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Effects of the Morphology of a ZnO Buffer Layer on the Photovoltaic Performance of Inverted Polymer Solar Cells

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The influences of morphology and thickness of zinc oxide (ZnO) buffer layers on the performance of inverted polymer solar cells are investigated. ZnO buffer layers with different morphology and thickness varying from several nanometers to ~55 nm are fabricated by adjusting the concentration of the precursor sol. The ZnO buffer layers with nearly same surface quality but with thickness varying from \approx 7 to \approx 65 nm are also fabricated by spinning coating for comparison. The photovoltaic performance is found to be strongly dependent on ZnO surface quality and less dependent on the thickness. The use of dense and homogenous ZnO buffer layers enhances the fill factor and short-circuit current of inverted solar cell without sacrificing the opencircuit voltage of device due to an improvement in the contact between the ZnO buffer layer and the photoactive layer. Inverted devices with a dense and homogenous ZnO buffer layer derived from 0.1 M sol exhibit an overall conversion efficiency of 3.3% which is a 32% increase compared to devices with a rough ZnO buffer layer made from 1 M sol, which exhibited a power conversion efficiency of 2.5%. The results indicate that the efficiency of inverted polymer solar cells can be significantly influenced by the morphology of the buffer layer.

1. Introduction

Polymer solar cells (PSCs) based on polymer–fullerene composites have attracted considerable attention as a promising alternative to conventional silicon-based solar cells due to their cost effectiveness and potential applications requiring light weight materials on flexible substrates.^[1–7] Much effort has been made toward improving the power conversion efficiency (PCE) of PSCs, which has recently reached over 8% through a use of novel polymers and control of the active layer morphology with a conventional structure.^[8] These conventional bulk heterojunction

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(BHJ) PSCs are designed with an active layer sandwiched by a hole conducting poly(3,4 ethylenedioxylenethiophene):poly (styrene sulfonic acid) (PEDOT:PSS) layer on top of an indium tin oxide (ITO) glass as the anode and a low-work-function metal (typically aluminum) as the cathode. However, in spite of the high PCE, there are several drawbacks with the conventional device architecture. The oxidation of the air-sensitive, low-work-function metal (usually Al) cathode and etching of ITO by the acidic PEDOT:PSS hole-transporting layer are the most common reasons for instability in conventional device architecture.^[9-12] One strategy to solve this issue and to improve the device lifetime is to use an inverted device architecture where the nature of charge collection is reversed.^[13,14] In the inverted structure, the interface of ITO/PEDOT:PSS can be avoided and the air-sensitive, low-workfunction Al can be replaced with air-stable, high-work-function metals such as Au and Ag. Recently, an inverted structure with a

transparent electron-collecting electrode has demonstrated significant improvement in the air stability of the solar cell.^[13–15] However, it has been reported that PSCs with an inverted device structure based on poly(3-hexylthiophene):phenyl-C₆₁-butyric acid methyl ester (P3HT:PCBM) composite exhibited PCEs from 2–4%,^[16–18] which is lower than that obtained in PSCs with normal device structure. Further improvement in device structure is required for the inverted structure PSCs to reach its full potential.

In solar cells with an inverted structure, a high work function metal is used as a hole-collecting electrode, while the ITO electrode is inserted with a thin film of an n-type metal oxide such as zinc oxide (ZnO), titanium oxide (TiO_x), cesium carbonate (Cs₂CO₃), or aluminum oxide (Al₂O₃) as the buffer layer.^[5,19–23] The buffer layer works as an electron-collecting electrode and a hole-blocking layer, which is essential for achieving high efficiency PSCs.^[5,23] Recently, ZnO has drawn much attention in serve as the buffer layer because it has good transparency across the whole visible spectral range, relatively high electron mobility, and environmental stability.^[24,25] In addition, in inverted devices, the ZnO layer can enhance the operational stability of PSCs by blocking the UV-light-induced



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photodegradation of organic materials.^[14] Another merit of ZnO as the buffer layer is that it can be easily processed via a solution method followed by thermal annealing at relatively low temperature, making ZnO fully compatible with roll-to-roll type fabrication onto flexible substrates.^[7,26–28] In fact, ZnO is the only buffer layer material that has been widely explored in PSCs and fabricated by a roll-to-roll processing technique.^[6,29–31] All of these features make ZnO an ideal buffer layer material for PSCs with inverted structures. Recently, many methods have been employed for producing the ZnO buffer layer in inverted structure PSCs. These methods include solution-processed sol-gel,^[32] nanoparticles approaches,^[33] sputtering, and atomic layer deposition (ALD).^[17,34,35]

The overall performance of PSCs with an inverted device structure is sensitive to the electrical properties of the interfaces between the buffer layer and the photoactive layer.^[20] The contact resistance between the photoactive layer and the electrode buffer laver can strongly impact the charge collection.^[36] The morphology of the ZnO buffer layer plays a critical role in determining the contact quality because of the significant difference in surface energy between the ZnO buffer layer and the P3HT:PCBM blend active layer.^[37] However, studies on the influences of the morphology of ZnO buffer layers on photovoltaic properties of inverted PSCs have been very limited.^[38,39] Moreover, the effects of the morphology and thickness of the ZnO buffer layer on the device performance are still not clear. Thus, it is crucial to investigate the influences of both the thickness and the morphology of the ZnO buffer layer on device performance.

This paper reports a systematic experimental study of the influences of morphology and thickness of ZnO buffer layers on the photovoltaic properties of inverted PSCs, ITO/ZnO/P3HT:PCBM/PEDOT:PSS/Ag with a stacked structure, as shown in **Figure 1a**. The energy level diagram of the inverted cell is depicted in Figure 1b. The sol-gel method was employed to fabricate the ZnO buffer layers on the top of the ITO substrates. The sol-gel method was chosen because the growth of the ZnO layer based on this method has very well-controlled morphology and thickness on the nanometer scale. In addition, different from traditional deposition by physical methods, the sol-gel method offers a simple, low-cost, and highly controlled method for ZnO film preparation.^[40,41]

The ZnO layers with different morphology and thickness varying from several nanometers to ≈55 nm were prepared by adjusting the concentrations of sol from 0.02 to 1 mol L^{-1} (M). The ZnO layers with nearly the same morphology but thickness ranging from ≈7 to ≈65 nm were also fabricated by spin-coating 0.1 M sol with increasing times for comparison. The morphology of the ZnO buffer layers was investigated using scanning electron microscopy (SEM) and atomic force microscopy (AFM). A correlation between the morphology and the PCE in inverted PSCs could then be established with the possibility to enhance the device performance for a specific change of the surface morphology. As for the 3.3% efficiency, compared with the reported inverted PSCs based on P3HT:PCBM composites, which exhibited PCEs around 2–4%,^[16–18] the 3.3% efficiency is still of interest. The experimental results showed that the morphology of the ZnO buffer layers have a significant impact on the photovoltaic properties of the inverted devices, with a 32% increase in PCE.

2. Results and Discussion

For all the inverted devices investigated in this study, the only changes made from device to device were the morphology and thickness of the ZnO buffer layers; all the other components, including the chemical composition and microstructures, were controlled to be exactly the same as far as the lab facilities permit. Here, two sets of ZnO layers were fabricated to investigate the influence of the morphology and thickness on a device's photovoltaic performance. The first set of devices, A, B, C, D, E, and F, with ZnO buffer layers were fabricated by spin-coating 0.02, 0.05, 0.1, 0.3, 0.6, and 1 M sol one time, respectively. The second set of devices, G, H, I, and J, with ZnO buffer layers were obtained by spin-coating 0.1 M sol 3, 5, 7, and 10 times, respectively.

The current–voltage (*J*–*V*) curves of the two sets of inverted devices are shown in **Figure 2**a,b and extracted devices parameters are summarized in **Table 1** and **2**. In addition, the thickness and roughness of the ZnO buffer layers, as well as the series resistance (R_S) and shunt resistance (R_{SH}) of all the devices, are also included in the tables. For the first set of devices (A–F), the photovoltaic performance was found to be dependent on the



Figure 1. a) Device structure of the inverted PSCs with the ZnO buffer layer and b) the corresponding energy level diagram of the components of the device.



Figure 2. *J*–*V* characteristics of devices with ZnO buffer layers. a) ZnO buffer layers of devices A, B, C, D, E, and F, which are derived from 0.02, 0.05, 0.1, 0.3, 0.6, and 1 M sol, respectively. b) ZnO buffer layers of devices G, H, I, and J are derived from 0.1 M sol with spin-coating 3, 5, 7, and 10 times, respectively.

concentration of ZnO sol, with two regimes below and above 0.1 м. From Figure 2a and Table 1, one can see that the devices with ZnO buffer layers that were deposited by spin coating 0.02, 0.05, and 0.1 M sol showed a significant enhancement in fill factor (FF) from 0.35 to 0.56 and an appreciable increase in $I_{\rm SC}$ from 8.76 to 9.59 mA cm⁻². The open circuit voltage, $V_{\rm OC}$, was also seen to increase from 0.59 to 0.61 V. Consequently, the PCE increased from 1.82% to 3.3%. When the ZnO laver was obtained from the sol with concentration over 0.1 M, the increase in the sol concentration resulted in a decrease in the FF decreased from 0.56 to 0.44 and the J_{SC} was reduced from 9.59 mA cm⁻² to 9.15 mA cm⁻²; the $V_{\rm OC}$ remained unchanged. Figure 2b and Table 2 show that for the second set of devices (G–J) with ZnO buffer layer, obtained by spin-coating 0.1 M sol for different times, the photovoltaic performances of the devices are nearly the same.

It is known that the transmittance of the oxide buffer layer plays an important role in the device performance of invented polymer solar cells.^[32] **Figure 3** shows the optical transmittance spectra of two sets of ZnO buffer layers in the UV–visible wavelength range (300–900 nm).

From Figure 3a,b, it can be observed that all the ZnO layers show good optical transmittance. In the case of uncoated ITO, the transmittance is about 80% over the visible wavelength range. After coating with ZnO films, the sharp absorption edge of the ITO/ZnO layers exhibits a gradual shift towards 380 nm, corresponding to the energy gap, 3.2 eV for ZnO, with increased film thickness. Inversely, the transmittances of the ITO/ZnO layers at around 450 nm are higher than the bare ITO and increase with the increasing ZnO layer thickness. This increase in transmittance of the ITO/ZnO layers at around 450 nm should be attributed to the antireflection caused by the ZnO coatings on the surface of the ITO substrates.^[42] The increased transmittance of the ITO/ZnO layers should be beneficial to the devices' photovoltaic properties. Here, we first proposed a new parameter and name it the "relative optical transmittance" (T_R); it quantitatively investigates the effects of the buffer layer transmittance on the optical absorption of the given active layer in PSCs. The T_R can be calculated from the measured transmittance of a given active layer (here the blend of P3HT/PCBM layer) using the formula:

$$T_{\rm R} = \frac{\int_{\lambda_2}^{\lambda_1} I_{\lambda} t_{\lambda} d\lambda}{\int_{\lambda_2}^{\lambda_1} I_{\lambda} d\lambda}$$
(1)

where t_{λ} is the measured transmittance spectrum of the ITO/ ZnO buffer layer at λ wavelength, I_{λ} is the absorption spectrum intensity of the P3HT:PCBM active layer at wavelength λ , and the λ_1 and λ_2 correspond to 300 and 900 nm in this work.

Based on the above-mentioned definition, the T_R reveals the influence of the ZnO buffer layer transmittance on the optical absorption of active layer. A higher T_R means the more optical absorption of the active layer, resulting in the better

Table 1. Average devices performance of inverted PSCs with the first set of ZnO buffer layers deposited by spin-coating 0.02, 0.05, 0.1, 0.3, 0.6, and1 M sol one time. The averages were obtained by testing three devices.

Device	ZnO RMS [nm]	ZnO Thickness [nm]	V _{oc} [V]	J _{sc} [mA cm ⁻²]	FF	PCE [%]	$R_{ m S}$ $[\Omega~{ m cm}^2]$	$R_{ m SH}$ $[\Omega~ m cm^2]$
A	4.25	≈2	0.59	8.76	0.35	1.82	47.9	375.3
В	3.71	≈4	0.60	9.17	0.52	2.90	20.6	785.7
С	2.86	≈7	0.61	9.59	0.56	3.30	10.7	1007.7
D	3.49	≈20	0.61	9.48	0.51	2.99	11.7	763.5
E	4.00	≈35	0.61	9.42	0.51	2.94	18.6	700.1
F	4.02	≈55	0.61	9.15	0.44	2.50	31.7	551.6



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Table 2. Devices performance of inverted PSCs with the second set of ZnO buffer layers deposited by spin-coating 0.1 M sol 3 (G), 5 (H), 7 (I) and 10 (J) times.

Device	ZnO RMS [nm]	ZnO Thickness [nm]	V _{oc} [V]	J _{sc} [mA cm ⁻²]	FF	PCE [%]	$R_{ m S}$ $[\Omega~{ m cm}^2]$	R _{SH} [Ω cm²]
G	2.68	≈20	0.62	9.34	0.54	3.10	11.6	951.2
н	2.52	≈30	0.62	9.10	0.56	3.12	11.8	1015.0
I	2.50	≈50	0.61	9.38	0.54	3.06	12.2	1098.3
J	2.06	≈65	0.61	9.27	0.54	3.05	13.8	1034.4

device performance. Based on the measured transmittance and absorption spectra, the $T_{\rm R}$ values were calculated to be 0.72, 0.71. 0.71, 0.70, 0.71, and 0.73 for ZnO buffer layers derived by spin-coating, respectively, 0.02, 0.05, 0.1, 0.3, 0.6, and 1 M sol one time. The values of $T_{\rm R}$ for the ZnO buffer layers deposited by spin-coating 0.1 M sol with 3, 5, 7, and 10 times were 0.70, 0.69, 0.68, and 0.67, respectively. The standard deviations in $T_{\rm R}$ for the two sets of devices were 0.012 and 0.014, respectively, which demonstrated very small variations in $T_{\rm R}$ for both sets. Therefore, the strong variation in the first set of inverted devices performance observed in our solar cells is unlikely to be determined by the transmittance of the ZnO buffer layer in the devices.

Surface morphology and roughness were studied using SEM and AFM to examine their impact on the device performance. Figure 4 shows the SEM images of ZnO layers derived from sols with different concentrations. It can be seen that the ultrathin ZnO films derived from 0.02 $\,{\mbox{\tiny M}}$ and 0.05 $\,{\mbox{\tiny M}}$ sol are so thin that the morphology still shows that of the ITO surface. When the sol concentration is increased to 0.1 M, a dense and homogenous ZnO layer formed with nanoscale ZnO particles can be observed. Further increase of the sol concentration to 0.3, 0.6, and 1 M resulted in an increase of both the ZnO particles size and the pore size of the ZnO layers. The morphology differences revealed from the SEM images is consistent with characterization of the root mean square (RMS) surface roughness measured using AFM analyses are presented in Table 1. The root mean square (RMS) values of the ZnO layers decrease with the increase in sol concentration from 0.02 M to 0.1 M. This means that the increased sol concentration increases the thickness of the ZnO layer and thus decreases the surface roughness of the ITO surface. When the sol concentration is exceeding 0.1 M,



Figure 3. The transmittance spectra of ITO (reference) and ITO/ZnO buffer layers. a) ZnO buffer layers of devices A, B, C, D, E, and F. b) ZnO buffer layers of devices G, H, I, and J.

the RMS slightly increases due to the large ZnO particles and increased pore size in the ZnO layers.

Figure 5 shows the SEM images of ZnO layers obtained by spin-coating 0.1 \mbox{M} sol for different times. All the ZnO layers are dense with a smooth surface, while the ZnO particles size slightly increases with increasing spin-coating time. As a result, the RMS values (presented in Table 2) of all the ZnO layers remain nearly the same with different times for the spin-coatings. In addition, the thickness of the ZnO layers increases from \approx 20 nm to \approx 65 nm with increasing spin-coating time.

The surface morphologies of ZnO layers were also investigated using AFM. All samples were scanned over areas ranging from 500×500 nm² to 2×2 um² at two different locations on the films' surfaces. The AFM 3D images presented in **Figure 6** indicate the surface roughness variation as the ZnO sols increase. This is consistent with the results of SEM analysis shown in Figure 4.

By comparing the performance parameters of two sets devices presented in Table 1 and 2, it is clear that there is an obvious correspondence between the device performance and the ZnO buffer layer surface quality, but not the thickness. In general, the smoother and denser fully covered ZnO layers result in the higher J_{SC} , FF, and PCE. Therefore, we suggest that the surface quality of the buffer layer can make a direct impact on the contact between the active layer and the ZnO layer and, thus, influence the photovoltaic performance of the device.

The contact quality between the ZnO buffer layer and the P3HT:PCBM active layer can be reflected by the values of series resistance (R_S) and shunt resistance (R_{SH}) of the inverted OPCs. It is known that the existence of contact resistance and charge recombination at the interface are the major reasons that give rise to the increase in R_S and the drop in R_{SH} , respec-

tively.^[43] According to literature,^[44,45] the R_{SH} and R_S can be independently calculated from the inverse slope of the *J*–*V* curves of the device at $I = I_{SC}(V = 0)$ and $V = V_{OC}(I = 0)$, respectively. The R_S and R_{SH} of the two sets of devices with the ZnO buffer layer derived from sol with different concentrations or obtained by spin-coating the same sol for different times are shown in Table 1 and 2.

Interestingly, when a ZnO buffer layer was derived from sols with concentration increasing from 0.02 M to 0.05 M, the $R_{\rm SH}$ increased from 375.3 Ω cm² to 785.7 Ω cm². Meanwhile, the $R_{\rm S}$ decreased from 47.9 Ω cm² to 20.6 Ω cm². It is known that the ZnO





Figure 4. SEM images of ZnO buffer layers derived from sol concentrations of A) 0.02, B) 0.05, C) 0.1, D) 0.3, E) 0.6, and F) 1 M.



Figure 5. SEM images of ZnO buffer layers derived from 0.1 M sol and by spin-coating G) 3 times, H) 5 times, I) 7 times, and J) 10 times.



layer can effectively suppress the leakage current at the interface of the active layer and ITO.^[14] Thus, according to the SEM analysis, it is very likely that the increased R_{SH} with increasing sol concentration in the range of 0.02–0.1 M is because the increased coverage of the ZnO buffer layer on the ITO surface effectively prevents the direct contact between the P3HT:PCBM and ITO. On the other hand, the decreased $R_{\rm S}$ results from the improved electron collection and transportation caused by the ZnO laver. However, the ZnO lavers made from both 0.02 м and 0.05 м sol are too thin to obtain a full coverage of the ITO surface, leaving a portion of uncovered ITO in direct contact with the active layer to create a current leakage pathway. This is the reason for the still relatively low R_{SH} . By increasing the concentration of sol to 0.1 M, a complete coverage of the ITO surface was obtained and

the ZnO buffer layer reached a minimum RMS. Such a dense and homogenous surface effectively suppress the leakage current across the direct contact of the P3HT:PCBM/ITO interface and thus increases the R_{SH} . The decrease in R_S indicates that the electron collection and transportation benefits from the high-quality contact between the P3HT:PCBM active layer and the dense and homogenous ZnO buffer layer. As a result, the decreased $R_{\rm S}$ and elevated $R_{\rm SH}$ contribute to the device performance by improving the FF and J_{SC} . The decreased R_S and increased $R_{\rm SH}$ improved the FF to 0.56 in the device with the 0.1 M derived ZnO buffer layer, contributing to the improvement of the devices PCE from 1.82% to 3.3%. When the sol concentration exceeded 0.1 M, the full coverage ZnO buffer layer was also obtained. However, the RMS and the voids size in the ZnO layer were also increased. From the device parameters in Table 1, it could be observed that a further increase of the sol concentration to 0.3, 0.6, and 1 M leads to increased R_S . The increased R_S leads to the FF and the J_{SC} decreased to 0.44 and 9.15 mA cm⁻², respectively, in the device with the 1 M derived ZnO buffer layer. It is evident that this decrease in FF and J_{SC} directly results in the decrease of the PCE from 3.3% to 2.5%. It is worth noting



Figure 6. 3D AFM iamges of the ZnO buffer layers of devices A, B, C, D, E, and F, which were deposited by spin-coating 0.02, 0.05, 0.1, 0.3, 0.6, and 1 M sol one time.

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Figure 7. Device structures and P3HT:PCBM/ZnO interfaces conditions for the inverted PSCs with ZnO buffer layers derived from a) 0.1 ${\rm M}$ and b) 1 ${\rm M}$ sol.

that the contact resistance between the ZnO buffer layer and the photoactive layer affects the R_s more significantly than the resistance of the ZnO buffer layer itself. Due to the large difference in surface energy between the ZnO buffer layer and the P3HT:PCBM blend active layer,^[37] it is diffcult for the blend of P3HT:PCBM solution to fully penetrate the voids in the ZnO buffer layers. As a result, the ZnO buffer layer, with its dense and homogenous surface, allows an intimate contact with the blend of the P3HT:PCBM photoactive layer, while a rough surface may trap some voids leading to inferior contact. **Figure 7** is a simplified cross-section schematic showing the P3HT:PCBM/ ZnO interfaces with different ZnO surface morphology; it is suggested that the voids exist at the interface when ZnO has a rough surface, resulting in increased R_s and deceased R_{SH} .

As shown in Table 1, all the devices with ZnO layers derived from 0.1 $\,_{M}$ sol, regardless of coating time, have almost the same $R_{\rm S}$ and $R_{\rm SH}$. As a result, all the devices have a high PCE of \approx 3.1%. The ZnO buffer layers in these devices have similar dense and homogenous surfaces but increase in thickness with the increasing ZnO sol concentration, as the analysis results of the SEM images in Figure 5 show. Therefore, the above results suggest again that the surface quality, but not the thickness, of the ZnO buffer layer has a direct impact on the photovoltaic performance of solar cells.

It should be note that, in Figure 2a, some inflection points, or the so-called "s-shaped" kink, can be observed on the J-V curves of devices (A) and (B), which are based on ZnO buffer layers derived from 0.02 M and 0.05 M sol, respectively. A possible reason is that the ZnO buffer layers derived from 0.02 M and 0.05 M sol are so thin (several nanometers) that the presence of oxygen at the grain boundaries reduces the conductivity of these layers.^[17,46] In the literature, the inflection points in polymer solar cells have been explained to be due to the low conductivity of the ZnO layer.^[17,46] UV illumination is a method that can remove the inflection point by enhancing the electrical conductivity of the ZnO layer.^[46] However, for the practical application of PSCs, an UV filter is usually employed to



Figure 8. The EQE of the device with the ZnO buffer layer derived from 0.1 $\ensuremath{\mathsf{M}}$ sol.

prolong the lifetime of the device and, therefore, the UV illumination cannot work for the purpose of removing the inflection points. In this respect, doping of ZnO to enhance the conductivity of the buffer layer is another promising route to solve the inflection point problem.^[47,48] The doping of ZnO can also improve the morphology of the ZnO buffer layer by providing a smoother surface with adjustment of the doping parameters.^[38,49] This benefits the contact of the ZnO/polymer interface and thus improves device performance.

Shown in **Figure 8** is the spectrum of the external quantum efficiency (EQE) of the device with the ZnO buffer layer derived from 0.1 M sol. The figure shows this device, (C), which has the optimum ZnO buffer layer, has a maximum EQE of 69% at the wavelength of 550 nm.

3. Conclusions

Inverted polymer solar cells with sol-gel derived ZnO buffer layers with varying morphology and thickness were investigated. The device performance was found to be strongly dependent on the ZnO morphology rather than the thickness. The analysis of the ZnO layers' optical transmittance and the calculations of $T_{\rm R}$ indicate that the thickness of the ZnO buffer layers has only a negligible impact on the device performance. However, the morphology of the ZnO layers plays a direct, important role in the contact quality between the active layer and the ZnO buffer layer. The dense and homogenous ZnO layer results in a better contact between the photoactive layer and the ZnO layer, which effectively lowers the contact resistance and causes a decreased $R_{\rm S}$ of the device. The existence of voids and large surface roughness of the ZnO buffer layers causes an increase in the $R_{\rm S}$ due to the inferior contact between the ZnO buffer layer and photoactive layer. The inverted devices showed an overall conversion efficiency of 3.3% with a dense and homogenous ZnO buffer layer derived from 0.1 M sol. This conversion efficiency is enhanced by 32% compared to the devices with a rough ZnO buffer layer made from 1 M sol, which exhibited a PCE of 2.5%. All the results indicate that the morphology of the ZnO buffer layer plays an important role in the device performance.

4. Experimental Section

Materials: Regioregular P3HT (4002-E grade) was purchased from Rieke Metals, Inc. PCBM (99.0% purity) was purchased from American Dye Source, Inc., Canada. The PEDOT:PSS (Clevios 4083) was purchased from H. C. Starck. Zinc acetate (Zn(CH₃COO)₂, 98.0%), 2-methoxy ethanol (CH₃OCH₂CH₂OH, 99.0%), and monoethanolamine (NH₂CH₂CH₂OH–2H₂O, 99.0%) were purchased from Sigma-Aldrich. All the chemicals were used as received without further purification. The ITO-coated glass (10–15 Ω sq⁻¹) substrates were purchased from Colorado Concept Coatings LLC. Samples were prepared on ITO substrates (~2.25 cm²), which were cleaned prior to use by ultrasonic agitation in a detergent solution, acetone, and isopropyl alcohol, and then dried under nitrogen flow.

Preparation of the ZnO Buffer Layers: Zinc acetate dehydrate was first dissolved in a mixture of 2-methoxy ethanol and monoethanolamine at room temperature. The concentration of zinc acetate was adjusted from 0.02 M to 1 M and the molar ratio of monoethanolamine to zinc acetate was kept at 1:1. The resulting solution was stirred using a magnetic stirrer at 60 °C for 2 h to yield a homogeneous, clear, and transparent sol. The ZnO layers were spin-coated after the prepared solution was aged at room temperature for one day in order to make it more glutinous. The sols were dropped onto ITO glass substrates, which were then spun at 3000 rpm for 30 s. After processing, the samples were immediately baked at 300 °C for 10 min and subsequently annealed at 350 °C for 20 min in air to convert the zinc acetate to ZnO. Throughout the device fabrication process, we fixed all the process parameters except the concentration of sol.

Device Fabrication and Characterization: The chlorobenzene solution of P3HT:PCBM (1:0.8 by weight) containing (20 mg mL⁻¹) P3HT and (16 mg mL $^{-1})$ PCBM) was stirred in glovebox at 60 $^\circ C$ overnight. The solution was allowed to cool to room temperature and then filtered through a 0.2 µm polytetrafluoroethylene (PTFE) filter. First, the P3HT:PCBM blend solution was spin-coated onto the ITO substrates with the ZnO buffer layer at 1000 rpm for 30 s, which were first pretreated with air plasma for 10 min. Then the samples were baked at 225 °C for 1 min to help self-organization of P3HT, as well as to drive away residual solvent and assist the polymer contact with the ZnO buffer layer. Then, the diluted PEDOT:PSS (Clevios P VP AL 4083) solution was spin-coated onto the active layer to form the hole-transport layer. The films were then baked at 120 °C for 10 min. A 100 nm thick Ag film was finally deposited under a vacuum of 2×10^{-6} Torr as the top electrode. The *J*–V characteristics of the solar cell were tested in a glovebox using a Keithley 2400 source measurement unit and an Oriel Xenon lamp (450 W) coupled with an AM1.5 filter. A silicon solar cell certificated by the NREL was used as a reference to calibrate the measurement conditions. The light intensity used in this study was 100 mW cm⁻².

ZnO Buffer Layer Characterization: The surface morphologies of the specimens were obtained using SEM (Philips, JEOL JSM7000) and AFM. AFM measurement s were carried out on an Asylum Research (MFP-3D Stand Alone AFM) operated in tapping mode. Optical transmittance spectra were recorded using a Thermo Fisher Scientific (EVO30 PC) UV–vis recording spectrophotometer over the wavelength range between 300 and 900 nm.

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