2) Inorganic materials have also been studied extensively in OPDs because of their high stability. However, the particle size of the material needs to be further reduced, and there are still relatively few p-type inorganic nanomaterials for EBLs. How to achieve the preparation of high-quality inorganic blocking layers at low temperature or even room temperature is the focus of our attention.

(3) Doping is one of the straightforward ways to modify the carrier blocking layer. The method of inorganic nanoparticle doping in organic interface materials is expected to be used in the future research of OPD because it combines the advantages of the two types of materials.

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