Effect of boric acid doped PEDOT:PSS layer on the performance of P3HT:PCBM based organic solar cells

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A B S T R A C T

In this study, we fabricated PEDOT:PSS film with different concentrations 0–5 mg/ml of boric acid (H₃BO₃) doped PEDOT:PSS film as hole collector layer. Undoped and boric acid doped PEDOT:PSS films are prepared with spin coating technique and characterized by XRD, UV, AFM, FTIR and electrical conductivity measurements. We fabricated polymer solar cells in the form of ITO/PEDOT:PSS:H₃BO₃/P3HT:PCBM/Al. Results show that the open-circuit voltage (Voc) and the fill factor (FF) increased by introducing H₃BO₃ as dopant into the PEDOT:PSS layer due to an increase in the work function of PEDOT:PSS layer and improvement of surface roughness, respectively. The solar cells without H₃BO₃ showed a power conversion efficiency PCE of 1.79% whereas the cells with H₃BO₃ concentration of 1.25 mg/ml in PEDOT:PSS, showed a higher performance resulting in a PCE of 2.14% under AM 1.5G illumination.

1. Introduction

In recent years, there is an increasing level of interest in organic-based solar cells as an alternative energy source. Organic solar cell/photovoltaic (OPV) devices fabricated from the blends of poly(3-(hexylthiophene) (P3HT) and [6,6]-phenyl C61-butyric acid methyl ester (PCBM) are the most widely studied bulk heterojunction systems because of their relatively good photovoltaic (PV) properties. Although the P3HT:PCBM devices exhibit excellent PV properties compared to other bulk heterojunction OPV devices, their power conversion efficiency is still too low compared to that of the conventional silicon PV cells [1]. Annealing by a laser [2], light harvesting by a use of a low band gap molecule [3], incorporation of nanocrystals [4] or the use of crystallizable solvent [5] have been foreseen as methods to improve the PV efficiency of P3HT:PCBM based organic solar cells. The conventional polymer:fullerene solar cells include poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) as hole collector buffer layer because of its high work function, transparency in the visible range, high conductivity, mechanical flexibility, and easy processing ability which is inserted between transparent electrode, typically ITO and light-absorbing organic layer [6–11]. PEDOT:PSS is thought to be beneficial for device performance in a number of ways. It not only decreases the surface roughness of indium-tin oxide (ITO) transparent electrodes, reduces the short cuts in the device, but also improves the selectivity of the anode due to the higher work function relative to ITO, enhancing electron blocking and therefore maintaining higher open-circuit voltage. There are many approaches which demonstrated that properties such as the electrical conductivity and the work function of PEDOT: PSS can be changed by the addition of additives (e.g. WO₃, MoO₃, V₂O₅, NiO₂, Fe₂O₃ NPs, ethylene glycol (EG) and multi-walled carbon nanotubes (MWCNT)) which in turn affects the device performance significantly [7–13]. In these studies, the efficiency of the organic solar cells increased with the addition ethylene glycol (10%) [6], NiO₂ (5:1 ratio) [7], Fe₂O₃ NPs (0.7 wt%) [14], and MWCNT (4%) [15] in PEDOT:PSS which used as hole collector layer, 29%, 10%, 32%, 23%, respectively, also observed that increases in FFs. However, these additives are more expensive and requires difficult and long production processes [16]. The use of boric acid is an alternative way for boron doping. Boric acid is one of the most important boron compounds and has strategic and industrial importance. It is a low-cost material and can be easily fabricated [17]. It is mostly used in industrial applications, such as glass, ceramics, textiles, detergents, and nuclear power, as well as in the agricultural, medical, pharmaceutical and electronics related sectors [18]. However, boric acid has not been widely used in solar cell studies to best of our knowledge. In one of the studies on boric acid, Ruan et al., examined the photoelectrochemical properties of highly ordered titanium dioxide nanotube-array
photoanodes, fabricated by anodization of titanium in a nitric acid/hydrofluoric acid electrolyte, with and without the addition of boric acid. They reported the presence of boric acid in the electrolyte resulted in a TiO₂ nanotube-array possessing significantly greater photoelectrochemical properties, under both UV–vis spectrum illumination [17]. Rahman et al., investigated the effect of boric acid composition on the morphology, thickness, elemental composition, optical absorption, structure, photoluminescence of ZnO nanotubes and the performance of the DSSC utilizing the ZnO samples. They reported that the diameter and thickness of ZnO nanotubes decreased with the increasing composition of boric acid. The DSSC utilizing ZnO nanotubes prepared at 2 wt% boric acid demonstrated the highest $J_{SC}$ and $η$ of 2.67 mA/cm² and 0.29%, respectively [19]. The use of boric acid as a dopant in titanium dioxide nanotubes based dye sensitized solar cells have been investigated by Subramanian et al., They introduced boron into the interstitial sites of TiO₂ lattice and contributed to the shift of conduction band. The boron-doped TiO₂ nanotube arrays showed an enhanced performance compare to those of undoped TiO₂ nanotubes [20].

In this work, we introduced a new boron doped PEDOT:PSS layer to improve the PV performance of P3HT:PCBM based organic solar cells. We have shown that boron can be used as a dopant to the PEDOT:PSS films for organic solar cells as hole collector layer. It has been shown that the devices employing boron showed a better FF and efficiency.

2. Experimental

As substrates, 1.5 cm × 1.5 cm ITO covered glass sheets with a sheet resistance <15 Ω/cm, from KINTEC company, were used as substrates. The ITO was patterned by etching with an acid mixture of HCl:HNO₃:H₂O (4.5 ml:1 ml:3 ml) for 30 min. The sheet resistance of the ITO substrate was 13 Ω cm. The part of the substrate which forms the contact is covered with a Scotch tape to prevent etching. The tape was removed after etching and the substrate was then cleaned using acetone and isopropanol in an ultrasonic bath.

The blends of P3HT:PCBM were prepared by dissolving 12 mg of P3HT and 6.5 mg PCBM in 1 ml chlorobenzene. For the preparation of the PEDOT:PSS:H₃BO₃ buffer layer, various ratios of H₃BO₃ (0–5 mg/ml) was added in PEDOT:PSS solution. All the prepared solutions were stirred in dark for 24 h.

For the preparation of the solar cells, PEDOT:PSS:H₃BO₃ was spin coated on ITO substrates at 2000 rpm for 60 s and annealed at 150 °C for 4 min under ambient conditions. The film thickness was determined using Veeco Dektak profilometer. The film thickness did not change very much with boric acid doping. The active layer of P3HT:PCBM was spin cast onto PEDOT:PSS:H₃BO₃ film at 800 rpm for 60 s in glove box N₂ atmosphere. Finally aluminum (Al) contact metal was deposited by thermal evaporation on active layer about 100 nm. The final device structure was in the form of ITO/PEDOT:PSS:H₃BO₃/P3HT:PCBM/Al (see Fig. 1). A reference device was fabricated without H₃BO₃ addition to check whether H₃BO₃ had an effect on the PV performance of P3HT:PCBM based devices. Reference device structure was in the form of ITO/PEDOT:PSS:H₃BO₃/Al.

The current–voltage (I–V) characteristics were measured with a Keithley 2400 source meter under simulated 100 mW/cm² (AM 1.5G) irradiation. Optical characterizations of P3HT:PCBM active layer, undoped and boric acid doped PEDOT:PSS films were determined in the wavelength range of 300–1100 nm using PerkinElmer Lambda2 UV–vis spectrophotometer. AFM measurements were performed using ezAFM Atomic Force Microscope system for characterization of the film morphology. X-ray diffraction studies were carried out using the Panalytical Diffractometer with CuKα radiation of 1.5418 Å XRD system. The resistivity of undoped and boric acid doped PEDOT:PSS films coated on glass was measured by two probe method for performed to compare the electrical properties of the undoped and doped films. Electrical characterization of the resistance of the films was obtained using Keithley 2400 sourcemeter. For Fourier transfer infrared spectrum (FTIR) of undoped and boric acid doped PEDOT:PSS solution were recorded by a PerkinElmer spectrometer-ATR mode.

Table 1

<table>
<thead>
<tr>
<th>Boric acid concentration in PEDOT:PSS (mg/ml)</th>
<th>Film thickness (nm)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{SC}$ (mA/cm²)</th>
<th>FF%</th>
<th>PCE%</th>
<th>$R_{sh}$ (kΩ)</th>
<th>$R_{op}$ (kΩ)</th>
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<td>0</td>
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<td>56.33</td>
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<td>1.83</td>
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<td>8.000</td>
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<td>5.00</td>
<td>56.23</td>
<td>0.640</td>
<td>5.10</td>
<td>39.0</td>
<td>1.27</td>
<td>1.400</td>
<td>9.803</td>
</tr>
</tbody>
</table>

Fig. 1. Schematic of the device architecture with PEDOT:PSS:H₃BO₃ buffer layer.

Fig. 2. XRD diffraction pattern of (a) PEDOT:PSS, (b) 1.25 mg/ml boric acid doped PEDOT:PSS, (c) 5.00 mg/ml boric acid doped PEDOT:PSS, (d) ITO substrate.
3. Results and discussion

Fig. 2 shows the XRD pattern of undoped, boric acid doped PEDOT:PSS films and bare ITO substrate. A weak and broad peak was observed between $2\theta = 25–26^\circ$ which belongs to (0 2 0) plane of PEDOT:PSS polymer [15,21,22]. The broadness of the peaks reflects the semi-crystalline nature of PEDOT:PSS. This $2\theta$ value corresponds to the d-spacing of approximately 3.56 Å, which can be attributed to the inter-chain distance of PEDOT [23]. When closely examined, the broad peaks of the undoped and doped PEDOT:PSS are slightly shifted with respect to one another. The peak positions of PEDOT:PSS, PEDOT: PSS (1.25 mg/ml) and PEDOT:PSS (5 mg/ml) have been extracted using a Gaussian peak fitting after a linear background subtraction. This yields the $2\theta$ values of the peaks as 25.04, 25.28, 25.47, corresponding to the d-spacing values of 3.56, 3.53 and 3.50 Å, respectively. The lowest D-spacing is obtained from the films of PEDOT:PSS (5 mg/ml), which indicates the closest packing of the PEDOT chains.

As also can be seen from Fig. 2, the ITO peak at $2\theta = 30^\circ$ disappears for the boric acid doped PEDOT:PSS films that is attributed to the homogeneous film formation on the ITO substrate which is in accordance with the AFM studies.

Atomic force microscopy images of undoped and boric acid doped PEDOT:PSS films are shown in Fig. 3. The peak to valley height values were 13.40, 11.61 and 8.68 for undoped PEDOT:PSS, PEDOT:PSS (1.25 mg/ml boric acid), PEDOT:PSS (5 mg/ml boric acid)/PEDOT:PSS films, respectively whereas the RMS values were 1.37 nm, 1.36 nm, 1.15 nm, respectively. By the help of the AFM images, it has been observed that the additional H$_3$BO$_3$ into the PEDOT:PSS layer led to a smoother surface and therefore a better morphology. A better film forming property led to an improved the fill factor of the solar cells.

The results of resistivity of undoped and doped PEDOT:PSS films are shown in Fig. 4. They demonstrate the reduction of sheet resistance by 5–20% compared to undoped PEDOT:PSS film with increased boric acid concentration up to 1.75 mg/ml. The amount of doping concentration is increased above 1.75 mg/ml increasing resistance with the B—O peak observed in FTIR spectra shown in Fig. 5.

Fig. 5 shows the FTIR spectra of undoped and boric acid doped PEDOT:PSS at room temperature. On the PEDOT:PSS films FTIR spectra can clearly see one peak at about 1400 cm$^{-1}$ caused by asymmetric B—O stretching [24] with boric acid added after 1.25 mg/ml boric acid doping concentration. We observed that decreased resistivity with boric acid doping up to 1.75 mg/ml concentration than increased resistance with increasing doping concentration.
additional H$_3$BO$_3$ on the performance of the organic solar cells. The calculated cell parameters in order to determine the effect of boric acid on the characteristics of photovoltaic cells are given in Table 1.

The reference device where no H$_3$BO$_3$ is employed in the device exhibited a short-circuit current density ($J_{sc}$) of 8.75 mA/cm$^2$ and an open-circuit voltage ($V_{oc}$) of 535 mV. A fill factor of 0.39 was calculated which led to a power conversion efficiency of 1.79%. For the solar cells employing 1.25 mg/ml of H$_3$BO$_3$ in PEDOT:PSS layer exhibited a $J_{sc}$ of 7.57 mA/cm$^2$ and a $V_{oc}$ of 602 mV. A fill factor of 0.46 was calculated which led to a PCE of 2.14%. It has been observed that at a specific concentration of H$_3$BO$_3$ (1.25 mg/ml) the solar cells showed the best PV performance. From photovoltaic parameters point of view, the main effect of the additional H$_3$BO$_3$ was to increase the $V_{oc}$ and the fill factor. The increase in the $V_{oc}$ is explained in terms of the work function difference (Fig. 11) whereas the increase in the fill factor is attributed to the better morphology (Fig. 3) achieved by an additional H$_3$BO$_3$ into the PEDOT:PSS layer.

The power conversion efficiency of an organic solar cell is calculated using the following formula:

$$\eta = \frac{I_{oc}V_{oc}FF}{P_{in}}$$

where $I_{sc}$ is the short-circuit current, $V_{oc}$ is the open-circuit voltage and FF is the fill factor. The open-circuit voltage is a sensitive function of energy levels of the used materials as well as their interfaces [25]. It has been previously demonstrated that interfacial effects at the metal/organic semiconductor interface (such as oxide formation) change the work function of the electrodes and influence the open-circuit voltage [26,27] which has been also supported by KPFM results in this study.

In the ideal, loss free contacts, the short-circuit current, $I_{sc}$, is determined by the product of the photoinduced charge carrier density and the charge carrier mobility within the organic semiconductors:

$$I_{sc} = ne\mu E$$

where $n$ is the density of charge carriers, $e$ is the elementary charge, $\mu$ is the mobility, and $E$ is the electric field. Assuming the 100% efficiency for the photoinduced charge generation in a bulk heterojunction mixture, $n$ is the number of absorbed photons per unit volume. For a given absorption profile of a given material, the bottleneck is the mobility of charge carriers. Mobility is not a material parameter but a device parameter. It is sensitive to the nanoscale morphology of the organic semiconductor thin film [28–33]. In a van der Waals crystal, the final nanomorphology depends on film preparation. Parameters such as solvent type, the solvent evaporation (crystallization) time, the temperature of the

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**Fig. 4.** Variation of resistivity of undoped PEDOT:PSS and PEDOT:PSS films with different concentrations of boric acid.

**Fig. 5.** FTIR spectra of undoped PEDOT:PSS and PEDOT:PSS with different concentrations of boric acid.

**Fig. 6.** $i$–$V$ curves of the investigated devices in linear scale.

**Fig. 7.** Absorption of PEDOT:PSS/P3HT:PCBM with (a) undoped, (b) 1.25 mg/ml doped PEDOT:PSS, (c) 5 mg/ml doped PEDOT:PSS.
substrate, and/or the deposition method can change the nanomorphology [34,35].

In this study it has been observed that the blend film of PEDOT:PSS and boric acid improves the interfacial effects between the ITO and PEDOT:PSS as compared to bare PEDOT:PSS films and therefore improves the open-circuit voltage of the herein investigated devices however, the prize paid is the complicated nanomorphology of the blend that is difficult to optimize and control which results in a lower short-circuit current density. Since the efficiency is directly proportional to the product of \( V_{oc} \) and \( I_{sc} \), although the \( I_{sc} \) of the devices involving boric acid decreased non-dramatically, the overall efficiency increased upon additional boric acid. What matters for the performance of an organic solar cell is the overall power conversion efficiency.

Also, as it is seen in Fig. 4 the reduction in the resistivity of the PEDOT:PSS films with boric acid doping confirms the improvement in the shunt resistance of the cells.

An increase of \( R_{sh} \) and a decrease of \( R_s \) or both can cause an increase in FF for photovoltaic devices. The \( R_{sh} \) values for cells which contained boric acid in PEDOT:PSS increased from 3 kΩ to 11.47 kΩ. The increase in the \( R_{sh} \) led to a higher FF and PCE% upon additional boric acid.

Fig. 7 shows the absorption graph of PEDOT:PSS/P3HT:PCBM layers with different concentration of H\(_3\)BO\(_3\) in PEDOT:PSS. It has been seen that the additional H\(_3\)BO\(_3\) in PEDOT:PSS leads to a small red shift in the absorption. It is well known that, the PEDOT:PSS layer is almost transparent in the visible region of the solar spectrum. The major role of the conducting PEDOT:PSS layer in organic solar cells is to modify and increase the work function of

Fig. 8. The external quantum efficiency of organic solar cells with (1) undoped PEDOT:PSS, (2) 1.25 mg/ml doped PEDOT:PSS, (3) 5 mg/ml doped PEDOT:PSS.

Fig. 9. The relationship between the photovoltaic parameters of the solar cell and boric acid concentration.
ITO electrode, for facilitating charge transfer between ITO and organic active layer. In this study, the transparency of the PEDOT:PSS layer in the visible portion of the solar spectrum is diminished upon addition of H$_3$BO$_3$ which in turn leads to a decrease in the short-circuit current density.

Fig. 8 shows the external quantum efficiency (EQE) of OSCs measurement. We compared the curve of the external quantum efficiency (EQE) between PEDOT:PSS and PEDOT:PSS: H$_3$BO$_3$ (different concentration) device. The spectrum span between 300 and 750 nm and is in accordance with the photovoltaic data.

Fig. 9 shows the H$_3$BO$_3$ concentration dependence on the principal cell parameters of the device such as the open-circuit voltage ($V_{oc}$), the short-circuit current density ($J_{sc}$), FF and power conversion efficiency. It is clear that the doping H$_3$BO$_3$ has an influence on all the device parameters. With increasing H$_3$BO$_3$ concentration the device fill factor and open-circuit voltage increased despite the decreased the short-circuit current density. The maximum PCE and FF were obtained at the 1.25 mg/ml concentration ratio of H$_3$BO$_3$.

Fig. 10 shows lifetime of OPV cell prepared with undoped and 1.25 mg/ml boric acid doped PEDOT:PSS film was investigated in a glove box. At the end of 600 h it has been observed that boric acid doped solar cells still have a good stability.

Energy level alignment is crucial for the performance of organic solar cells and depends on the work function of the individual electrodes [36,37]. In order to understand the influence of H$_3$BO$_3$ blending in PEDOT:PSS on the contact potential difference, we used scanning Kelvin probe microscopy (SKPM), Local contact potential difference (CPD) between doped and undoped PEDOT:PSS films formed on ITO substrates and AFM conductive tip (TiN) was investigated. The local contact potential difference between TiN tip and bare-ITO was measured as $–0.281$ V and it was obtained as $–0.0375$ V for undoped PEDOT:PSS whereas $0.12$ V and $0.124$ V were obtained for 1.25 mg/ml and 5 mg/ml doped PEDOT:PSS, respectively. The values obtained from KPFM measurements clarified that the work function of the ITO surface increased as a result of the doping of PEDOT:PSS with boric acid. One of the major roles of the PEDOT:PSS layer is to increase the work function of the ITO to facilitate the charge transfer from the organic layer to the ITO (see Fig. 11). The increase in the work function leads to an increase in the $V_{oc}$. The increase in the $V_{oc}$ is attributed to the higher work function of 1.25 mg/ml boric acid doped PEDOT:PSS.

4. Conclusion

We have investigated the influence of addition of H$_3$BO$_3$ in the PEDOT:PSS solution and its consequence on the performance of P3HT:PCBM based photovoltaic devices. Results show that the power conversion efficiency was significantly improved by inserting H$_3$BO$_3$ in the PEDOT:PSS layer using as hole collector layer for OPV. An increase in power conversion efficiency and FF approximately 20% and 23% were obtained between the bare device and optimized device due to the addition of H$_3$BO$_3$. The main effect of H$_3$BO$_3$ in the device structure was the increase in $V_{oc}$ and FF. With the help of the Kelvin probe microscopy studies the increase in the $V_{oc}$ is attributed to an increase in the work function of ITO upon additional boric acid. The increase in the fill factor is attributed to the better morphology of the herein investigated films achieved by an additional boric acid in PEDOT:PSS layer.

Acknowledgement

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References

photoelectrochemical response

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