ITO-Free Flexible Indoor Organic Solar Cells using PEDOT: PSS Conductive Electrode Demonstrating PCE over 10% On a Polyethylene Naphthalate (PEN) Substrate

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Abstract—Solution-processed flexible organic photovoltaics (OPVs) have gained tremendous popularity worldwide during the last two decades. Indium tin oxide (ITO) is commonly used as a transparent conductive electrode in OPVs due to its large conductivity and good transmittance but it is fragile, rigid, and quite expensive. In this paper, flexible solar cells, with Poly (3, 4-ethylenedioxythiophene): poly(styrene-sulfonic acid) (PEDOT: PSS) transparent conductive electrodes are successfully demonstrated on a Polyethylene Naphthalate (PEN) substrate. Prior to PEDOT: PSS electrode, a buffer layer of polyvinyl alcohol (PVA) is added to PEN substrate. The OPV with PEDOT:PSS anode produced power conversion efficiency (PCE) average values of (12.0 % ± 0.1%) while the reference device with ITO exhibited PCE values of (8.0 % ± 0.0%) under a 500-lux-light emitting diode (LED) lamp. Besides PCE improvement, a flexible OPV device also exhibits superior flexibility over ITO as it can retain its PCE up to 85% even after 500 bending cycles in air while the PCE of ITO-based device declined to 15 % of its original value during a similar bending condition. To our knowledge, this excellent bending flexibility and PCE value are the highest recorded, under a 500-lux LED lamp on a PEN substrate.

Keywords—organic photovoltaics, ITO-free, solution-processed, flexibility, dim lighting conditions.

INTRODUCTION

Organic photovoltaic has become one of the promising sustainable economic solutions as a renewable energy source over the last few decades [1-9]. The solar cell has been widely used in modern applications like robotics, greenhouses, portable electronics, consumer products, and electronic textiles due to its enormous advantages of low-cost, high-throughput, easy fabrication processes for large area solar cells, lightweight and suitable for flexible substrates [10-17].

Apart from the use of solar cells in outdoor environments, many low-power applications such as sensors, chargers, actuators, and wireless sensor nodes (WSN) etc. in houses and offices are also operating under low light conditions [18-25]. The irradiation spectrum and intensity of the light sources used for indoor applications are different from that of under 1-sun [26-28]. Various artificial sources like a light emitting diode (LED), fluorescent lamp, halogen lamp and incandescent lamps are usually used for dim light applications [29-35]. Flexibility is one of the important factors for the commercialization of organic photovoltaic technology in consumer applications [36-37]. Flexible organic devices need a flexible transparent bottom electrode, which should exhibit high conductivity, better mechanical flexibility and transmittance [38-42]. Currently, Indium Tin Oxide (ITO) is a standard transparent bottom electrode widely used in photovoltaic devices but its high cost, low conductivity on plastic substrates, and poor bending capabilities hinder its use for flexible optoelectronic systems [43-47]. There are alternative transparent conductive electrodes such as carbon nanotubes, conductive polymers, silver nanowires, graphene and many others that have been used on different flexible substrates [48-55]. Single-walled carbon nanotube network has been used as transparent electrode with average transmittance and sheet resistance of 85% of 200 Ω/sq respectively [56-58]. Metal Nanowires such as Cu and Ag are also good alternatives of ITO substrate [59-60]. Yang et al. with PCE of 2.5 % using conventional geometry have fabricated AgNW on PET substrate. Their device presented transmittance of 80% with a comparatively lower sheet resistance of 30.8 Ω/sq [61]. In 2016, Wang et al., increased transmission of Cu NWs electrode...
to 90% by applying hydrogen plasma treatment at room temperature while sheet resistance declined to 19 Ω/sq [62]. Graphene is also an ideal contender for next-generation flexible electrodes due to its mechanical stability, high carrier mobility \(2 \times 10^5 \text{ cm}^2/\text{V}s\), low cost, large specific area \(2.6 \times 10^3 \text{ m}^2/\text{g}\) and better transmittance [63-66].

Conductive polymer like PEDOT: PSS is extensively used polymer for fabrication of solar cells. Different strategies including surface treatment by acids, spin-rinsing, and dry transfer of PEDOT: PSS, has been proposed to increase the electrical conductivity, and optical transmittance of flexible electrode employed by PEDOT: PSS [67-68]. Zhou et al. used a combination of PH500 and PEDOT (EL) as a conductive electrode. The structure of their device was PET/polymer anode/APFO-3: PCBM/LiF/Al, which demonstrated PCE of 2.2 % [69]. All the previously described transparent electrodes are investigated under 1-sun conditions while few issues for example high surface roughness of the electrodes, costly and complex fabrication methods, still exists for the use of these electrodes under low light conditions [70-74]. Recently, we reported ITO-free flexible organic solar cell employing ZnO/Ag/ZnO as the transparent conducting anode for indoor light applications with high optical transmittance up to 92% and very low sheet resistance of 4.8 Ω/sq. The inverted structure (PET/ZnO/Ag/ZnO/PEIE/P3HT: ICBA/MoO\textsubscript{x}/Ag).

In the current study, ITO free flexible organic solar cell is fabricated using PEDOT: PSS (PH1000) as transparent anode on a PEN substrate. The flexible device with P3HT: ICBA active layer showed higher power conversion efficiency (PCE) of ~11% under 500-lux-LED approximately 25% higher than the reference ITO based device, which exhibits 8% under similar conditions. Furthermore, it shows superior mechanical flexibility over ITO up to 500 bending cycles and can withstand 85% of its PCE at a bending radius of 7.99 mm without mechanical deformation.

**WORKING MECHANISM AND ANALYSIS**

The work function values of ITO and PEDOT: PSS electrodes with and without PEIE layer were calculated using Kelvin probe (KP) in ambient air. Highly oriented pyrolytic graphite (HOPG) and ITO\textsubscript{glass} were used as a reference which displayed WF values of \(5.14 \pm 0.058 \text{ eV}\) and \(4.87 \pm 0.027 \text{ eV}\) respectively. The schematic of the OPV device with an inverted structure is shown in Figure 1.

![Fig. 1. Schematic of various participating layers of organic photovoltaic (OPV) device.](image)

The WF value of the reference PEN-ITO was found to be \(4.82 \pm 0.074 \text{ eV}\) while the anode PEDOT: PSS (PH1000) on PEN substrate exhibited higher WF value of approximately \(5.02 \pm 0.043 \text{ eV}\). There was a huge difference between the WF values of anodes and electron affinity (EA) \(3.57\text{eV}\) of the acceptor ICBA to provide suitable energy-level alignment [23]. Therefore, to resolve this issue, a buffer layer of PEIE for surface modification was added on both anodes. The inclusion of this PEIE layer, resulted in an improved energy-level alignment of anodes with EA of the ICBA by decreasing the WF values of PEN-ITO and PEN_PEDOT: PSS films to \((4.05 \pm 0.039 \text{ eV})\) and \((4.12 \pm 0.054 \text{ eV})\) respectively. The optical transparency of the OPVs presented in Figure 2. Transmittance for PEN_PEDOT: PSS and PEN-ITO in visible spectral range \((390-700 \text{ nm})\) is found to be ~75 and ~85 % respectively.

![Fig. 2. Transmittance spectra of electrodes.](image)

The J-V curve of both devices under 1-sun and in the dark is depicted in Figure 3. Under 1-sun, PEN-ITO reference device exhibited PCE of \((2.3 \pm 0.3\%)\) with \(J_{sc} (6.9 \pm 0.8 \text{ mA/cm}^2)\) and \(V_{oc} (826 \pm 2 \text{ mV})\). Whereas, the device PEN_PEDOT: PSS showed PCE \((1.5 \pm 0.1\%)\) and comparatively smaller \(J_{sc} (6.3 \pm 0.5 \text{ mA/cm}^2)\). \(V_{oc}\) also drops to \((638 \pm 24 \text{ mV})\).
PEN_PEDOT: PSS device is significantly smaller than that of PEN_ITO device under 1-sun, which could be the reason of inferior PCE. $V_{oc}$ of fullerene based OPVs is generally determined by difference between HOMO and LUMO energy levels of donor and acceptor respectively. In this study, the difference in energy levels of PEN_ITO_PEIE (4.05 eV) and PEN_PEDOT:PSS_PEIE (4.12 eV) with ICBA (3.57 eV) is 0.48 and 0.57 eV respectively. Relative higher difference in energy level of PEN_PEDOT: PSS compared with that of PEN_ITO, results in smaller $V_{oc}$ followed by decline in PCE under 1-sun. Another reason for smaller $V_{oc}$ could be the higher sheet resistance ($R_{sH}$) of PEN_PEDOT: PSS because higher sheet resistance (132 Ω/cm$^2$) could induced the surface recombination instead of drift of charge carriers which results in higher leakage current and smaller $R_{sh}$ values.

Regarding $J_{sc}$, one of the reason for lower current density $J_{sc}$ in PEN_PEDOT: PSS could be the fairly higher $R_{sA}$ value of (88±12 Ω/cm$^2$) when compared with $R_{sA}$ value of PEN_ITO (42±3 Ω/cm$^2$). To validate, the shrinkage in $J_{sc}$ of PEN_PEDOT: PSS device, the external quantum efficiency (EQE) of both devices was measured by using incident photon-to-current efficiency (IPCE) system as represented by figure 4. EQE spectra of PEN_PEDOT: PSS was little lower than that of reference device which confirms the small difference in the $J_{sc}$ values of both devices under 1-sun. The cross-section view of the OPV device is shown in Figure 5.

CONCLUSION

In this study, solution-processed BHJ organic solar cells with flexible ITO and PEDOT: PSS (PH 1000) as bottom electrodes are fabricated on PEN substrate successfully. PEN_PEDOT: PSS device exhibited superior performance over PEN_ITO in terms of power conversion efficiency and mechanical durability up to 500 bending cycles under indoor light conditions at different bending curvatures. The optimized PCE values for both PEN_PEDOT: PSS and PEN_ITO devices are (11 % $\pm$ 0.1%) and (8% $\pm$ 0.1%) under LED respectively. On top of that, PEN_PEDOT:PSS OPV demonstrated excellent mechanical stability compared to PEN_ITO device as it retained its PCE and FF values up to ~85 and ~ 90% respectively even after 500 bending cycles. These results provide an effective pathway toward the use of low-cost ITO-free flexible optoelectronic devices for indoor light applications.

REFERENCES


