Improvement of photovoltaic performance and stability of AnE-PV:PCBM based organic solar cells using solution processed inverted geometry

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Organic bulk heterojunction and inverted type solar cells were fabricated using AnE-PVstat:PCBM blends as photoactive layers. The device was inverted using thin films of TiO2 as hole blocking and electron conducting layers. The power conversion efficiency (PCE) of organic bulk heterojunction solar cells increased from 1.70% to 2.59% when inverted device configuration was used instead of regular organic bulk heterojunction solar cell configuration. Stability studies reveal that the inverted type devices are more stable than the herein investigated regular organic bulk heterojunction solar cells fabricated using AnE-PVstat:PCBM blends as photoactive layers.

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Organic solar cells have received considerable attention. Flexibility, transparency, cost effectiveness, manufacturing potential in a continuous printing process, easy large area coating can be counted as the biggest advantages of organic solar cells [1–3]. Power conversion efficiencies (PCE) up to 8–10% are reported for organic solar cells employing semiconducting polymers or dyes [4–6]. These breakthroughs in the field prove that the organic solar cells are indeed developing. Recent theoretical studies reveal that the PCE values can be further improved [7–9]. At the same time silicon based hybrid solar cell, their photovoltaic parameters and charge separation - transport mechanisms have been attracted number of workers [10–13].

One of the reasons behind the focus on achieving highly efficient organic solar cells is to compete with the mature silicon technology which has already proven itself in the photovoltaic (PV) market. Although efficiency is an important issue, stability problems of organic solar cells still remain as a challenge to be overcome. Most of the commonly used organic solar cell device architecture consists of organic materials sandwiched between two metal electrodes. In this geometry, Aluminum is one of the mostly used top metal electrodes. It is known that both organic materials and aluminum are sensitive to oxygen and moisture and the devices suffer from rapid degradation under the ambient conditions [14]. Water molecule and oxygen are important degradation agent and there can be diffused different pathways into the active layer which start degradation. Water molecules diffuses through the aluminum electrode and adsorbed into this electrode. Adsorbed water molecules diffuses towards the ITO and leading to the degradation of all interfacial layer. And also under the illumination active layer of the organic solar cell enter into photochemical reaction with atmospheric gas or agent [15–17].

Encapsulation of the device after production is an approach to overcome the stability problems [18]. This impedes oxygen and...
water diffusion into the device and react active layer but not use recycle [17], So, sealed glass container [19] or high vacuum chamber techniques [20] used instead of encapsulation but devices degrada-
tion is not stopped.

Another approach is to invert the device geometry. With the inverted geometry, stability problems can be eliminated by using metal electrodes which are less sensitive to oxygen. Compact layer and thin film of TiO2, ZnO, Nb2O5, Cs2CO3, V2O5, CdS are mostly used between ITO and the top electrode in the inverted geometry [21–25] and this transparent electrode coted ITO act as cathode. Also porous and nanoporous TiO2 film used as charge separator for dye-sensitive solar cell [26,27].

In this study, organic photovoltaic cells were prepared in two different geometries one of which is conventional (ITO/PEDOT:PPS/Active Layer/Al) and the other is inverted (ITO/TiO2/Active Layer/ PEDOT:PPS:IPA/Ag or Au). PEDOT:PPS:IPA used as hole transport layer on top of the active layer such as PEDOT:PPS:IPA, MoO3, V2O5, VOx [28–31]. Anthracene-containing polymer AnE-PVstat and PCBM blend was used as the photoactive layer. Anthracene contain-
ing polymers have been studied by several groups, previously [32–35]. In Ref. [32] reported a maximum efficiency (PCE) of 2.13% for conventional geometry with anthracene containing polymers as active layer and stable cathode Cs/Ag cathode instead of only aluminum cathode. A comparative study about the stability of conventional and inverted geometry organic solar cell was reported [36] using conducted based on the same buffer/electrode combinations under highly damp conditions. In this work PCE for normal (ITO/MoOx/P3DTPT:PC70BM/TiO2/Al) and inverted (ITO/TiO2/ P3DTPT:PCBM70/MoO3/Al) architecture are reported 4.6% and 5%, respectively. In some work [37] both devices allow the high performance the PCE of the inverted geometry was 3.1% compared to a PCE value of 3.6% for the conventional geometry with LiF/Al electrode but the better fill factor (FF) and life time of inverted geometry compared.

In this work polymer solar cells with Anthracene-containing polymer AnE-PVstat and PCBM blend as active layer of into both conventional and inverted type solar cell were fabricated, charac-
terized and compared performances. The novelty of this work comes from the employment of Anthracene-containing polymer AnE-PVstat and PCB blend was used as active layer for the first time with ITO/TiO2/AnE-PVstat:PCBM/PEDOT:PPS:IPA/Ag: Au configuration in the literature, in which different type of higher work function metal electrode (Au and Ag). In the inverted geometry, AnE-PVstat:PCBM is sandwiched between TiO2 and PEDOT:PPS:Ag: Au whereas in the conventional geometry AnE-
PVstat:PCBM is sandwiched between ITO and Al. We performed Kelvin Probe Force Microscopy studies to investigate the contact potential differences between AnE-PVstat:PCBM layer and Al metal electrode and also PEDOT:PPS:IPA and Ag/Al metal electrode. We determine the contact potential by investigating the influence of the electrode material on the electrical performance of different geometries polymer solar cells. We observed that photovoltaic performance and life time of inverted type cells (ITO/TiO2/AnE-PVstat:PCBM/PEDOT:PPS:IPA/Ag or Au) higher than herein investig-
ted conventional type cells (ITO/PEDOT:PPS/AnE-PVstat:PCBM/ Al).

The synthesis of the polymer has been described elsewhere [38]. Chemical structure of AnE-PVstat is given in Fig. 2.

As substrates, ITO (indium tin oxide) coated glass sheets of 1.5 cm × 1.5 cm with sheet resistances smaller than 12 Ωcm−2, from Kintec Company, Honkong, were used. The ITO was patterned with etching with an acid mixture of HCl:HNO3:H2O (4:6: 0: 4: 5) for 30 min. The part of the substrate which forms the contact was covered with a scotch tape to prevent etching. The tape was removed after etching and the substrate was then cleaned using acetone and isopropanol (IPA) in an ultrasonic bath. The blends for the active layer with 1:4 wt ratio was prepared by 5 mg of AnE-PVstat and 20 mg of PCBM in 1 ml of chlorobenzene (CB).

For the conventional bulk heterojunction solar cells (see Fig. 2), poly(3,4-ethylenedioxythiophene)–poly(styrenesulfonate) (PEDOT:PPS) was spin coated at 2000 rpm on the glass–ITO substrate. The PEDOT:PPS layers were annealed in a furnace at 180 °C for 15 min. ITO used as anode with PEDOT:PPS layer for conventional geometry. Active layer of AnE-PVstat:PCBM was spin coated onto PEDOT:PPS coated ITO substrates at 800 rpm in a glove box. Finally, 120 nm Al was thermally evaporated in vacuum at a pressure 1 · 10−5 mbar as top contact used as cathode.

For the inverted devices (see Fig. 2), TiO2 solutions were prepared according to [39]. The films were coated at 8000 rpm and then baked in the oven for 30 min at 450 °C. ITO used as the cathode with TiO2. Active layers of AnE-PVstat:PCBM were spin coated at 800 rpm onto TiO2 coated ITO substrates in a glove box. PEDOT:PPS was diluted with IPA in 1:20 volume ratio and spin coated onto the active layer at 800 rpm for 30 s. Finally, either 120 nm of gold (Au) or silver (Ag) were thermally evaporated in vacuum at a pressure 1·10−5 mbar as top contacts.

Current-voltage (I–V) characteristics of the photovoltaic de-
vice were measured using Keithley 6484D in dark and under illu-
mination with Solar Light XPS 150 solar simulator (AM 1.5–100 mWcm−2) in a glove box. Incident Photon to Current Ef-


microscopic view of AnE-PVstat:PCBM films on different substrates (Fig. 1f).

The photovoltaic characterizations and stability measurements of both conventional and inverted type devices were performed at room temperature in a glove box (oxygen level < 10 ppm). Devices were not encapsulated. The current voltage characteristics of the investigated devices are shown in Fig. 2(a–d).

Conventional organic solar cell exhibited a short circuit current density ($J_{sc}$) of 5.2 mA/cm$^2$ and an open circuit voltage ($V_{oc}$) of 840 mV, a fill factor (FF) of 0.39 was calculated which led to a PCE of 1.7%. Inverted type devices employing Au as the top metal electrode exhibited a $J_{sc}$ of 8.71 mA/cm$^2$, a $V_{oc}$ of 595 mV, a FF of 0.41 was...
calculated whereas a $J_{sc}$ of 9.71 mA/cm$^2$, a $V_{oc}$ of 640 mV was achieved and a FF of 0.46 was calculated for the inverted type devices with Ag as the top metal electrodes which led to PCEs of 2.39% and 2.56%, respectively.

The overall PV performance of the devices depends on the configuration and also the top metal electrodes which is attributed to the changes in the energy level alignments. Ohmic contacts between the photoactive layer and the metal electrodes may lead to higher $J_{sc}$ and $V_{oc}$ due to better charge extraction. On the other hand, Ag is realized to be the most suitable top electrode, since its slow oxidation shifts its work function from about 4.3 eV to about 5 eV, favoring hole extraction. It has no absorption in the visible range contrary to the evaporated Au layer which has a slight absorption in the visible and a higher reflectivity [41,42].

On the other hand, the $V_{oc}$ of inverted type devices are affected by the work functions of the layers adjacent to the donor and the acceptor [43]. In the inverted geometry, AnE-PVstat:PCBM is sandwiched between TiO$_2$ and PEDOT:PSS/Au whereas in the conventional geometry AnE-PVstat:PCBM is sandwiched between ITO and Al. The difference between the $V_{oc}$’s is attributed to the difference of the contact potential between the metals where the donor-acceptor blend is in contact.

We performed Kelvin Probe Force Microscopy studies to investigate the contact potential differences between organic layer (AnE-PVstat:PCBM) and Al metal electrode and also PEDOT:PSS:IPA and Au metal electrode. Fig. 3 shows the magnitude versus contact potential difference curves. A contact potential difference of 1.612 eV was calculated for organic layer and Al metal electrode whereas 0.921 eV contact potential difference was achieved for PEDOT:PSS/Au metal surface. Since the lower contact potential difference is favorable for charge extraction, the better performance of inverted solar cells is attributed to the lower contact potential difference between the organic layer and the metal electrode.

Stability measurements of two configuration cells were examined in glove box for 40 h and shown in Fig. 4. As shown in Fig. 4d the power conversion efficiency of conventional cell was degraded quickly comparison with inverted type cell. The inverted cell preserved about 50% of PCE% and short circuit current after 40 h which is much better than that of the conventional device.

Fig. 5 shows both the IPCE results of the investigated inverted and conventional organic solar cells (left scale) and also the absorption spectra of the thin films comprising the both types of organic solar cells.

![Fig. 2. Current voltage characteristics of (a) ITO/PEDOT:PSS/Active Layer/Al, (b) ITO/TiO$_2$/Active Layer/PEDOT:PSS/Ag, (c) ITO/TiO$_2$/Active Layer/PEDOT:PSS/Au, (d) Photovoltaic performance the same devices in the linear regime and (e) Chemical structure of AnE-PVstat. and schematic description of herein investigated conventional BHJ and inverted type organic solar cells.](image-url)
devices (right scale). By means of IPCE measurements, the contribution of the species present in the device to the total photocurrent generation can be investigated. UV–vis absorption spectra of TiO$_2$ thin film is shown in Fig. 5b. The thin film is high transparency in the visible region and absorption edge at about 330 nm. The optical band gap of TiO$_2$ thin film was determined by Tauc relation for direct transition $^{[44,45]}$

$$a^2 = \frac{A(h\nu - E_g)}{(h\nu)^2}$$  \hspace{1cm} (1)

where $a$ is absorption coefficient, $E_g$ is the optical band gap, $\nu$ is the frequency of incident photons, $h$ is the Planck’s constant, and $A$ is a constant called the band tailing parameter. Tauc plot of $(a\nu)^2$ versus $h\nu$ photon energy are shown in Fig. 5c to determine of energy band gap of TiO$_2$ films. The intercept of the extrapolated linear part of the curve with $h\nu$ axis gives the energy band gap. The optical energy band gap of TiO$_2$ thin film was determined to be about 3.72 eV. The absorption spectra of the AnE-PVstat:PCBM blend covers the spectral range over the wavelengths ca. 250–700 nm. The IPCE spectrum of the inverted type device spans the spectral range over the wavelengths 300 and 700 nm and matches very well with the absorption of the AnE-PVstat:PCBM blend. It was not possible to measure the IPCE spectrum below 300 nm due to the
limitations of the measurement set-up. There is a slight red shift between the IPCE of the inverted device and the absorption spectrum of the TiO2 film which is attributed to the intimate contact of TiO2 with the organic layer [46]. A slight blue shift around 600 and 700 nm was observed for the IPCE of the conventional organic solar cell and the absorption spectrum of the AnE-PVstat:PCBM blend which is attributed to the PEDOT:PSS layer that has an absorption in the UV region.

In this study, we have compared two different types of devices in the configuration of conventional type ITO/PEDOT:PSS:AnE-PVstat:PCBM/Al and inverted type ITO/TiO2/AnE-PVstat:PCBM/PEDOT:PSS:IPA/Ag. The originality of this study comes from the ITO/TiO2/AnE-PVstat:PCBM/PEDOT:PSS:IPA/Ag:Al inverted configuration was used for the first time in the literature with AnE-PVstat:PCBM blend as active layer. Previously in the literature, AnE-PVstat:PCBM blend based polymer solar cells have been studied as ITO/PEDOT:PSS:AnE-PVstat:PCBM/Al [32] and ITO/TiO2/AnE-PVstat:PCBM/V2O5/Al configuration [33]. Also power conversion efficiencies are determined as 2.13% and 3.26%, respectively with encapsulated devices under different condition. In this work, power conversion efficiencies of 1.70% for the conventional and 2.59% for the inverted type devices have been reported under the same experimental conditions and same work for the first time in the literature. The inverted device preserved about 50% of its PCE and short circuit current even after 40 h which was much better than that of the conventional device in glove box and unencapsulated form. Also, the better performance of the inverted devices is attributed to the more stable top electrodes which is Ag as compared to that of conventional cell which is Al that can be easily oxidized in air. In the inverted configuration, the TiO2 films prepared by sol–gel processed technique showed high transparency and less phase separation of the active layer on the TiO2 layer as compared to that of the PEDOT:PSS layer improved the photovoltaic performance of the inverted type devices especially increased electron transport as compared to the herein investigated conventional organic solar cells. Also, we determined the contact potential differences between active layer and Al metal electrode as 1.612 eV and also PEDOT:PSS:IPA and Au metal electrode as 0.921 eV for conventional and inverted geometry, respectively by Kelvin probe Force Microscopy technique to explain the differences of Voc. The higher performance of inverted solar cells is attributed to the lower contact potential difference between the active layer and the metal electrode because of the lower contact potential difference is suitable for charge extraction.

Fig. 5. IPCE spectra of (1) Inverted cell (ITO/TiO2/AnE-PVstat:PCBM/PEDOT:PSS:Ag) (2) Conventional cell (ITO/PEDOT:PSS:AnE-PVstat:PCBM/Al) (left scale) and absorption spectra of (a) AnE-PVstat:PCBM, (b) TiO2 thin films (right scale) (c) Tauc plot for TiO2 thin films.

References


