

Hendrik C.Swart¹, Odireleng M. Ntwaeaborwa^{1*}, Pontsho S. Mbule^{2*}, Mokhotjwa S. Dhlamini² and Bakang B.Mothudi²

1. Department of Physics, University of the Free State, Bloemfontein 339, 9300, South Africa

2. Department of Physics, University of South Africa, Pretoria 392, 0003, South Africa

Abstract: Today, BHJ (bulk heterojunction) OSCs (organic solar cells) dominate modern age research in renewable solar energy. In recent developments, the ultimate goal is to improve the general performance of the BHJ-OSCs to enable them to compete on an equal footing basis with conventional silicon photovoltaic cells. In this presentation, we review the fundamental parameters that have been reported to improve the general performance of the BHJ-OSC devices. These parameters include, among other things, the use of ZnO nanoparticles ETL (electron transport layer) inserted between the top electrode and the photoactive layer, annealing procedure and device geometry. The BHJ-OSC devices constructed in this study comprised of successive (bottom up) layers of (3,4ethylenedioxythiophene):poly (styrenesulfonate) or PEDOT:PSS, a blend of poly (3-hexylthiophene) or P3HT and [6,6]-phenyl butyric acid methyl ester or PCBM, zinc oxide or ZnO nanoparticles and aluminum (Al) metal top electrode. These layers were deposited on ITO (indium tin oxide) coated glass substrates. The device construction was also inverted (top down) in order to evaluate the effect of inversion on the power conversion efficiency and the general performance of the devices. The devices were annealed at 155 °C either before (pre-annealed) or after (post-annealed) the deposition of the Al top electrode. Post-annealed devices showed improved PV (photovoltaic) characteristics when compared to pre-annealed devices. Furthermore, we discuss the performance of inverted geometry in comparison to ZnO nanoparticles and nanoflakes as buffer layers.

Key words: P3HT:PCBM, solar cells, ZnO, buffer layer.

1. Introduction

1.1 Fundamental Aspects of Organic Solar Cells

OSCs (organic solar cells) research has developed during the past 30 years, especially in the last decade, it has attracted scientific and economic interest triggered by a rapid increase in power conversion efficiencies [1]. Many organic solar cell devices use polymers as integral part of their construction. For example, conjugated polymers often play a role of electron donors and hole conductors in the active layer of organic solar cell devices. However, basic organic solar cell research and device development still have a long way to go to be able to compete on an equal footing basis with conventional inorganic solar cells. The efficiency of inorganic solar cells can top 20% and the development of inorganic thin layer and multi-junction devices will likely lead to even better performance [2].

Further steps to improve the power conversion efficiencies of organic solar cells are made by solution-processed polythiophene: fullerene and efficiencies between 6% and 8% by use of novel materials as well as additives optimizing the phase separation have been obtained [3-5]. The research and development of organic solar cells focuses mostly on two concepts: either soluble blends of conjugates polymers with fullerene derivatives or the combination

Corresponding authors: 1 Odireleng Ntwaeaborwa, professor, research field: nanomaterials for PV devices. E-mail: ntwaeab@ufs.ac.za. 2 Pontsho Mbule, doctor, research field: Nanomaterials for PV devices. E-mail: mbuleps@unisa.ac.za.

of small molecular donor and acceptor materials, a material combination which can be thermally evaporated [6, 7]. The first attempt to create organic solar cells was made by sandwiching a single layer of organic material between two dissimilar metal electrodes of different work function. In these cells, the photovoltaic properties strongly depend on the nature of the electrodes [7, 8]. These are called single layer organic photovoltaic cells and are the simplest form among various organic photovoltaic cells. By the absorption of light, strongly coulomb bound electron-hole pairs are created and their binding energy in organic semiconductors inhibiting much lower effective dielectric constants is usually between 0.5 and 1 eV. The excitons have to be separated to finally generate a photocurrent. In order to overcome the exciton binding energy, one either has to rely on the thermal energy or dissociate the exciton at the contacts [9]. Unfortunately, both processes have a rather low efficiency under the operating conditions of solar cells and the temperature is not high enough, so the sample thickness is much higher than the exciton diffusion length. Not all the excitons are dissociated and as the consequence, the single layer organic solar cells had power conversion efficiencies far below 1%.

The second organic semiconductor layer was introduced and the first organic bilayer solar cell was reported by Tang in the mid-1980s [10]. In bilayer devices, the light is usually absorbed in the donor material and the photo generated excitons diffuse within the donor towards the planar interface to the second material, the acceptor, which is usually chosen to be strongly electronegative. The acceptor material provides the energy needed for the excitons to be separated, as the electrons can go to a state of much lower energy within the acceptor. In combining electron donating (p-type) and electron accepting (n-type) materials in the active layer of a solar cell, a BHJ (bulk heterojunction) was described by Yu et al in 1995 [11]. They reported that the bulk heterojunction significantly improved organic solar cells power

conversion efficiencies by increasing the excitons access to the donor/acceptor interfaces. BHJ is presently the most widely studied photoactive layer and the name bulk-heterojunction solar cell has been chosen because the interface (heterojunction) between both components is all over the bulk, in contrast to the classical (bilayer) heterojunction. Polymer-fullerene solar cells were among the first to utilize this bulk-heterojunction principle and have an advantage because of their much larger interface between the donor and acceptor [12].

1.2 BHJ-OSCs Device Geometry

Since the introduction of the organic photovoltaics, several structures and materials have been used for design and fabrication of efficient and stable devices. In the construction of a working organic solar cell, the organic layer is just one of the necessary components. The device must also be designed to effectively get light in and charge out. The standard organic solar cell consists of glass substrate pre-coated with ITO (indium tin oxide), an organic layer PEDOT:PSS, the active layer (a blend of P3HT:PCBM) and a top metal electrode, normally an aluminium metal. It is also notable that in this study, ZnO is used as a buffer layer or electron selective layer in both geometries of organic solar cells. Fig. 1 (a, b), show the schematic diagram of the organic solar cell geometry. On the side where light will come in there is a transparent conducting electrode, ITO. There are two different organic solar cells geometries used in this study, i.e. normal/conventional and inverted. In the normal cells, ITO is the anode or positive electrode and a metal with a lower work function than ITO usually aluminium is the cathode or negative electrode, while ITO is the cathode in inverted cells and a metal with a work function greater than ITO (usually silver or gold) is the anode. However, there are advantages and drawbacks for each geometry. Normal orientation results in relatively high efficiencies, while inverted cells are both more stable and more responsive to solution processing.

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Fig. 1 (a) Conventional schematic device structure, (b) Inverted structure and their energy level diagrams (c and d). The energies are referenced to the vacuum level.

There is also often a glass substrate that provides mechanical support and anti-reflection coatings can also help to minimize losses due to non-absorption. On the other dark side, the electrode usually consists of a thin film of metal such as Au or Al for a conventional device and Ag for inverted devices that has been evaporated onto the organic layer. Care must be taken with the attachment of the electrodes to the organic materials, lest an insulating layer forms. Strategies have been developed for certain materials, such as adding buffer layers to solve the problem of instability and degradation [13]. The energy level alignment in the organic solar cells is schematically shown in Fig. 1(c, d) (The energies are referenced to the vacuum level). While P3HT and PCBM form a donor-acceptor heterojunction that facilitates the dissociation of photo-generated excitons (bound electron-hole pairs), the lower conduction band edge of ZnO as compared to the LUMO (lowest unoccupied molecular orbital) of P3HT may also lead to dissociation of excitons in P3HT via rapid electron transfer to ZnO. The similar electron affinities of ZnO and PCBM also suggest that there is a negligible barrier height for electron transport from PCBM towards the Al cathode. Furthermore, the

very deep valence band of ZnO creates a large barrier height to block hole injection from the P3HT: PCBM active layer into ZnO [14].

1.3 The Role of the Buffer Layer in Thin Film Heterojunction Solar Cells

Inserting metal oxides (ZnO or TiO₂) nanostructures into the interface between the active layer and the cathode electrode in organic solar cells as a buffer layer is regarded as one of the most effective strategies in interface engineering to improve the device performance, in combination with some hole-transporting and electron blocking materials as an anode buffer layer [15]. The primary function of a buffer layer is to form a junction with the absorber layer while admitting a maximum amount of light to the junction region and absorber layer [16]. In addition, this layer should have minimal absorption losses and should be capable of driving out photo generated carriers with minimum recombination losses and electrical resistance. The band gap should be as high as possible and layer should be as thin as possible to maintain low series resistance.

The beneficial effects of the buffer layer ranges from modifying the absorber surface to protecting the sensitive interface during the subsequent deposition of cathode electrode and the favourable properties of the interface are suggested to be related to the match of lattice parameters [17]. The current understanding is that candidates for buffer layers should hold a wide band gap for limited light absorption and the process of deposition should be capable of passivating the surface states of the absorber layer and provide an alignment of the conduction band with the absorber to yield high efficiencies. Buffer layers also enhance the stability of the solar cells as the active layer is usually sensitive to air and this may lead to material degradation due to penetration of oxygen and water molecules through the top electrode. Solution processed ZnO has been successfully applied as an interfacial layer/buffer layer in both conventional and inverted organic solar cells

because of its high transparency in the visible light spectrum [18-20]. With the aim of discerning the effect of ZnO electron-selective layer/buffer layer on the overall performance of organic bulk-heterojunction solar cells, we prepared a series of devices with conventional structure (ITO/PEDOT:PSS/P3HT:PCBM/ZnO/Al) (where PEDOT:PSS = Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate), P3HT = poly (3-hexalthiophene) and PCBM = [6,6]-phenyl-C60 butyric acid methyl ester) in which ZnO was deposited on top of an absorbing layer. Another series of devices with inverted structure (ITO/ZnO/P3HT:PCBM/PEDOT:PSS) was prepared. Both kinds of devices comprise a similar cathode structure formed by ZnO layers, with the main difference being the order in which they are deposited, the particle shape and the concentration of ZnO nanostructures.

1.4 Overview of Efficiency Degradation Mechanisms in Organic Solar Cells Devices

Bv introducing metal oxides in organic photovoltaics, the organic solar cells show great potential in terms of device performance with high exciton dissociation, the favourable charge transport ability and the air stability [21]. One of the key solar cell parameters affecting the cell PCE (power conversion efficiency) is the series resistance or internal resistance, R_s . The series resistance represents the total resistance of the cell and is a composite of (i) the active and interfacial layer resistances, (ii) electrode resistances and (iii) the various contacts and interconnect resistances [22]. Conventional geometry of BHJ organic solar cells can suffer degradation of the top electrode, which is normally made of a low-work function metal (Al) that is reactive and oxidize easily in air. The exposure of Al cathode can cause oxidation and degradation of the active layer due to the diffusion of oxygen and moisture through pinholes and grain boundaries [23]. There are different factors that can cause degradation of the OSC device and these factors

can be classified as physical and/or chemical. Generally, large serial resistances due to degradation of the bulk of a material or the quality of the metal electrode reduce the performance of the device. Additionally, the degradation can be localized in the electrode layer itself or at the electrode/ZnO layer/active layer interfaces. In this last case, the degradation mechanism generally leads to a decrease of the interface quality between the active layer/ZnO layer and the electrode, therefore leading to a reduction of the charge transfer and extraction. This reduction of electrode/active layer interface can be due to physical loss of contact between the layers due to delamination [24], creation of voids or the formation of electrically insulating patches at the interface due to change of chemical reactions at the surface of the metal electrode [25].

To optimize the device lifetime or stability, one needs to understand how the device degrades during operation. Materials degrade and as a consequence so do in many instances their physical, electrical, and mechanical properties. Photovoltaic devices that rely on the delicate interplay between the electronic structure of the material, and the energy levels in external electrodes connecting the functional material in the device to the outside world, are highly sensitive to even small degrees of degradation. For an electronic device based on organic materials that rely on both bulk and interface phenomena, it is clear that degradation becomes highly critical for device function and thus must be removed or at least minimized to improve stability. Degradation comprises a complex range of mechanisms of which presumably not all have been identified. Known degradation mechanisms involve: diffusion of molecular oxygen and water into the device, degradation of interfaces, degradation of the active material, interlayer and electrode diffusion, electrode reaction with the organic materials, morphological changes, and macroscopic changes such as delamination, formation of particles, bubbles, and cracks. Some of these degradation mechanisms are

interrelated and take place at the same time, some during operation of the solar cell, and some during storage. Some degradation mechanisms are fast, and others are slow. It is thus a challenging task to identify degradations mechanisms, and even more difficult to quantify to what extent each mechanism contributes to the overall deterioration of the solar cell performance. It has been known for a long time that diffusion of molecular oxygen and water into the device leads to some of the most significant degradation mechanisms for organic solar cells [26].

2. ZnO Nanostructures: Background, Synthesis and Characterization for Applications in Organic Solar Cells

In recent years, there has been increasing interest in ZnO nanostructures due to their variety of morphologies and availability of simple and low cost processing [27]. In addition, nanostructured ZnO has distinguished performance in electronics, optics and photonics. Since the 1960s, synthesis of ZnO has been an active field and study of low dimensional materials has become a leading edge in nanoscience and nanotechnology. With reduced particle size, novel electrical, mechanical, chemical and optical properties have been observed and these are results of surface and quantum confinement effects [28]. While there are still unanswered questions concerning fundamental properties of ZnO, in particular those related to defects and visible luminescence lines, great progress has been made in synthesis methods and device applications of ZnO nanostructures. ZnO is a versatile functional material that has a diverse group of growth morphologies such as nanorods, nanowires or nanoflakes for applications in transparent electrodes in solar cells, UV (ultraviolet) light emitters, diode lasers and spin-electronics [29, 30]. Moreover, it has a direct wide band gap (3.37 eV at room temperature) and high exciton binding energy (60 meV) making it the best candidate for applications particularly in solar cells [31]. ZnO nanostructures can be synthesized in a number of ways such as chemical bath deposition, laser ablation, hydrothermal process, co-precipitation and sol-gel method [32-36]. However, most of these synthesis techniques involve processes of many complex steps requiring sophisticated equipment and extremely thorough experimental conditions. Wet-chemistry colloid preparation as opposed to other methods, have its own attractiveness and ZnO nanostructures can be synthesized easily at low costs. Wet-chemistry route also allow the control of particle size, size distribution, shape and structures under different experimental conditions [37]. Therefore, typical growth mechanisms and wet-chemistry synthesis methods of ZnO nanostructures for applications in organic solar cells are discussed. Furthermore, the kinetics in nanostructure formation such as change in morphology by monitoring the reaction time, temperature, pH and evaporation rate of ammonia in a solution are also discussed.

2.1 Synthesis of ZnO Nanostructures

While relationship between the growth conditions, native defects concentrations and measured properties is not entirely clear, there are very few controversial topics when it comes to the growth of ZnO nanostructures. In this section, ZnO nanostructures synthesized by wet-chemical method are discussed. Spherical nanoparticles, nanoflakes and nanoflowers structures are presented for the applications in organic solar cells as electron selective layers/buffer layer.

2.1.1 ZnO Spherical Nanoparticles

ZnO nanoparticles were synthesized by hydroxylation of zinc acetate dihydrate (ZnAc.2H₂O) by tetramethylammonium hydroxide (TMAH). In a typical preparation, TMAH dissolved in 30 ml of ethanol was added dropwise to 0.1M zinc acetate dihvdrate dissolved in 30 ml of DMSO (dimethylsulfoxide) followed by vigorous stirring for 1 h at room temperature. Nanoparticles were precipitated by adding ethyl acetate. The precipitate was separated by centrifugation and was washed at least three times

by a mixture of heptane and ethanol in the volume ratio of 2:1 and then in heptane only. The ZnO nanoparticles were either dispersed in ethanol/methanol or dried in an oven kept at 110 °C for 1 h. The synthesis is illustrated in Fig. 2. All chemicals were purchased at sigma Aldrich and used without any further purification.

2.1.2 ZnO Nanoflakes and Nanoflowers

ZnO nanoflakes were synthesized by adding a mixture of PEG (polyethyleneglycol) (Mw = 1000) and ammonia water (NH₃.H₂O) dropwise to 0.2 M solution of zinc nitrate hexahydrate (Zn (NO₃)₂.6H₂O) resulting in a white mixture with pH of 12. The mixture was rapidly stirred at 60 °C for 1 h. The precipitate was centrifuged and washed at least three times with ethanol and distilled water and was then dried in an oven at 110 °C for 1 h. Similar experimental procedure was followed to prepare ZnO nanoflowers structures except that the mixture was vigorously stirred for 10 h. The synthesis is illustrated in Fig. 2. All chemicals were purchased at sigma Aldrich and used without any further purification.

2.1.3 ZnO Crystal Structure, Morphology and Kinetics in Nanostructure Formation

XRD (D8 Advanced AXS GmbH diffractometer) patterns of ZnO nanostructures are shown in Fig. 3. The diffraction peaks at scattering angles (2θ) of 31.8° , 34.4°, 36.3°, 47.5°, 56.5°, 62.7°, 66.3°, 67.9° and 69.0° correspond to the reflection from (100), (002), (101), (102), (110), (103), (200), (112) and (210) crystal planes, respectively, matching well with the standard JCPDS data, card number 80-0075. Furthermore, XRD indicates that ZnO nanostructures exhibit the hexagonal wurtzite structure. Impurity peaks were observed from diffraction patterns of nanoflakes and this could be due to the precursor concentration super-saturation or short reaction times. The Debye-Scherrer equation [38, 39] which uses the width of the peak at half of its maximum height (FWHM) of the wide angle x-ray scattering was used to estimate the crystallite size. The crystallite sizes of nanoparticles and nanoflakes were found to be ~ 5 ± 0.2 nm and ~20

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Fig. 2 Schematic diagram showing the wet-chemistry synthesis of ZnO nanostructures.



Fig. 3 XRD spectra of ZnO nanostructures.

 \pm 0.2 nm, respectively, and that of nanoflowers ~35 \pm 0.2 nm. Fig. 4(a-e) shows the FE-SEM (FE-SEM, Nova-nano SEM200, FEI)images of ZnO nanoparticles, nanoflakes and nanoflowers. Spherical nanoparticles

and randomly oriented nanoflakes were observed (Fig. 4 (a, b)). Flower-like clusters were also observed (Fig. 4 (c-e)), they have symmetric arms in level directions. Every arm consists of cluster of nanoparticles.

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Fig. 4 FE-SEM images of (a) ZnOnanoparticles , (b) Nanoflakes and (c-e) Nanoflowers.

ZnO nanostructures are expected to crystallize by the hydrolysis of Zn salts in basic solution that can be formed using strong or weak alkalis. Zn^{2+} is known to coordinate in tetrahedral complexes. Due to the $3d^{10}$ electron configuration, it is collarless and has zero crystal field stabilization energy. Zn^{2+} is able to exist in a series of intermediates and ZnO can be formed by the dehydration of these intermediates. Chemical reactions in aqueous systems are usually considered to be in a reversible equilibrium and driving force is the minimization of the free energy of the entire reaction system, which is the intrinsic nature of wet chemical methods [40]. The main reactions involved in the growth of ZnO nanostructures are illustrated in the following equations [41, 42]:

$$Zn^{2+} + 20H^- \leftrightarrow Zn(0H)_2 \tag{1}$$

$$Zn(OH)_2 + 2OH^- \leftrightarrow [Zn(OH)_4]^{2-}$$
(2)

$$[Zn(OH)_4]^{2-} \leftrightarrow ZnO_2^{2-} + 2H_2O \quad (3)$$

$$ZnO_2^{2-} + H_2O \leftrightarrow ZnO + 2OH^-$$
(4)

$$ZnO + OH^- \leftrightarrow ZnOOH^-$$
 (5)

In the condition where ammonia is used, the mechanism of the formation of ZnO is usually accepted as follows:

$$NH_3 + H_20 \leftrightarrow NH_3 H_20 \leftrightarrow NH_4^+ + H0^-$$
 (6)

$$Zn^{2+} + 4NH_3 \rightarrow Zn(NH_3)_4^{2+}$$
 (7)

$$Zn(NH_3)_4^{2+} + 20H^- \rightarrow ZnO + 4NH_3 + H_2O$$
 (8)

$$Zn^{2+} + 40H^- \to Zn(0H)_4^{2-}$$
 (9)

$$Zn(OH)_4^{2-} \to ZnO + H_2O + 2OH^-$$
 (10)

It can be seen that ZnO nuclei are obtained by the dehydration of $Zn(OH)_4^{2-}$ or $Zn(NH_3)_4^{2+}$. In the presence of PEG, growth units $Zn(NH_3)_4^{2+}$ or $Zn(OH)_4^{2-}$ are easily adsorbed by the atom O in the C-O-C chain. $Zn(OH)_4^{2-}$ or $Zn(NH_3)_4^{2+}$ can be carried and transformed into ZnO crystalline nanoparticles/nanoflakes and grow on active sites around the surface of ZnO nuclei. When the reaction temperature is low (60 °C), the rate of production of NH₃ is slow and more Zn²⁺ are transformed in to ZnO nuclei in the function of hydroxyl. Thus, more ZnO nuclei with active sites aggregate spontaneously in hexagonal symmetry direction, which provides more

chances for the formation of flower-like ZnO. When the synthesis temperature rises to 80 °C, more productions of NH₃ make $Zn(NH_3)_4^{2+}$ increase in the reaction system, which decreases the rate of formation of ZnO nuclei compared with that at 60 °C. When the rate of growth matches the rate of formation of nuclei, single/bundled nanorods structure is formed. In the case of 80 °C, the quantity of activity sites increases with the rise in temperature, which gives an advantage for more rods growing around ZnO nuclei [43, 44].

3. Effects of Particle Morphology of ZnO Buffer Layer on the Performance of Organic Solar Cells

The organic solar cell devices consisting of successive layers of poly (3,4-ethylenedioxythiophene) (styrenesulfonate) or PEDOT:PSS (hole poly extraction layer), a blend of poly(3-hexyltheopene): [6,6]-phenyl C61-butyric acid methyl ester or P3HT:PCBM (photo-active layer), ZnO nanoparticles/nanoflakes (electron extraction layer) and aluminum (Al) top electrode (cathode) spin-coated on a glass substrate pre-coated with a layer of transparent indium-tin-oxide or ITO (anode) were fabricated. The glass substrate was cleaned ultrasonically using isopropanol, acetone and isopropanol again, consecutively for each 10 min, then followed by drying at ~80 °C for 20 min and was lastly treated in an ultraviolet ozone generator for 20 min. A thin layer of poly (3,4-PEDOT:PSS (CLEVIOS™ AI 4083) was spin-coated on the cleaned ITO pre-coated glass substrate at the speed of 4000 rpm for 35 s followed by drying in an oven/hot plate at 110 °C for 10 min. The active layer of P3HT:PCBM blend with a weight ratio of 1:0.6, dissolved in chlorobenzene, was spin-coated at the speed of 1000 rpm for 15 s. This was followed by the deposition of the layer of methanol solution of ZnO nanoparticles/nanoflakes at 4000 rpm for 35 s. Electron extraction layers of ZnO nanoparticles/nanoflakes were spin-coated with four different concentrations of 0.5, 1, 2 and 20 mg/ml. The

top Al metal electrode (100 nm) was thermally evaporated at $\sim 1 \times 10^{-6}$ Torr pressure through a shadow mask and the device area was 0.12 cm². All the devices were then thermally treated at 155 °C for 10 min.

The surface topography of the device layers was examined using contact-mode AFM (AFM, Shimadzu SPM-9600). Figs. 5(a-f) show topographic images of PEDOT:PSS, P3HT:PCBM, ZnO nanoflakes electron extraction layer, ZnO nanoparticles electron extraction and Al layer scanned layer, from P3HT:PCBM/ZnO/Al and Al layer scanned from P3HT:PCBM/Al device geometries, respectively. The lowest rms value of $1.02 (\pm 0.01)$ nm demonstrates surface smoothening effect of PEDOT:PSS. The other layers (P3HT:PCBM and Al, Fig. 5(b) and (f)) show a distribution of particles and their rms roughnesses were 5.2 (\pm 0.2) nm and 5.4 (\pm 0.4) nm, respectively. The ZnO nanoparticles and nanoflakes (2mg/ml concentration) rms roughnesses were 52 (\pm 3.6) nm and 3.5 ± 0.5 nm, respectively, and the Al layer (Fig. 5e), shows the roughness of 58 (± 3.2) nm.

The layers in Fig. 5(b), (d) and (e) shows much coarser texture with broad hill-like features and an increased surface roughness compared to the other films. This is most likely due to annealing and ordered structure formation in the film [45]. It has been reported that rougher interface between the photo-active layer and the top electron can improve efficiency of organic solar cell devices by increasing light harvest in the photo-active layer and by subsequently preventing the formation of shunt paths [46, 47]. As discussed, it is reasonable to attribute high PCE value of 3.08% from the OSC device with ZnO nanoflakes to increased light harvest by rougher interfacial morphology. However, Qian et al [14] reported improved efficiency from OSC devices with relatively smooth interface morphology. They reported that the improved electrical contact between the cathode and the photoactive layer enabled the efficient collection of photo-generated electrons.

Fig. 6 compares the photovoltaic properties of the OSC devices with ZnO nanoflakes and nanoparticles electron extraction layers spin-coated from solutions of 0.5 concentration. The photovoltaic mg/ml performance parameters including short circuit current Jsc (dentsity), Voc (open circuit voltage), FF (fill factor) and PCE (power conversion efficiency) of the devices with different concentrations of the ZnO solutions are presented in Table 1. The J-V (current-density) EQEs characteristics and (external quantum efficiencies) of the devices are presented in Fig. 6(a) and (b), respectively. Although both devices recorded almost the same values of V_{oc} on average, the devices with the ZnO nanoflakes recorded relatively higher values of the J_{sc} and FF, and subsequently higher values of the PCE as shown in Table 1. The highest PCE values of 2.37 % and 3.08% were obtained from the devices spin-coated from the ZnO nanoparticles and nanoflakes solutions of 0.5 mg/ml concentration, respectively.

Other than the differences in particle morphology (shape and size), the high PCE value recorded from the device with the nanoflakes electron extraction layer suggests that the nanoflakesmade a relatively superior contact with the photo-active layer and the top electrode compared to the nanoparticles. Liang et al [48] have pointed out that the surface quality of the ZnO layer can lead to improved photovoltaic properties of the devices. The AFM data show that the nanoparticle layer with the rms value of 3.5 nm was by far smoother than that of the nanoflakes layer with the rms value of 52 nm. The photovoltaic performance was found to be dependent on the particle shape and concentration of ZnO. The device with the ZnO nanoflakes electron extraction layer showed a significant enhancement of the PCEs from ~1.38% to 3.08% as the ZnO concentration decreased from 20 mg/ml to 0.5 mg/ml. Similarly, the device with ZnO nanoparticles also showed such an increase of PCEs from $\sim 0.17\%$ to 2.37 % as the concentration decreased with the lower maximum PCE. When the ZnO concentration increases,



(e)

(f) Fig. 5 Contact-mode AFM topographic images of (a) PEDOT:PSS, (b) P3HT:PCBM, (c) ZnO nanoparticles electron extraction layer, (d) ZnO nanoflakes electron extraction layer, (e) Al layer from P3HT:PCBM/ZnOnanoflakes/Al and (f) Al Layer from P3HT:PCBM/Al device geometries.

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Fig. 6 (a) J-V characteristics and (b) external quantum efficiency of devices with ZnO nanoparticles/nanoflakes buffer layer. Table 1 Photovoltaic comparison of P3HT:PCBM solar cells with different concentrations of ZnO nanoparticles and nanoflakes.

Concentration (mg/ml)	ZnO nanoparticles				ZnO nanoflakes			
	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
0.5	7.18	0.67	49.5	2.37	7.63	0.67	60.6	3.08
1	6.67	0.65	45.8	1.98	7.45	0.67	59.2	2.94
2	6.38	0.67	35.7	1.52	6.94	0.66	52.8	2.43
20	0.74	0.64	36.3	0.17	6.01	0.61	37.8	1.38

the amount of solute particles increases in the solution, thereby increasing the probability of clustering together to form larger grains. In other words, at lower concentrations, clustering is minimal, which makes contact between the photoactive layer and the Al layer better.

In addition, From the AFM and SEM imaging, the ZnO nanoflakes film is much rougher than the ZnO nanoparticles film. It therefore demonstrates that the surface and film quality of the electron extraction layer can make a direct impact on the contact between the active layer and the ZnO layer, thus influencing the photovoltaic performance of the device [48]. It is therefore reasonable to conclude that the high PCE value of 3.08% recorded from the device with the nanoflakes buffer layer was a result of improved collection of the photon generated electrons from the rougher interface between the photo-active layer and the top electron, which may improve the efficiency of the device by increasing light harvest in the photo-active layer, and by subsequently preventing the formation of shunt paths.

The improvement in device performance is also observed from the EQE of the devices, as shown in Fig. 6(b). There is a significant increase in EQE for the device with the ZnO nanoflakes electron extraction layer with a maximum of ~55% at the wavelength of 505 nm versus ~47% for the ZnO nanoparticles electron extraction layer. Liang et al [48] reported that increased optical transmittance of the ZnO extraction layer should lead to enhanced absorption of the photoactive layer and better general performance of the OSC devices. While not measured in this study, it is reasonable to assume that the optical transmittance of the ZnO nanoflakes electron extraction layer was better than that of the nanoparticles and this could be one of the factors that contributed to improved photovoltaic properties of the devices.

4. Thermal Treatment and Surface Analysis of P3HT:PCBM Based Solar Cells

Significant advances in *PCE* are achieved by the improvement of the photoactive layer morphology and the challenge is to optimize the interfacial area of the donor/acceptor materials, charge mobility within the photoactive layer and the crystallinity of P3HT polymer within the blend. However, the processing

conditions such as thermal annealing of BHJ films can help improve the morphology and charge carrier mobility thereby increasing the quantum efficiency of the device [49]. In addition, the sequence of the thermal treatment is critical for the device performance. The organic solar cells with the cathode confinement in the thermal treatment (post annealing) show better performance than the cells without the cathode confinement (pre annealing) [50]. In manv multi-layered electronic devices, the interface between their layers governs their properties and changes such as oxidation and/or the formation of polar layers affect their functioning. Hence, to understand the BHJ structure, the study of these interfaces is important for organic solar cells development [51-53].

4.1 Device Fabrication

The device geometry was ITO/PEDOT:PSS/P3HT:PCBM/ZnOnanopaticles/Al with the device area of 0.12 cm^2 . A glass substrate precoated with ITO and modified by spin-coating a thin layer of PEDOT: PSS followed by drying in an oven/hot plate at 110 °C for 10 min was used as an anode electrode. The photoactive layer of P3HT:PCBM blend with a weight ratio of 1:0.6, dissolved in chlorobenzene, was spin-coated at the speed of 1000 rpm for 15 s. This was followed by the deposition of the layer of methanol solution of ZnO nanoparticles at 4000 rpm for 35 s. Finally, the top Al metal electrode (100 nm) was thermally evaporated at \sim 1 \times 10⁻⁶ Torr pressure through a shadow mask defining the device area. Two devices are compared in this study, i.e. Device A was then thermally treated before the evaporation of Al electrode (i.e. pre-annealing) and device B was thermally treated after the evaporation Al electrode (i.e. post-annealing) at 155 °C for 10 min.

4.2 Photovoltaic Performance Measurements

Current density versus voltage (J-V) characteristics were measured using a Keithley 2400 source meter and an Orielxenon lamp (150 W) coupled with an AM1.5 filter to simulate sunlight. The light intensity was calibrated with a silicon reference cell with a KG2 filter following standard solar cell testing procedures. All J-V measurements were conducted at the light intensity of 100 mW/cm². The EQE as a function of wavelength were measured using an IPCE (incident photon-to-current efficiency) measurement system (PV measurement, Inc). The wavelength of the bias light was controlled with optical filters (Andover Corporation).

4.3 SIMS Depth Profiling and Imaging

Complete devices, device A and B, were characterized by ion-tof TOF-SIMS⁵. Two depth profiling ion beams operating in the dual beam mode were used. While a primary current of 70 nA of Cs⁺ ions is sputtering the crater, the 0.3 pA Bi_3^{++} ion is progressively analyzing the crater bottom, with impact energies of 1 keV (Cs^+) and 30 keV (Bi_3^{++}) and the sputter area of $300 \times 300 \,\mu\text{m}$ with the sputter time of 10 sec/scan. Both positive and negative mode of SIMS measurements were performed directly on the Al cathode. The surface imaging was performed with a $Cs^+ 0.3$ pA primary beam, and was rastered over area of $100 \times 100 \ \mu m$ on the sample surface. The two-dimensional images were recorded with a resolution of 512 \times 512 pixels. The measurements were performed at the base pressure of 1.5×10^{-9} mbar.

The Photovoltaic response characteristics of device A and B are summarized in Table 2. The device performance is greatly improved by the thermal treatment after the deposition of the Al cathode (post-annealing). The *PCE* is significantly increased from 1.57% to 2.93%. In addition, the V_{oc} of device B increased marginally from 0.43% to 0.65%. The improvement of the PV properties can be attributed to combined effects of the ZnO buffer layer and

post-annealing treatment. This trend is similar to results reported by Ntwaeaborwa et al [46] and Kim et al [54], where they observed that the device with thermal treatment after cathode deposition shows a better performance. The increase of V_{oc} in device B may be attributed to a decrease in ohmic contact at the interface between ZnO layer and Al electrode. The change in ohmic contact at the interface may be a result of energy level re-alignment due to a post annealing treatment as stated by Zhao et al [55]. The change of ohmic contact in organic solar cells is considered to have a strong impact on the V_{oc} and FF of the cell. The external quantum efficiency gave the maximum photocurrent contribution at ~ 501 nm and an improvement of device performance of about 10% is obtained for device annealed after Al deposition.

Positive mode, SIMS depth profiling results of device A and B are presented in Fig. 7(a, b). Signals arising from ²⁷Al, ¹⁶O, ¹²C, ³²S, ⁶⁴Zn, ²⁸Si, ¹²⁰Sn and ¹¹⁵In ions allowed a clear identification of the Al/ZnO/P3HT: PCBM/PEDOT: PSS and ITO/glass layers, respectively. Although there is no significant difference of depth profile distribution between device A and B except slight concentration intensity of carbon, the formation of aluminum oxide is possible and this has been reported before by Bulle-Lieuwma et al [56]. The Al signal that decreases slowly and diffuses in to the active layer (P3HT: PCBM) originates from the Al metal. The annealing of devices leads to a slight shift and diffusion of Al into to the active layer. The interface between Al and P3HT: PCBM is found to be oxygen-rich, as it is visible from the ¹⁶O signal observed. Interestingly, within the active layer the ⁶⁴Zn signal which originates from ZnO layer is observed. Again the intensity of ¹⁶O signal increases at the Al/P3HT: PCBM interface and significantly decreases within the active layer and then stays constant throughout

 Table 2
 Photovoltaic comparison of device A and device B.

Device A				Devie			
J_{sc}	V_{oc}	FF	PCE	J_{sc}	V_{oc}	FF	PCE
(mA/cm^2)	(V)	(%)	(%)	(mA/cm^2)	(V)	(%)	(%)
7.027.18	0.433	51.69	1.57	7.10	0.654	63.07	2.93

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Fig. 7 (a-b)TOF-SIMS depth profiles (Intensity as function of a sputter time) obtained directly on the Al cathode for Devices A (Positive SIMS).

to the ITO/glass substrate. The presence of ¹⁶O is attributed to ZnO or the formation of aluminum oxide (or hydroxide) during Al evaporation as a result of a chemical reaction with the present residual gas (water) in the vacuum chamber [57, 58] and water that might be present on the sample surface. Sulfur (³²S) depth profile, which originates from P3HT, PSS and PEDOT and carbon (¹⁶C) from P3HT: PCBM are stable at the Al region, and then simultaneously increases towards the P3HT: PCBM region. While ¹⁶C is uniformly distributed within the active layer, then significantly

decreases towards the PEDOT: PSS layer, ³²S slightly increased, slowly decreased and then is uniformly distributed throughout the PEDOT: PSS layer, then decreased towards the ITO/glass region.

The diffusion of tin (¹²⁰Sn) and indium (¹¹⁵In) into the active layer from ITO/glass region has been recognized as one of the main factors that are detrimental to the lifetime of organic solar cells. The diffusion of ¹¹⁵In and ¹²⁰Sn depends on the nature of the layers present. In the case of PCBM/PEDOT: PSS/ITO, ¹²⁰Sn and ¹¹⁵In signals are found within the PEDOT:

PSS until they reach the P3HT:PCBM/PEDOT:PSS interface, where signals drops. De Jong et al [59] showed with RBS technique that the diffusion of ¹¹⁵In into the PEDOT:PSS layer strongly increases upon the exposure to air using the explanation that water present in the atmospheric air and taken up by the PEDOT:PSS liberates the acidic protons of PSS. Acidic etching then result in indium ions dissolving in the PEDOT:PSS. This may possibly cause in both indium and tin diffusing to the P3HT:PCBM layer. Because our samples were exposed to air and kept for few months

without encapsulation or were kept at ambient laboratory conditions, findings in this study may be in accordance with the results of de jong et al [59]. The silicon (²⁸Si) signal originating from the underlying glass substrate used is low throughout the layers and increases at the ITO/glass region.

Fig. 8(a, b) shows that the concentration of 27 Al and 16 C for device A are slightly intense compared to the device B. This could be due to the heat treatment effect on devices. Fig. 9(a, b) shows the surface imaging of device A after 60 scans. Images show the Zn⁻ and O⁻



Fig. 8 TOF-SIMS depth profiles (Intensity as function of sputter time) of (a)²⁷Al and (b)¹⁶C.

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Fig. 9 Ion mapping of Zn⁻ and O⁻ for Device A, after 60 scans (a, c) and after 180 scans (b, d).

elemental or chemical distribution across the surface observed within 300 μ m × 300 μ m dimension. These images reveal the secondary ion intensities as a function of the location on the sample surface and after the first 60 scans, low concentrated Zn⁻ and O⁻ ions are homogenously distributed on the surface as indicated by a side bar scale. However, there are clear large particles on the surface of O⁻ indicating the inhomogeneous distribution. After 180 scans (Fig. 9(b, d)), the distribution of secondary ions detected intensified and showed more inhomogeneity across the surface.

5. Inverted Organic Solar Cells with Solution Processed ZnO Nanoparticles/Nanoflowers

In the conventional structure of organic solar cells, a

layer of poly (3,4-ethylene dioxythiophene): poly (styrene sulfonate) (PEDOT:PSS) is usually used to modify the transparent ITO electrode for efficient collection of holes [60, 61]. However, owing to the strong acidic nature of PEDOT: PSS, the degradation of ITO/PEDOT: PSS interface is inevitable [62]. Furthermore, widely used low work-function metal cathodes such as Al cathode in conventional organic solar cells are sensitive to air. The exposure of an Al cathode to air can cause oxidation and degradation of the active layer due to the diffusion of oxygen and moisture through pinholes and grain boundaries of the metal cathode [63]. To overcome these problems, one approach is to use an inverted structure. By modifying the polarity of ITO with an n-type functional buffer layer and using less air sensitive, high work-function metals such as Ag or Au, collection of electrons and holes can be improved considerably. In this type of structure, the elimination of PEDOT: PSS and prevention of air and moisture diffusion from the high work-function metal top electrode can improve the device stability [64]. In organic solar cells, it is important to determine the appropriate energy level of the collecting electrode to match that of the active layer. Thus, various materials for modifying the polarity of ITO have been proposed. Inorganic semiconducting materials such as TiO₂ or ZnO deposited on the ITO electrode can be used as buffer layers for accepting electrons which can also increase the stability of inverted organic solar cells [64, 65]. Compared with TiO₂, ZnO have high electron mobility, which makes it an ideal electron selective contact layer in inverted organic solar cells structures [66]. In addition, TOF-SIMS measurements are performed to monitor 3D molecular compositions and metal/organic interface.

Fig. 10 shows the cross-sectional view of ZnO nanoparticles and nanoflowers on the ITO-coated glass substrate. The nanoparticles are uniformly distributed across the surface while the nanoflowers were scattered unevenly on the surface. PV (photovoltaic) characteristics comparison between the device with

ZnO nanoparticles and nanoflowers are shown in Fig. 11(a, b) and extracted parameters are summarized in Table 3. The device with ZnO nanoparticles shows a J_{sc} of 8.33 mA/cm², V_{oc} of 0.58 V and *FF* of 46.45%, resulting in the *PCE* of 2.26%.

However, as shown in Table 3, the PV values of from the device with ZnO nanoflowers were comparatively low. It is evident from the J-V curve that the device with nanoflowers suffers the high series resistance. Since these devices are fabricated with the same materials and the same procedure and the only difference is the electron extraction layer morphology, the increased current density is unlikely to account for other reasons, but it is possibly due to reduced series resistance in the case of ZnO nanoparticles. Shim et al [67], have demonstrated that the tuning of ZnO buffer layer improves the photovoltaic performance. On the other hand, when the ZnO buffer layer becomes thick, a high intrinsic resistance increasing the series resistance and reducing the charge carrier transport ability can decrease the photovoltaic performance of the device.

The EQE of these two devices are compared in Fig. 11(b). The device with the ZnO nanoparticles clearly has a higher EQE, especially for wavelengths longer than ~ 450 nm. The EQE of the device with ZnO nanoparticles exceeds that of the nanoflowers by



Fig. 10 FE-SEM cross-section view of (a) ZnO nanoflowers on a glass/ITO substrate and (b) ZnO nanoparticles on a glass substrate.

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Fig. 11 (a) J-V characteristics and (b) external quantum efficiencies of the devices with ZnO nanoparticles and nanoflowers electron selective layers.

 Table 3 Photovoltaic comparison of P3HT: PCBM solar cells with ZnO nanoparticles and nanoflowers electron selective layers.

Inverted Device	ZnO Layer	$J_{sc} (\mathrm{mA/cm}^2)$	$V_{oc}\left(\mathrm{V} ight)$	FF (%)	PCE (%)
(1)	Nanoparticles	8.331	0.5848	46.45	2.26
(2)	Nanoflowers	7.379	0.3763	38.81	1.08

approximately 10%. A slight red-shift of spectrum is also observed. The enhanced or red-shift is believed to be the result of improved polymer chain ordering from the growth process [68]. The SIMS depth profile was performed on the device with ZnO nanoparticles to determine the distribution in depth of the device components. This is presented in Fig. 12 (a). The peak intensity of ¹⁰⁷Ag signal remained constant for the first few minutes and then decreased. The profile pattern indicated the moderate diffusion of ¹⁰⁷Ag into the P3HT:



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Fig. 12 (a) TOF-SIMS depth profiles (Intensity as function of a sputter time) obtained directly on the Ag electrode for the inverted device with ZnO nanoparticles and 3-D surface imaging of (b) Silver, (c) Carbon, (d) Oxygen and (e) Sulfur.

PCBM region. ⁶⁴Zn, ¹²C and ¹⁶O signals simultaneously increased as the ¹⁰⁷Ag signals decreases. They all remain constant in the P3HT:

PCBM region except for the ¹⁶O signal which dropped and increased again towards the P3HT: PCBM/PEDOT: PSS interface. This suggests that the

surface is oxygen rich towards the ZnO/ITO/glass region. In addition, ³²S signal also increases and remains constant through the P3HT: PCBM/DEDOT: PSS regions and it drops at the ITO/glass region, indicating that these regions are sulfur enriched originating from both P3HT and PSS. As indicated in the previous discussion (section 1.8), ¹²⁰Sn and ¹¹⁵In signals are observed in the P3HT: PCBM region and this is attributed to the acidic nature of PEDOT: PSS etching away the organic layers thereby allowing the penetration of ¹²⁰Sn/¹¹⁵In into other layers. The ²⁸Si signal which is pronounced in the ITO/glass region comes from the glass substrate. Fig. 12 (b-e) shows the 3D surface images of silver, carbon, oxygen and sulfur. It is evident from the images that there is guite a high concentration of ¹²C, ¹⁶O and ³²S. This is consistent with the composition depth distribution presented in Fig. 12(a).

6. Summary and Conclusions

In this review, photovoltaic characteristics of P3HT: PCBM based solar cells are presented in a context of evaluating the effects of post-annealing treatment, inverted structure with ZnO buffer layer on the solar efficiency. ZnO spherical nanoparticles, nanoflakes and nanoflowers synthesized by wet chemistry method were used as electron extracting layer/buffer layer. The performance of both conventional and inverted devices was found to depend on the concentration and morphology of ZnO. In the conventional device, ZnO nanoparticles and nanoflakes concentrations were varied from 0.5 to 20 mg/mL. The surface topographic images of PEDOT: PSS, P3HT: PCBM, ZnO nanoparticle and nanoflakes and Al layers with rms roughness values of 1.02 ± 0.01 nm, 5.2 ± 0.2 nm, $52 \pm$ 3.6 nm, 3.5 ± 0.5 nm and 58 ± 3.2 nm, respectively, were analyzed. The lower rms values show the smoothening effect of layers while the broad hill-like layers with higher rms value were ascribed to annealing and the formation of highly ordered film structure. Although the devices had the same ZnO concentration, the device with ZnO nanoflakes recorded relatively higher values of PCE, J_{sc} , V_{oc} and FF. The highest PCE values of 2.37 % and 3.08 % were obtained from the devices spin-coated from the ZnO nanoparticles and nanoflakes solutions of 0.5 mg/mL concentration, respectively. Furthermore, a comparison between the inverted devices with ZnO nanoparticles and nanoflowers as electron extraction layers was made. In this case, the devices were fabricated using the same materials and the same procedure except that the particle morphology of the ZnO electron extraction layer was different. The photovoltaic response was high for device with ZnO nanoparticles, even if the ZnO nanoflowers showed slightly higher transparency. The EQE of devices mostly exhibits maximum photon absorption in the visible range of the spectrum in the range of 300-600 nm wavelength.

Compositional depth profiling and surface imaging of OSCs were discussed. For both conventional and inverted devices, different layers of the OSCs, namely, the Al/Ag, the P3HT: PCBM layer, the ZnO nanoparticles layer, PEDOT: PSS layer and ITO/glass layer were clearly identified by TOF-SIMS depth profiling. TOF-SIMS revealed signals arising from ²⁷Al, ¹⁶O, ¹²C, ³²S, ⁶⁴Zn, ²⁸Si, ¹²⁰Sn and ¹¹⁵In ions. Enrichment of oxygen at the interface between Al and the photoactive layer was observed. Furthermore, depth-profiling showed that during preparation diffusion of indium into the PEDOT: PSS occurred and this was probably due to the influence of water molecules from the atmosphere.

In conclusion, the research conducted in this project has established new perspectives regarding the effects of ZnO particle morphology on the performance of organic solar cells. Combined with the recent advances in the efficiency of solar cells, the prospects for fabricating efficient organic solar cell devices using ZnO nanostructures as electron extracting layers are excellent. However, it should be noted that the reproducibility issue of OSCs has not yet been clearly addressed because of several reasons. Firstly,

establishing highly reproducible performance of OSCs requires tremendous trial and errors, and poorly reproducible performance is believed to be an intrinsic drawback of organic electronics devices. Secondly, in the device fabrication, there are several process variables: blend solution preparation method, blend ratio, blend layer thickness, PEDOT: PSS thickness, various kinds of PEDOT: PSS with different conductivity, spin casting conditions, cathode structure, annealing conditions and method, oxygen and moisture exposure, encapsulation, illumination set-up and characterization set-up. As a result, it is quite difficult to consistently reproduce the same or relative photovoltaic output from one device to the other. Therefore, many researchers experience significant performance variation even though the devices were fabricated using a consistent procedure. Finally, the results reported here indicated that more fundamental questions concerning the influence of ZnO morphology on the performance of organic solar cells must be addressed before rational improvement can be expected.

7. Future Outlook

Organic solar cells offer many advantages due their fundamental properties, mechanical flexibility and resilience, light weight, processability and immense customizability in their optoeletronic characteristics. Efficiencies have improved considerably due to a greater understanding of basic organic semiconductor operations, tailored device architectures and improved material synthesis and selection, with current state-of-the-art device efficiencies exceeding 8%. Despite advances, numerous challenges still remain to make OSCs a commercially viable competitor to thin film inorganic materials. To this point, most research efforts have been focused on increasing device efficiency at the laboratory scale and the lifetime of OSCs is also a concern and requires more investigation. In addition, as materials synthesis and control over device morphology improve, attention must be turned

to module performance as a whole, including optical effects. Altering substrate optical properties has already been shown to improve the exciton diffusion bottleneck and increase performance and further developments could increase the performance further.

In the past three decades, organic photovoltaics have emerged from a niche research topic to a promising competitor in the photovoltaic market. Inexpensive, rugged, and high efficiency organic photovoltaics have the potential to revolutionize solar energy around the world and diligent research effort will realize this goal. Finally, the future work that can be done to continue the research of P3HT: PCBM based solar cells is to look into approaches of light harvesting by choosing low band gap photo-active materials and band gap tuning of conjugated polymers or extending to NIR to maximize the efficiency of OSCs. Moreover, ZnO has a lot of defects that might cause instability in the devices. Treatment of ZnO in the UV-Ozone may get rid of some of these defects and significantly change the conductivity thereby enhancing the absorption efficiencies or the overall performance of OSCs.

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