Research Article

Fabrication and Optimization of Polymer Solar Cells Based on P3HT:PC₇₀BM System

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Efficient bulk heterojunction (BHJ) polymer solar cells (PSCs) based on P3HT:PC₇₀BM were fabricated by optimizing the processing parameters. The optimized thickness and annealing temperature have been found to be about 200 nm and 130°C. The effect of cathode interfacial layers on device performance is related to the formation of interfacial dipole. Furthermore, the effect of optimum ZnO interfacial thickness (~30 nm) on device performance is attributed to good interfacial conductivity and its optical property. The metal electrode deposited in the slow rate has a better influence on device performance. Based on these optimal conditions, the best power conversion efficiency (PCE) of 3.91% was obtained under AM 1.5G and 100 mW/cm² illumination. This detailed investigation provides an important reference for the fabrication and optimization of polymer photovoltaic devices.

1. Introduction

In recent years, polymer solar cells (PSCs) have been attracting much attention due to their low cost, ease of processing, flexibility, and light weight compared to traditional inorganic counterparts [1–6]. Actually, the most promising PSCs are based on the bulk heterojunction (BHJ) structure where the polymer donor is intimately mixed with a fullerene derivative acceptor increasing the charge separation and transportation in PSCs. The power conversion efficiency (PCE) of BHJ PSCs has also been improved greatly in the past years [7–11]. However, they still have not realized commercialization compared to conventional photovoltaic cells based on silicon. Many investigations on operating mechanism, novel device structures, fabrication process, and synthesis of multifunctional materials have been carried out in order to improve the device performance [2, 9, 12–16]. Among them, the preparation process of the solar cells is very important. The processes of energy conversion from light into electricity in PSCs usually include photon absorption, exciton formation/diffusion, exciton dissociation, carrier transport towards the electrodes, and charge collection by respective electrodes. These processes are subtly controlled by active

layer thickness, intrinsic properties of materials, thermal treatment, and interface modification, for example, inserting different interface layers between active layer and electrode. Therefore, it is noted that efficient devices are hardly achieved by optimizing only one single aspect.

In this report, we report the fabrication and optimization of polymer solar cells based on P3HT and PC₇₀BM by changing the thickness of the active layer, annealing temperature, types and thickness of cathode interface layers, and metal electrode deposition rate. The reasons of influence of these factors on device performances are also discussed.

2. Experimental

2.1. Materials. Regioregular electron-donor P3HT (poly(3-hexylthiophene)) and acceptor PC₇₀BM ([6,6]-phenyl C₇₀-butyric acid methyl ester) were purchased from Luminescent Technology, Inc. PEDOT:PSS (Clevios 4083) was purchased from HC Starck. Zinc acetate (Zn(CH₃COO)₂, 98.0%), 2-methoxyethanol (CH₃OCH₂CH₂OH, 99.0%), and monoethanolamine (NH₂CH₂CH₂OH, 99.0%) were purchased from Sigma-Aldrich. All the chemicals were used as received without further purification. 1,2-Dichlorobenzene

FIGURE 1: (a) The molecular structures of P3HT, PC₇₀BM, and PEDOT:PSS. (b) The typical device structure of polymer solar cell based on P3HT:PC₇₀BM. (c) Energy level diagram of the component materials used.

(DCB) solution of P3HT:PC₇₀BM (1:0.8 by weight) containing (20 mg mL⁻¹) P3HT and (16 mg mL⁻¹) PC₇₀BM was stirred in glovebox at 60°C overnight. Upon cooling to room temperature, the solution was filtered through a 0.2 μm polytetrafluoroethylene (PTFE) filter. The ZnO precursor was prepared by dissolving zinc acetate and monoethanolamine in 2-methoxyethanol under vigorous stirring for 12 h for the hydrolysis reaction in air.

2.2. Device Fabrication and Measurement. Prior to device fabrication, the ITO substrates (CSG Holding Co. Ltd., Shenzhen, China) were cleaned by sonication using detergent, deionized water, acetone, and isopropanol sequentially for 15 min. After drying in an oven for a few hours, the ITO surface was treated with plasma treatment for 10 min. Then, a layer of PEDOT:PSS (~40 nm) was spin-coated onto the cleaned ITO as an anode buffer layer of the PSCs and baked at 120°C for 15 min. Then, the active layer and ZnO film were spin-coated in the glovebox by employing the P3HT:PC₇₀BM blend solution and ZnO precursor solution, respectively.

The Al (LiF or Ca) electrode was deposited in a deposition chamber under vacuum pressure of 2×10^{-4} Pa.

The current density-voltage (*J-V*) characteristics of the fabricated devices were performed using a computer controlled Keithley 2400 SourceMeter under illumination with calibrated AM 1.5G (100 mW/cm²) sun simulator in a nitrogen condition at room temperature. A xenon light source was used to give simulated irradiance of 100 mW/cm² (equivalent to AM 1.5G irradiation) at the surface of the solar device. The shadow mask was used during thermal evaporation to define the active area of 0.15 cm². All thickness measurements were analyzed using alpha-step surface profiler.

3. Results and Discussion

3.1. Effect of Active Layer Thickness on Device Performance. Figure 1 shows the chemical structures of the materials used, the typical device structure of polymer photovoltaic cells fabricated, and energy level diagram of the component materials used in this study. The thickness of active layer has

FIGURE 2: J - V characteristics under illumination for different thicknesses of the active layers. The structure of the devices is ITO/PEDOT:PSS/P3HT:PC₇₀BM/Al.

been reported to play an important role in determining the electrical properties of the device [17–19]. In order to optimize the performance of the PSCs, first we fabricated devices with the structure of ITO/PEDOT:PSS/P3HT:PC₇₀BM/Al by use of different thicknesses of P3HT:PC₇₀BM. Figure 2 shows the current density versus voltage (J - V) characteristics of the devices measured under 100 mW/cm² illumination (AM 1.5G). The performances of the devices with different active layer thickness are listed in Table 1 for comparison. The device with the thickness of 200 nm shows the best performance with the highest PCE of 2.64%, an open-circuit voltage (V_{oc}) of 0.56 V, a short-circuit current density (J_{sc}) of 8.74 mA/cm², and fill factor (FF) of 0.54. It is worth noting that FF and V_{oc} of the devices do not change significantly with the increase of the thickness of the active layer from 100 nm to 200 nm (FF keeps 0.55 ± 0.01 and V_{oc} keeps 0.57 ± 0.01 V), but J_{sc} of the device is obviously increased from 6.34 mA/cm² to 8.74 mA/cm² with the active layer thickness from 100 nm to 200 nm, resulting in the increasing of PCE from 2.05% to 2.64%. Further increasing the active layer thickness (300 nm) makes the device performance decay sharply with a PCE of 1.19%.

In PSCs, the thickness improvement of active layer may lead to more absorbed photons, so J_{sc} of the device is obviously increased with the active layer thickness from 100 nm to 200 nm. However, the relatively low carrier mobility in the disordered materials leads to more carrier recombination before reaching the electrodes. Thus, further enhancement of active layer thickness results in an increase of charge recombination and series resistance, which leads to lowering

TABLE 1: Photovoltaic parameters of the devices with different active layer thicknesses, measured under 100 mW/cm² illumination (AM 1.5G). The structure of the devices is ITO/PEDOT:PSS/P3HT:PC₇₀BM/Al.

Thickness of active layer	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)
100 nm	6.34	0.58	0.56	2.05
200 nm	8.74	0.56	0.54	2.64
300 nm	6.08	0.53	0.37	1.19

TABLE 2: Photovoltaic parameters of the devices with different annealing temperatures, measured under 100 mW/cm² illumination (AM 1.5G). The structure of the devices is ITO/PEDOT:PSS/P3HT:PC₇₀BM (200 nm)/Al.

Temperature	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)
As cast	8.74	0.56	0.54	2.64
110°C	9.10	0.56	0.56	2.87
130°C	10.70	0.55	0.60	3.53
150°C	8.52	0.53	0.52	2.36

of the fill factor and short-circuit current. The above results are in good agreement with those reported previously [19, 20].

3.2. Effect of Annealing Treatment on Device Performance.

Thermal treatment of the devices is commonly used to improve the phase segregation of the donor and acceptor materials in order to gain the optimal morphology of the bulk heterojunction [21]. However, this technique is versatile because the degree of phase separation depends on many factors. In order to investigate the influence of annealing treatment on device performance, the devices were annealed at different annealing temperatures after cathode deposition.

Figure 3 shows the J - V characteristics of the devices under AM 1.5G illumination at an irradiation intensity of 100 mW/cm². All devices have the same structure of ITO/PEDOT:PSS/P3HT:PC₇₀BM/Al with the optimal active layer thickness of 200 nm, and the performance parameters of the devices are shown in Table 2. Clearly, the performance of the devices depends greatly on the annealing temperatures. For as-cast condition, the devices show the best performance with PCE of 2.64%. After the annealing process, the devices show the better performance with PCE of 3.53%, V_{oc} of 0.55 V, and J_{sc} of 10.70 mA/cm² at 130°C. This increase can be related to the well-known improvement of the crystallization behavior of the blend components and the optimal nanophase segregation, which leads to higher charge mobility in PSCs [22, 23]. However, with further increasing annealing temperature to 150°C, devices show a lower PCE of around 2.36%, V_{oc} of 0.53 V, J_{sc} of 8.52 mA/cm², and FF of 0.52. This worse performance not only may be related to the organization of P3HT and/or PC₇₀BM but also involved other processes during annealing treatment; for example, excessive thermal annealing will lead to unfavorable coarsening of the acceptor and donor domains, resulting in phase segregation at length scales larger than the exciton diffusion length [22–24].

FIGURE 3: J - V characteristics of the devices with different annealing temperatures, measured under 100 mW/cm^2 illumination (AM 1.5G). The structure of the devices is ITO/PEDOT:PSS/P3HT:PC₇₀BM (200 nm)/Al.

FIGURE 4: J - V characteristics of the devices with different CILs, measured under 100 mW/cm^2 illumination (AM 1.5G). Devices are based on ITO/PEDOT:PSS/P3HT:PC₇₀BM (200 nm)/CILs/Al (with no thermal treatment).

TABLE 3: Photovoltaic parameters of the devices with different CILs, measured under 100 mW/cm^2 illumination (AM 1.5G). The structure of the devices is ITO/PEDOT:PSS/P3HT:PC₇₀BM (200 nm)/Al (with no thermal treatment).

CILs	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)
Al (110 nm)	8.74	0.57	0.54	2.64
LiF (1 nm)/Al (100 nm)	9.60	0.58	0.58	3.23
Ca (5 nm)/Al (100 nm)	10.64	0.59	0.61	3.83

3.3. Effect of Different Cathode Interface Layers on Cells Performance. For the conventional PSCs, cathode interface layers (CILs) require low work functions (WFs) to match with LUMO levels of acceptor materials for charge extraction and transportation. In order to obtain a comprehensive understanding of different CILs influences on device, we chose Al, LiF/Al, and Ca/Al as the cathode and studied the performances for the conventional device structures of ITO/PEDOT:PSS/P3HT:PC₇₀BM (200 nm)/CILs/Al (with no thermal treatment). Figure 4 shows the J - V characteristics of the devices with different CILs under AM 1.5G illumination at an irradiation intensity of 100 mW/cm^2 . Device performance with various CILs is summarized in Table 3.

As shown in Figure 4 and Table 3, the performances of devices change sharply with different CILs. The best device has a PCE of 3.83% with the Ca/Al CIL. The devices based on P3HT:PC₇₀BM with only Al cathode give a PCE of 2.64%. In contrast, the PCE for the device with LiF/Al and Ca/Al cathodes are all enhanced to 3.23% and 3.83%,

respectively. This improvement can be mainly related to the increase of the short-circuit current density and fill factor, which leads to the enhancement of the PCE of the device. The mechanism for the enhanced performance of solar cells upon the implantation of the cathode interlayers might be the formation of a thin dipole layer, leading to lowering of the metal work function and thus to a better energy level alignment at the organic/cathode interface, and the better performances have been achieved. Moreover, Ca is a kind of active metal and may react with C atoms of P3HT, so the stronger interfacial dipole forms across this interface between active layer and Ca/Al CIL, which will facilitate “barrier-free” electron extraction from the LUMOs of PC₇₀BM and improve J_{sc} and FF of devices. Therefore, the best performance has been achieved with a PCE of 3.83% using Ca/Al CIL.

3.4. Effect of ZnO Interfacial Thickness on Device Performance. Transition metal oxides (TMOs) have been widely applied in organic optoelectronic devices [25–27]. Among these TMOs used in polymer solar cells, ZnO is one of the most promising candidates for cathode buffer layer [28]. So in order to understand the effect of thickness of ZnO CIL under the optimized conditions (active layer thickness 200 nm), we fabricated devices with various thickness of ZnO. J - V characteristics under illumination are plotted in Figure 5, and parameters are listed in Table 4.

As shown in Table 4, the parameters of the devices vary significantly with various ZnO thickness except that V_{oc} remains at about $0.57 \pm 0.01 \text{ V}$. The PCE varies from

TABLE 4: Photovoltaic parameters of the devices with different thicknesses of ZnO, measured under 100 mW/cm² illumination (AM 1.5G).

Thickness of ZnO	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)
0 nm	8.74	0.56	0.54	2.64
15 nm	9.07	0.57	0.59	3.05
30 nm	10.87	0.58	0.62	3.91
45 nm	8.46	0.57	0.57	2.75

FIGURE 5: J - V characteristics of the devices with different ZnO thicknesses, measured under 100 mW/cm² illumination (AM 1.5G). The structure of the devices is ITO/PEDOT:PSS/P3HT:PC₇₀BM/ZnO/Al.

3.05% (for the device with ZnO thickness, $L = 15$ nm) to 3.91% (for $L = 30$ nm, the optimum thickness) and back to 2.75% (for $L = 45$ nm). The oscillatory behavior of PCE as a function of ZnO thickness can be attributed to the ability to facilitate efficient electron transfer and extraction from the polymer:fullerene blends with the effect of thickness on ZnO layer conduction. The improved device performance is due to the electron selective interface and ohmic cathode contact, which provides the excellent ability to extract and transfer electron with the increase of ZnO thickness to the optimum thickness; further increasing ZnO thickness leads to lower conduction and an increase of the series resistance [29, 30].

In addition, ZnO can also be used as an optical spacer layer in organic solar cells. Here, the incorporation of ZnO layer between P3HT:PC₇₀BM active layer and aluminum metal electrode might enhance light absorption as a result of redistribution of the optical electrical field in the device, and

FIGURE 6: Active layer thickness dependent simulated spatial distribution of normalized electric field intensity $|E^2|$, assuming a unity IQE and illumination with AM 1.5G for different thicknesses of the ZnO layer.

thus higher photocurrents are obtained. To further understand the effect of ZnO thickness on the electric field distribution in the device, the simulation of the spatial distribution of the squared optical electric field (normalized to the incoming plane wave) for 520 nm light illumination with different ZnO thickness was calculated by the transfer matrix method. The optical constants of PEDOT:PSS, P3HT:PC₇₀BM, ZnO, and Al are obtained with ellipsometry measurements and those of glass substrate ITO have been determined and reported in the literature [31].

Figure 6 shows calculated spatial distribution of the squared optical electric field $|E^2|$ in the active layer of devices with ZnO interfacial layer. Without ZnO optical spacer, the thin photoactive layer with the thickness of 140 nm is situated well in the maximum optical electrical fields. After inserting the ZnO layer, two maxima are observed in the position near 60 and 180 nm. While increasing ZnO spacer thickness the position of the maximum shifts towards thicker active layer. From Figure 6, it is clear to see a modest improvement of the optical electric field intensity by inserting 30 nm ZnO layer. A great increase of exciton generation rate can also be found in ZnO-modified devices. This demonstrates that optical modeling is an accurate tool to predict the improvement of light absorption in the devices with 200 nm active layers and 30 nm ZnO layers as a result of redistribution of the optical electric field inside the device. Thus, we can conclude that the insertion of ZnO layer into devices may be the possible reason for the improved efficiency.

3.5. Effect of Electrode Metal Deposition Rate on Device Performance. In addition, we find that the deposition rate of Al electrode has a great influence on the performance of the device. So the devices with the structure

FIGURE 7: J - V characteristics of the devices with different deposition rates.

TABLE 5: Photovoltaic parameters of the devices with different deposition rate, measured under 100 mW/cm^2 illumination (AM 1.5G).

Deposition rate	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
Fast	8.06	0.54	0.52	2.27
Slow	9.34	0.58	0.56	3.34

of ITO/PEDOT:PSS/P3HT:PC₇₀BM (200 nm)/Al were fabricated, depositing Al onto the active layer at 2.0 Å/s and 14.0 Å/s , respectively. The deposition processes of the materials were carried out in a vacuum chamber at the base pressure of around $2 \times 10^{-4} \text{ Pa}$. The deposition rates of the materials were detected with quartz crystal monitor. The PCE of the devices improves from 2.27% to 3.34% with J_{sc} of 8.06 mA/cm^2 and 9.34 mA/cm^2 under the fast and slow deposition rates, respectively. This suggests that the performance of devices prepared under the slow rate is better. J - V characteristics under illumination are plotted in Figure 7, and parameters of the devices are listed in Table 5.

We attribute this phenomenon to the following aspects. Structural disorders are responsible for intrinsic traps which are mainly related to and controlled by growth conditions for deposited Al electrodes [32]. Slower deposition growth rate leads to reduction in the density of trap states. Fast deposition growth rate, however, results in higher trap density owing to the structural defects. These trap states strongly affect carrier recombination dynamics. Trap-assisted recombination is monomolecular recombination which is aggravated by the presence of high trap density. Therefore, it is clear that the devices prepared under slower deposition growth rate achieve higher performance than those prepared under

faster deposition growth rate. Another reason is the effect of grain size and surface roughness, which can be explained by the fundamental characteristics of the island growth mode. It was found that the root mean square (rms) roughness of the Al films increases with the deposition rate, and the film prepared in fast deposition rate had larger grain size. That is to say, the electrical contact between the Al electrodes and the active layer in the fast deposition rate is worse for the charge collection and transition than that in the slow deposition rate.

3.6. The Stability of the Devices. Due to polymer solar cell made of organic materials, these materials are very prone to react with the water or oxygen in the air, which seriously degrades the performance of the device [33–35]. Diffusion of water or oxygen in atmosphere into the devices causes photo-oxidation of the organic layers, leading to photochemical decomposition of the polymer or the formation of charge transfer complex. These bring about an alteration in the stacking shape of the polymer structure from higher degree of polymer ordering to lower degree of polymer ordering and improve the traps for charge transport [35–37]. The organic/metal electrode interface is also vulnerable towards molecular oxygen and water, and low work function electrodes such as aluminum and calcium can form metal oxides in the interface that consequently will act as a transport barrier causing deterioration of the photovoltaic performance [33, 37, 38]. The lifetime of organic solar cells is affected by the many factors above, and many problems need to be further researched, but in recent years, under the efforts of the researchers, the lifetime of the solar cells exceeds many thousands of hours in favorable circumstances [33, 35]. This progress has been gained by several developments, such as inverted device structures of the devices, the choice of more photostable active materials, and the introduction of interfacial layers [38, 39].

4. Conclusion

The PSCs based on P3HT:PC₇₀BM system have been fabricated and optimized by changing the fabrication processing parameters. The optimized thickness and annealing temperature to achieve the higher PCE are about 200 nm and 130°C , respectively. More absorbed photons and increased crystallization behavior of the blend components lead to the excellent device performance. The effect of cathode interface layers with different work function on cells performance is related to the probable formation of interfacial dipole. Furthermore, the effect of optimum ZnO interfacial thickness ($\sim 30 \text{ nm}$) on device performance is attributed to good interfacial conductivity and its optical property. Metal electrode deposited in the slow rate has a better influence on device performance. The best power conversion efficiency (PCE) of 3.91% was obtained under AM 1.5G 100 mW/cm^2 illumination.

Competing Interests

The authors declare that they have no competing interests.

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References

- [1] G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and A. J. Heeger, "Polymer photovoltaic cells: enhanced efficiencies via a network of internal donor-acceptor heterojunctions," *Science*, vol. 270, no. 5243, pp. 1789–1791, 1995.
- [2] Z. He, C. Zhong, S. Su, M. Xu, H. Wu, and Y. Cao, "Enhanced power-conversion efficiency in polymer solar cells using an inverted device structure," *Nature Photonics*, vol. 6, no. 9, pp. 591–595, 2012.
- [3] H. Z. Yu and J. B. Peng, "Performance and lifetime improvement of polymer/fullerene blend photovoltaic cells with a C_{60} interlayer," *Organic Electronics: Physics, Materials, Applications*, vol. 9, no. 6, pp. 1022–1025, 2008.
- [4] M. C. Scharber and N. S. Sariciftci, "Efficiency of bulk-heterojunction organic solar cells," *Progress in Polymer Science*, vol. 38, no. 12, pp. 1929–1940, 2013.
- [5] X. Guo, N. Zhou, S. J. Lou et al., "Polymer solar cells with enhanced fill factors," *Nature Photonics*, vol. 7, no. 10, pp. 825–833, 2013.
- [6] A. J. Heeger, "25th anniversary article: bulk heterojunction solar cells: understanding the mechanism of operation," *Advanced Materials*, vol. 26, no. 1, pp. 10–28, 2014.
- [7] Y. Liu, J. Zhao, Z. Li et al., "Aggregation and morphology control enables multiple cases of high-efficiency polymer solar cells," *Nature Communications*, vol. 5, article 5293, 2014.
- [8] Z. He, B. Xiao, F. Liu et al., "Single-junction polymer solar cells with high efficiency and photovoltage," *Nature Photonics*, vol. 9, no. 3, pp. 174–179, 2015.
- [9] J. You, L. Dou, K. Yoshimura et al., "A polymer tandem solar cell with 10.6% power conversion efficiency," *Nature Communications*, vol. 4, article 1446, 2013.
- [10] H. Zhou, Y. Zhang, C.-K. Mai et al., "Polymer homo-tandem solar cells with best efficiency of 11.3%," *Advanced Materials*, vol. 27, no. 10, pp. 1767–1773, 2015.
- [11] A. R. B. M. Yusoff, D. Kim, H. P. Kim, F. K. Shneider, W. J. Da Silva, and J. Jang, "A high efficiency solution processed polymer inverted triple-junction solar cell exhibiting a power conversion efficiency of 11.83%," *Energy and Environmental Science*, vol. 8, no. 1, pp. 303–316, 2015.
- [12] G. Li, R. Zhu, and Y. Yang, "Polymer solar cells," *Nature Photonics*, vol. 6, no. 3, pp. 153–161, 2012.
- [13] W. Cai, X. Gong, and Y. Cao, "Polymer solar cells: recent development and possible routes for improvement in the performance," *Solar Energy Materials and Solar Cells*, vol. 94, no. 2, pp. 114–127, 2010.
- [14] J. Mei, K. R. Graham, R. Stalder, and J. R. Reynolds, "Synthesis of isoindigo-based oligothiophenes for molecular bulk heterojunction solar cells," *Organic Letters*, vol. 12, no. 4, pp. 660–663, 2010.
- [15] H. Zhou, L. Yang, and W. You, "Rational design of high performance conjugated polymers for organic solar cells," *Macromolecules*, vol. 45, no. 2, pp. 607–632, 2012.
- [16] L. Lu and L. Yu, "Understanding low bandgap polymer PTB7 and optimizing polymer solar cells based on IT," *Advanced Materials*, vol. 26, no. 26, pp. 4413–4430, 2014.
- [17] W. Ma, C. Yang, X. Gong, K. Lee, and A. J. Heeger, "Thermally stable, efficient polymer solar cells with nanoscale control of the interpenetrating network morphology," *Advanced Functional Materials*, vol. 15, no. 10, pp. 1617–1622, 2005.
- [18] D. W. Sievers, V. Shrotriya, and Y. Yang, "Modeling optical effects and thickness dependent current in polymer bulk-heterojunction solar cells," *Journal of Applied Physics*, vol. 100, no. 11, Article ID 114509, 2006.
- [19] S. H. Park, A. Roy, S. Beaupré et al., "Bulk heterojunction solar cells with internal quantum efficiency approaching 100%," *Nature Photonics*, vol. 3, no. 5, pp. 297–303, 2009.
- [20] G. Li, V. Shrotriya, Y. Yao, and Y. Yang, "Investigation of annealing effects and film thickness dependence of polymer solar cells based on poly(3-hexylthiophene)," *Journal of Applied Physics*, vol. 98, no. 4, Article ID 043704, 2005.
- [21] N. M. Murari, M. J. Crane, T. Earmme, Y.-J. Hwang, and S. A. Jenekhe, "Annealing temperature dependence of the efficiency and vertical phase segregation of polymer/polymer bulk heterojunction photovoltaic cells," *Applied Physics Letters*, vol. 104, no. 22, Article ID 223906, 2014.
- [22] Y. Huangzhong, "Different solvents effect on the performance of the solar cells based on poly(3-hexylthiophene):methanofullerenes," *Synthetic Metals*, vol. 160, no. 23–24, pp. 2505–2509, 2010.
- [23] Y. Yao, J. Hou, Z. Xu, G. Li, and Y. Yang, "Effects of solvent mixtures on the nanoscale phase separation in polymer solar cells," *Advanced Functional Materials*, vol. 18, no. 12, pp. 1783–1789, 2008.
- [24] M. T. Dang, L. Hirsch, and G. Wantz, "P3HT:PC₇₀BM, best seller in polymer photovoltaic research," *Advanced Materials*, vol. 23, no. 31, pp. 3597–3602, 2011.
- [25] V. Shrotriya, G. Li, Y. Yao, Ch. W. Chu, and Y. Yang, "Transition metal oxides as the buffer layer for polymer photovoltaic cells," *Applied Physics Letters*, vol. 88, no. 7, Article ID 073508, 2006.
- [26] J. Meyer, S. Hamwi, M. Kröger, W. Kowalsky, T. Riedl, and A. Kahn, "Transition metal oxides for organic electronics: energetics, device physics and applications," *Advanced Materials*, vol. 24, no. 40, pp. 5408–5427, 2012.
- [27] H. Yu, Y. Ge, and S. Shi, "Improving power conversion efficiency of polymer solar cells by doping copper phthalocyanine," *Electrochimica Acta*, vol. 180, pp. 645–650, 2015.
- [28] Z. Liang, Q. Zhang, L. Jiang, and G. Cao, "ZnO cathode buffer layers for inverted polymer solar cells," *Energy and Environmental Science*, vol. 8, no. 12, pp. 3442–3476, 2015.
- [29] J.-P. Liu, K.-L. Choy, and X.-H. Hou, "Charge transport in flexible solar cells based on conjugated polymer and ZnO nanoparticulate thin films," *Journal of Materials Chemistry*, vol. 21, no. 6, pp. 1966–1969, 2011.
- [30] H. Y. Park, D. Lim, K. D. Kim, and S. Y. Jang, "Performance optimization of low-temperature-annealed solution-processable ZnO buffer layers for inverted polymer solar cells," *Journal of Materials Chemistry A*, vol. 1, no. 21, pp. 6327–6334, 2013.
- [31] P. Morvillo, E. Bobeico, and S. Esposito, "The influence of the fullerene on the optical constants of the photoactive blend film of a polymer solar cell," *Advances in Science and Technology*, vol. 74, pp. 164–169, 2010.
- [32] A. Sharma, S. Yadav, P. Kumar, S. Ray Chaudhuri, and S. Ghosh, "Defect states and their energetic position and distribution in organic molecular semiconductors," *Applied Physics Letters*, vol. 102, no. 14, Article ID 143301, 2013.

- [33] S. A. Gevorgyan, M. V. Madsen, B. Roth et al., "Lifetime of organic photovoltaics: status and predictions," *Advanced Energy Materials*, vol. 6, no. 2, Article ID 1501208, 2016.
- [34] G. Griffini and S. Turri, "Polymeric materials for long-term durability of photovoltaic systems," *Journal of Applied Polymer Science*, vol. 133, no. 11, Article ID 43080, 2016.
- [35] M. Jørgensen, K. Norrman, S. A. Gevorgyan, T. Tromholt, B. Andreasen, and F. C. Krebs, "Stability of polymer solar cells," *Advanced Materials*, vol. 24, no. 5, pp. 580–612, 2012.
- [36] J. J. Michels, M. Peter, A. Salem, B. van Remoortere, and J. van den Brand, "A combined experimental and theoretical study on the side ingress of water into barrier adhesives for organic electronics applications," *Journal of Materials Chemistry C*, vol. 2, no. 29, pp. 5759–5768, 2014.
- [37] M. Giannouli, V. M. Drakonakis, A. Savva, P. Eleftheriou, G. Florides, and S. A. Choulis, "Methods for improving the lifetime performance of organic photovoltaics with low-costing encapsulation," *ChemPhysChem*, vol. 16, no. 6, pp. 1134–1154, 2015.
- [38] K. Feron, T. J. Nagle, L. J. Rozanski, B. B. Gong, and C. J. Fell, "Spatially resolved photocurrent measurements of organic solar cells: tracking water ingress at edges and pinholes," *Solar Energy Materials and Solar Cells*, vol. 109, pp. 169–177, 2013.
- [39] H. C. Weerasinghe, D. Vak, B. Robotham, C. J. Fell, D. Jones, and A. D. Scully, "New barrier encapsulation and lifetime assessment of printed organic photovoltaic modules," *Solar Energy Materials and Solar Cells*, vol. 155, pp. 108–116, 2016.