Polymer Solar Cells with 90% External Quantum Efficiency Featuring an Ideal Light- and Charge-Manipulation Layer

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Rapid progress in the power conversion efficiency (PCE) of polymer solar cells (PSEs) is beneficial from the factors that match the irradiated solar spectrum, maximize incident light absorption, and reduce photogenerated charge recombination. To optimize the device efficiency, a nanopatterned ZnO:Al₂O₃ composite film is presented as an efficient light- and charge-manipulation layer (LCML). The Al₂O₃ shells on the ZnO nanoparticles offer the passivation effect that allows optimal electron collection by suppressing charge-recombination loss. Both the increased refractive index and the patterned deterministic aperiodic nanostructure in the ZnO:Al₂O₃ LCML cause broadband light harvesting. Highly efficient single-junction PSCs for different binary blends are obtained with a peak external quantum efficiency of up to 90%, showing certified PCEs of 9.69% and 13.03% for a fullerene blend of PTB7:PC₇₁BM and a nonfullerene blend, FTAZ:IDIC, respectively. Because of the substantial increase in efficiency, this method unlocks the full potential of the ZnO:Al₂O₃ LCML toward future photovoltaic applications.

Polymer solar cells (PSCs) hold great promise as clean and renewable energy sources due to their superior features, such as simple fabrication process, light weight, and potential application in flexible devices.^[1–11] In recent years, rapid progress in PSCs has been achieved with the certified power conversion

efficiency (PCE) exceeding 13% by employing new designed donor/acceptor materials,^[12–15] sophisticated morphology engineering,^[9,16–18] or novel device architectures.^[19,20] The external quantum efficiency (EQE), (or the incident-photon-to-converted-current efficiency, IPCE) is defined as the ratio of the number of collected photogenerated charges to the number of incident photons of a given wavelength, which represents the light harvesting capability in PSCs. Nevertheless, it is noteworthy that the peak EQE in the majority of single-junction PSCs consisting of either binary or ternary donor/acceptor bulk-heterojunction is still considerably below 80% due to limited light absorption in a thin active layer (<200 nm) and serious monomolecular/bimolecular charge recombination loss induced by low carrier mobility of organic materials

and poor interface contact for charge collection.^[16,21–24] In this respect, promoting charge collection and improving light absorption become important issues for further enhancing the efficiency of PSCs.

A variety of interface engineering methods have been explored to enhance the EQE with an ultrathin polyelectrolyte interlayer or a modified metal oxide layer (e.g., ZnO) between the electrode and active layer.^[23–27] The improved charge collection toward the electrodes has been achieved along with the reduced nonohmic contact losses, charge recombination losses and exciton quenching at the interfaces. Meanwhile, light manipulation has also been becoming a popular strategy to boost light absorption efficiency and increase the short-circuit current (J_{SC}). For example, the grating, nanobowls, or metal nanoparticles have been incorporated into substrate surface, charge extraction layers, or the active layers, which can induce the light trapping due to the antireflection, light scattering, or plasmonic resonance effect.^[28–33] Specially, our previous work has been demonstrated that the deterministic aperiodic nanostructure (DAN) can function as an efficient wavelength-/angle-independent light trapping scheme in PSCs.^[6]

Here, we demonstrate an effective method for the fabrication of highly efficient single-junction PSCs by using a nanostructure-patterned Al₂O₃-doped ZnO (denoted as ZnO:Al₂O₃) composite film as a light- and charge-manipulation layer (LCML) to simultaneously guide the incident light within the active layers for sufficient light absorption as well as to improve the electron

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collection with suppressed recombination loss (**Figure 1a**). The Al_2O_3 shells on ZnO nanoparticles offer the passivation effect and the formation of an interface dipole layer to optimize the electron collection with dramatically suppressed charge recombination loss. The increased refractive index and the incorporation of nanoimprinted DAN in the $\text{ZnO}:\text{Al}_2\text{O}_3$ LCML result in a broadband self-enhanced light absorption without sacrificing the fill factor (FF) and open-circuit voltage (V_{OC}). Highly efficient single-junction PSCs are obtained with peak EQE values approaching 90%, and certified PCEs of 9.69% and 13.03% for the fullerene-based active layer of thieno[3,4-*b*]thiophene/benzodithiophene:[6,6]-phenyl C71-butyric acid methyl ester (PTB7:PC₇₁BM) and the nonfullerene FTAZ:IDIC active layer, respectively (see the chemical structures in **Figure 1b**).

The $\text{ZnO}:\text{Al}_2\text{O}_3$ films were fabricated via a sol-gel method on indium-tin oxide (ITO) glass substrate by first preparing the

ZnO precursor as reported in the literature,^[34] and subsequently adding a defined amount of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ into the ZnO precursor. Then the modified ZnO precursor solution was stirred at 80 °C for 2 h. The film properties of various $\text{ZnO}:\text{Al}_2\text{O}_3(x\%)$ films were systematically characterized, where x is the molar concentration of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. As characterized by X-ray photoelectron spectroscopy (XPS) in **Figure 1c**, the peak intensity of Al 2p core level increases with the increasing Al_2O_3 content, and its peak position at 74.3 eV corresponds to the Al^{3+} cation of Al_2O_3 .^[35] Meanwhile, the Zn 2p_{3/2} peak remains at the almost same position. These results reveal the fact that the Al_2O_3 is only the production of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$.^[36] **Figure 1d** displays the second electron cut-off (SECO) region of ultraviolet photoelectron spectroscopy (UPS) spectra of various $\text{ZnO}:\text{Al}_2\text{O}_3(x\%)$ films, where the work function (ϕ) of $\text{ZnO}:\text{Al}_2\text{O}_3(x\%)$ films can be extracted

Figure 1. a) Device structure of PSCs incorporating a DAN-patterned $\text{ZnO}:\text{Al}_2\text{O}_3$ LCML. b) Chemical structures of FTAZ, IDIC, PTB7, and PC₇₁BM. c) XPS Al 2p and Zn 2p_{3/2} core level spectra, d) SECO region of UPS spectra, e) PL spectra, and f) SEM images of $\text{ZnO}:\text{Al}_2\text{O}_3(x\%)$ films with various molar concentrations.

from the SECO as summarized in Table S1 (Supporting Information). It is found that the increase of Al_2O_3 content from 0% to 15% causes a continuous decrease in ϕ from 4.2 to 3.9 eV. The ϕ change in $\text{ZnO}:\text{Al}_2\text{O}_3(x\%)$ films can be ascribed to the formation of an interface dipole layer between ZnO and Al_2O_3 due to their difference in oxygen areal density (OAD) that drives the oxygen ion diffusion from high OAD oxide of Al_2O_3 to the ZnO.^[37] As presented in Figure S1 (Supporting Information) of the schematic energy level diagrams, in which the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of PC_{71}BM were extracted from photoemission measurements,^[38] it can be found that the Schottky barrier height is minimized for electron collection from PC_{71}BM to the ITO with respect to the ϕ decrease in $\text{ZnO}:\text{Al}_2\text{O}_3$. Meanwhile, the photoluminescence (PL) spectra obtained from $\text{ZnO}:\text{Al}_2\text{O}_3(x\%)$ films in Figure 1e shows that the ZnO trap-state-induced emission decreases with respect to the increase in Al_2O_3 content. The suppressed trap-state emission implies that the Al_2O_3 coating on ZnO nanoparticles can effectively passivate these traps, which is in good agreement with the previous results.^[39] To understand the morphology of Al_2O_3 and ZnO, scanning electron microscopy (SEM) measurements were conducted as displayed in Figure 1f. The morphologies of various $\text{ZnO}:\text{Al}_2\text{O}_3(x\%)$ films show that the pinhole density on $\text{ZnO}:\text{Al}_2\text{O}_3$ surface decreases with the increasing Al_2O_3 content, indicating that the Al_2O_3 coating on ZnO nanoparticles fills the gaps between ZnO nanoparticles. These results are consistent with the atomic force microscopy (AFM) measurements in Figure S2 (Supporting Information),

showing the continuous morphology with increasing Al_2O_3 content. The X-ray diffraction (XRD) results of various $\text{ZnO}:\text{Al}_2\text{O}_3$ films in Figure S3 (Supporting Information) show the decrease in peak intensity as compared to bare ZnO (that is $x = 0$), confirming a possible increase in Al_2O_3 coverage on ZnO nanoparticles with the increasing Al_2O_3 content.^[40] On the other hand, it is noted in Figure 1f that some big bulges can be formed on the surface of $\text{ZnO}:\text{Al}_2\text{O}_3(20\%)$. According to the high-magnification SEM image in Figure S4 (Supporting Information), the significant morphology difference in $\text{ZnO}:\text{Al}_2\text{O}_3(20\%)$ is speculated to be related to the Al_2O_3 aggregation. As shown in the AFM image in Figure S2e (Supporting Information), the $\text{ZnO}:\text{Al}_2\text{O}_3(20\%)$ film has the Al_2O_3 aggregation with a bulge size of 450 nm in width and 120 nm in height. To evaluate the electron transporting property of the $\text{ZnO}:\text{Al}_2\text{O}_3$ films, the current density–voltage (I – V) characteristics of electron-only devices with a configuration of glass/ITO/ $\text{ZnO}:\text{Al}_2\text{O}_3(x\%)$ /Ag were measured. The almost identical device performances as plotted in Figure S5 (Supporting Information) indicate the negligible influence of the incorporation of Al_2O_3 on the electron transport property of the $\text{ZnO}:\text{Al}_2\text{O}_3$ films, which may be due to the presence of the continuous ZnO scaffold in the doped layers.

Single-junction PSCs were fabricated to assess the feasibility of $\text{ZnO}:\text{Al}_2\text{O}_3$ in devices. As depicted in Figure 1a, the PSCs were constructed with an inverted architecture of glass/ITO cathode/ $\text{ZnO}:\text{Al}_2\text{O}_3$ LCML/Active layer/ MoO_3 /Ag anode, where the $\text{ZnO}:\text{Al}_2\text{O}_3$ LCML without or with DAN patterns was used for electron collection and light manipulation. **Figure 2a**

Figure 2. Device performance of PTB7: PC_{71}BM -based PSCs on various $\text{ZnO}:\text{Al}_2\text{O}_3$ layers. a) I – V characteristics recorded under 100 mW cm^{-2} AM 1.5G illumination. b) EQE spectra, c) absorption spectra, and d) IQE spectra of various devices.

plots the I - V characteristics of PSCs constructed with a spin-coated PTB7:PC₇₁BM active layer, which were recorded under 100 mW cm⁻² air mass 1.5 global (AM 1.5G) illumination. The detailed photovoltaic parameters deduced from the I - V curves are summarized in **Table 1**. It is obvious in Figure 2a that the use of the ZnO:Al₂O₃ layers causes a remarkable improvement in J_{SC} and PCE as compared to the case of bare ZnO. Especially, J_{SC} is increased to a value of 16.70 mA cm⁻² and the PCE is enhanced to 9.52% with respect to an optimal ZnO:Al₂O₃(15%) layer.

It has been demonstrated that PSCs with corrugated ZnO layer can achieve the significantly enhanced absorption and EQE without scarifying the FF and V_{OC} .^[6] To further optimize the PSCs with a PTB7:PC₇₁BM active layer, the DAN pattern with a period of $\approx$ 400 nm was duplicated onto the ZnO:Al₂O₃ layer by adopting soft nanoimprint lithography (SNIL) technique. In previous reports,^[41] it has been demonstrated that the DAN pattern is advantageous for broadband light trapping over the full solar spectral range, while the SNIL technique is compatible with the large-area manufacturing of organic devices without material damage. The AFM image in Figure S6a (Supporting Information) displays that the quasi-periodic sub-wavelength nanostructures have been effectively patterned on ZnO:Al₂O₃ surface with an average period of 400 nm and a groove depth of 50–60 nm. It is also obvious in Figure S6b (Supporting Information) that corrugated surface morphology is well maintained by the subsequently spin-coated PTB7:PC₇₁BM layer. As presented in Figure 2a and Table 1, significant performance improvement can be achieved in the PSC with a DAN-patterned ZnO:Al₂O₃(15%) layer, exhibiting the further enhanced J_{SC} and PCE up to 18.02 mA cm⁻² and 10.11%, respectively. To verify the variation of J_{SC} , the EQE curves were measured and shown in Figure 2b for comparison. The calculated J_{SC} from the EQE spectra for the whole spectrum are 14.73, 15.88, 16.09, 16.18, 15.71, and 17.88 mA cm⁻² for PSCs based on ZnO:Al₂O₃(0%), ZnO:Al₂O₃(5%), ZnO:Al₂O₃(10%), ZnO:Al₂O₃(15%), ZnO:Al₂O₃(20%), and DAN-patterned ZnO:Al₂O₃(15%), respectively. The measured J_{SC} are $\approx$ 3% error to the calculated values. To further confirm the device performance, the optimal cells were tested by the National Center of Supervision and Inspection on Solar Photovoltaic Products

Quality of China (CPVT), and a certified PCE of 9.688% was obtained for the PTB7:PC₇₁BM-based device with the DAN-patterned ZnO:Al₂O₃(15%) layer (Table 1; Figure S7, Supporting Information). This is in agreement with the results obtained in our laboratory with $\approx$ 4% mismatch. In addition, it is noted that the PSC based on DAN-patterned ZnO:Al₂O₃(15%) achieved a peak EQE of 89% at 690 nm and an average EQE of 77.9% at the visible region (390–700 nm), suggesting that this device has a superior light harvesting capability.

To verify the origin of the performance improvement, the absorption spectra of PTB7:PC₇₁BM-based PSCs on various ZnO:Al₂O₃(x %) layers were extracted by measuring the reflection spectra with an integrated sphere equipped UV-visible spectroscopy. As shown in Figure 2c, the absorption of the devices based on ZnO:Al₂O₃ is remarkably enhanced at the whole visible region as compared to that on bare ZnO. In particular, the use of a DAN-patterned ZnO:Al₂O₃(15%) layer leads to the further enhanced absorption over a broadband wavelength range. These results are consistent with the EQE enhancement as shown in Figure 2b, implying that more incident light can be trapped in the active layer with the use of a ZnO:Al₂O₃ LCML. To verify the nature of the improved absorption in the ZnO:Al₂O₃ LCML, the film refractive index (n) was measured via an ellipsometer (Figure S8, Supporting Information) and summarized in Table S1 (Supporting Information). It is found that the n of ZnO:Al₂O₃(x %) films is significantly increased from 1.63 to 1.72 with respect to the increase in x from 0 to 15, although bare Al₂O₃ film has a low n of 1.52. We speculate that the increased n is because the ZnO:Al₂O₃(x %) films became denser with the increasing Al₂O₃ content.^[42] Theoretical simulation was carried out to estimate the n influence of ZnO:Al₂O₃(x %) on the photogeneration in PSCs by using the finite-difference-time-domain (FDTD) method (see the “Experimental Section” for the details of the optical modeling calculations). **Figure 3** presents the normalized cross-sectional near-field profiles of field distributions in PSCs for a transverse electric (TE) polarized incident light at a wavelength of 550 nm. The optical field distribution in the active layer of the ZnO:Al₂O₃(15%)-based device is apparently stronger than the case of ZnO:Al₂O₃(0%)-based device, implying that more

Table 1. Photovoltaic parameters of PSCs using various ZnO:Al₂O₃ layers without and with DANs. The average PCE values were obtained from four cells.

Devices	Active layer	V_{OC} [V]	J_{SC} [mA cm ⁻²]	FF [%]	PCE[best] [%]	PCE[avg.] [%]
ZnO	PTB7:PC ₇₁ BM	0.735	15.18	73.01	8.15	8.05
ZnO:Al ₂ O ₃ (5%)		0.74	16.40	73.67	8.94	8.82
ZnO:Al ₂ O ₃ (10%)		0.75	16.49	75.52	9.34	9.17
ZnO:Al ₂ O ₃ (15%)		0.75	16.70	76.01	9.52	9.35
ZnO:Al ₂ O ₃ (20%)		0.73	16.09	70.75	8.31	8.19
ZnO:Al ₂ O ₃ (15%) w/DAN		0.75	18.02	74.84	10.11	9.82
ZnO:Al ₂ O ₃ (15%) w/DAN ^{a)}		0.755	17.02	75.35	9.688	–
ZnO:Al ₂ O ₃ (0%)	FTAZ:IDIC	0.84	18.54	70.82	11.03	10.95
ZnO:Al ₂ O ₃ (15%) w/DAN		0.85	20.87	72.77	12.91	12.67
ZnO:Al ₂ O ₃ (15%) w/DAN ^{a)}		0.850	21.58	71.02	13.03	–

^{a)}The devices were certificated by the National Center of Supervision and Inspection on Solar Photovoltaic Products Quality of China (CPVT).

Figure 3. Optical simulation of normalized cross-sectional near-field profiles of TE polarized light at a wavelength of 550 nm for PSCs based on ZnO:Al₂O₃(0%), ZnO:Al₂O₃(15%), and DAN-patterned ZnO:Al₂O₃(15%) layers, respectively.

incident light can be trapped and thus absorbed in the active layer. Moreover, the modeled results show that the use of a DAN pattern in the ZnO:Al₂O₃ layer allows a further localization of photon flux in the active layer, which has been ascribed to the collective effects of light scattering and localized surface plasmonic resonance for the enhanced light harvesting.^[28–30] Consequently, the simulation results offer the theoretical understanding of the optical effect on the performance enhancement in PSCs based on the ZnO:Al₂O₃ layers without and with a DAN pattern. The internal quantum efficiency (IQE) spectra of PSCs based on various ZnO:Al₂O₃(*x*%) layers can be deduced from $\text{IQE} = \text{EQE}/\text{Absorption}$. As displayed in Figure 2d, all the ZnO:Al₂O₃-based PSCs show higher IQE values than the device with bare ZnO, indicating that the enhanced EQE for ZnO:Al₂O₃-based PSCs originates not only from the enhanced light absorption but also the improved electron collection.

Figure 4a plots the photocurrent density (J_{ph}) versus effective voltage (V_{eff}) characteristics on a double logarithmic scale. Here, J_{ph} is determined by $J_{\text{ph}} = J_{\text{L}} - J_{\text{D}}$, where J_{L} and J_{D} are the current densities under AM 1.5G 100 mW cm^{−2} illumination and in dark, respectively. V_{eff} is defined as $V_{\text{eff}} = V_0 - V_{\text{b}}$, where V_{b} is the bias voltage and V_0 is the compensation voltage at $J_{\text{ph}} = 0$. The $J_{\text{ph}} - V_{\text{eff}}$ curves in Figure 4a clearly show three regimes: a linear increase of J_{ph} with V_{eff} for small fields, a square-root dependence for middle fields, and then a gradual transition to saturation of J_{ph} at high fields. It is obvious that ZnO:Al₂O₃-based PSCs have higher saturation current density (J_{sat}) at the region of $V_{\text{eff}} > 0.2$ V. As J_{sat} is mainly dependent on the absorbed incident photon flux and independent of the bias and temperature, a noticeable enhancement in J_{sat} indicates that the ZnO:Al₂O₃ layer indeed improves the absorption of incident light in the active layer, which is in good agreement with the absorption measurements in Figure 2c and the optical modeling in Figure 3. On the other hand, the ZnO:Al₂O₃-based PSCs achieve higher J_{ph} at the low V_{eff} region, indicating that the electron collection property of the ZnO:Al₂O₃ layer is better than that of bare ZnO. The proportion of swept-out charges can be calculated by dividing J_{sat} by J_{SC} . Accordingly, the device with a ZnO:Al₂O₃(15%) layer exhibits a relatively

high J_{SC} , indicating that $\approx 94.5\%$ generated charges are swept out of the device prior to recombination and contribute to the photocurrent.

Figure 4. a) Photocurrent density (J_{ph}) as a function of the effective voltage (V_{eff}) for PSCs under 100 mW cm^{−2} AM 1.5G illumination. b) The experimental data (open symbols) of V_{OC} and J_{SC} of ZnO:Al₂O₃-based PSCs as a function of incident light intensity, together with the fits to the data (dashed lines).

To gain further insight into the influence of ZnO:Al₂O₃ on electron collection property, light intensity dependence of V_{OC} and J_{SC} were measured to verify the recombination processes in devices. As shown in Figure 4b, the V_{OC} varies logarithmically with incident light intensity ($\ln(I)$) by following the relationship

$$V_{OC} \propto (k_B T/q) \ln(I) \quad (1)$$

where k_B is the Boltzmann constant, T is the absolute temperature in kelvin, q is the electron charge, and I is the light intensity.^[43] The curve fitting show the slope values of $1.55 k_B T/q$, $1.42 k_B T/q$, $1.31 k_B T/q$, $1.13 k_B T/q$ and $1.17 k_B T/q$ for devices based on ZnO:Al₂O₃(0%), ZnO:Al₂O₃(5%), ZnO:Al₂O₃(10%), ZnO:Al₂O₃(15%), and ZnO:Al₂O₃(20%), respectively. The ZnO:Al₂O₃-based devices have a decreased slope with the increasing of Al₂O₃ content, indicating a weak dependence of V_{OC} on the I . As reported previously,^[44,45] a slope close to $k_B T/q$ means that the dominant recombination mechanism in ZnO:Al₂O₃-based device is bimolecular recombination. In other words, the monomolecular recombination, also termed the trap-assisted Shockley–Read–Hall (SRH) recombination, is significantly suppressed in the ZnO:Al₂O₃-based devices. In parallel, it is evident in the dark I – V characteristics (Figure S9, Supporting Information) that the reverse current is obviously reduced for the cases of incorporating Al₂O₃. It has been reported that the electron collection layer with low trap density in PSCs will presumably decrease the possibility of trap-assisted recombination and enhance the values of J_{SC} and FF, thereby improving the PCE.^[46] It is thus reasonable to infer that trap-assisted SRH recombination loss in ZnO:Al₂O₃-based PSCs is dramatically suppressed by taking into account the evidences of the light intensity dependent V_{OC} spectra (Figure 4b), the decrease in trap-induced PL emission (Figure 1d) and the reduced reverse current (Figure S9, Supporting Information). Thus, the suppressed charge recombination loss is attributed to the passivation effect due to the Al₂O₃ coating on ZnO, which decreases the trap density in the ZnO film.^[47] In addition, the weaker performance in ZnO:Al₂O₃(20%)-based device likely originates from the Al₂O₃ aggregation on ZnO:Al₂O₃(20%) film, which acts as insulating islands at the ZnO/PC₇₁BM interface and thus blocks the electron collection from the PC₇₁BM.

The incident light dependence of J_{SC} was recorded to further clarify the charge collection behaviors in ZnO:Al₂O₃-based PSCs. Figure 4b shows that the light intensity dependence of J_{SC} follows the power law as described as $J_{SC} \propto I^\alpha$, where α is the coefficient of the power law. The fitting of experimental data yields the α values of 0.950, 0.956, 0.962, 0.965, and 0.945 for devices with ZnO:Al₂O₃(0%), ZnO:Al₂O₃(5%), ZnO:Al₂O₃(10%), ZnO:Al₂O₃(15%), and ZnO:Al₂O₃(20%), respectively. The increased α value close to the ideal unity indicates that the electron collection property of the ZnO:Al₂O₃-based devices can be effectively improved by optimizing the Al₂O₃ content. An increasing α could result from the balanced mobility of charge carriers, the uniformed distribution of the density of states, the suppressed bimolecular recombination.^[48] In order to verify the influence of ZnO:Al₂O₃ on such issues, AFM measurement was carried out to study the morphology of the active layer. Figure S10 (Supporting Information) shows that height and phase images of PTB7:PC₇₁BM

active layer on various ZnO:Al₂O₃ layers exhibit the similar morphology, implying no influence of ZnO:Al₂O₃ on the morphology of active layer. Given that the active layers are almost identical in each case, the improved electron collection property in ZnO:Al₂O₃-based PSCs may be attributed to the suppression of bimolecular recombination loss, which is related to the electric field formed by the interfacial dipole with negative charge in ZnO and positive charge in Al₂O₃ (see Figure 1c) that can promote the electron drift from PC₇₁BM to ZnO and refrain the electron diffusion from ZnO to PTB7 at the short-circuit condition.^[49]

To verify the potential of the ZnO:Al₂O₃ layer as a LCML for various material systems, nonfullerene PSC based on a FTAZ:IDIC active layer was also fabricated (see the chemical structures in Figure 1b). Figure 5 presents the I – V characteristics and EQE of the corresponding devices under the illumination, and the detailed parameters are listed in Table 1. It is noteworthy that the J_{SC} of the FTAZ:IDIC device with a DAN-patterned ZnO:Al₂O₃(15%) LCML is increased to 20.87 mA cm^{−2}

Figure 5. Device performance of nonfullerene FTAZ:IDIC-based PSCs. a) I – V characteristics and b) EQE spectra recorded under 100 mW cm^{−2} AM 1.5G illumination.

with a peak EQE of 92% at 610 nm. Furthermore, a certified PCE of 13.03% was obtained for a representative device as tested by CPVT (see Table 1; Figure S11, Supporting Information), which is among the highest reported results for single-junction PSCs. These results confirm that the use of a ZnO:Al₂O₃ LCML is a simple and universal way to achieve the high-efficiency PSCs.

In conclusion, an efficient EQE enhancement strategy for PSCs has been demonstrated by using a sol-gel-derived ZnO:Al₂O₃ composite layer as an LCML for unique light and charge manipulation. Film characterization and electrical measurement reveal that the optimal Al₂O₃ content in ZnO:Al₂O₃ films offers the passivation effect to suppress the trap-assisted charge recombination loss during electron collection from the active layer to the contact. Optical measurement and theoretical simulation indicate that the combination of DAN pattern in the ZnO:Al₂O₃ LCML allows a broadband enhancement of light absorption. Highly efficient single-junction PSCs with different binary blends are achieved with a peak EQE up to 90%, showing certified PCEs of 9.69% and 13.03% for the fullerene blend of PTB7:PC₇₁BM and nonfullerene FTAZ:IDIC blend, respectively. Due to the ease of use and substantial increase in efficiency shown here, we anticipate that our method unlocks the full potential of the ZnO:Al₂O₃ LCML toward the future photovoltaic applications.

Experimental Section

Solution Preparation: The sol-gel-derived ZnO precursor solution was prepared by dissolving 220 mg zinc acetate dehydrate in 61 μ L ethanolamine and 2 mL 2-methoxyethanol with overnight vigorous stirring. Especially, for ZnO:Al₂O₃ precursor solutions, different amount of Al(NO₃)₃·9H₂O were added into the prepared ZnO precursor with 2 h stirring at 80 °C. PTB7 and PC₇₁BM were purchased from 1-material Chemscitech. The PTB7:PC₇₁BM blend solution was prepared by dissolving 10 mg PTB7 and 15 mg PC₇₁BM in 1 mL 1,2-dichlorobenzene with 3 vol% 1,8-iodooctane and stirring overnight at 60 °C. FTAZ and IDIC were synthesized as the previous reports.^[50] The FTAZ:IDIC solution was prepared by dissolving 6 mg FTAZ and 8 mg IDIC in 1 mL chloroform with 0.3 vol% 1,8-iodooctane and stirring 2 h at 60 °C.

Device Fabrication: ITO-glass substrates were in turn ultrasonic-cleaned in detergent, DI water, acetone, and isopropanol, and finally dried in an oven at 110 °C. ZnO and ZnO:Al₂O₃ precursor solutions were spin-coated onto UV-ozone-cleaned ITO-glass substrate at 3000 rpm for 40 s, and then annealed at 150 °C for 20 min, resulting in a film with a thickness of $\approx$ 40 nm. For the DAN-patterned ZnO:Al₂O₃ film, soft nanoimprint lithography with a polydimethylsiloxane mold was used to duplicate the pattern to ZnO:Al₂O₃ as our previous report.^[6] The size and height of DANs can be controlled by varying the imprinting conditions, e.g., the imprinting pressure and the annealing time. The active layers were formed by spin-coating PTB7:PC₇₁BM and FTAZ:IDIC blend solutions onto ZnO and ZnO:Al₂O₃ films at 1500 rpm for 120 s and 2500 rpm for 30 s, respectively, in the nitrogen-filled glove box. The devices were completed by subsequently evaporated 8 nm-thick MoO₃ and 100 nm-thick Ag on the active layer to form the top anode for hole collection, which were performed in an interconnected high vacuum evaporation chamber (base pressure: 2×10^{-6} Torr). Deposition rate and layers thickness were monitored by a quartz crystal microbalance. A shadow mask was used to define the Ag anode with an active area of 0.0725 cm².

Film and Device Characterization: The film properties of various ZnO:Al₂O₃ (x%) films were systematically characterized, where x is the molar concentration of Al(NO₃)₃·9H₂O in the mixture of

Zn(CH₃COO)₂·2H₂O and Al(NO₃)₃·9H₂O. Chemical compositions and electronic structures of the samples were measured by X-ray and ultraviolet photoemission spectroscopy (XPS and UPS) in a Kratos AXIS Ultra-DLD system, in which a monochromatic Al K α source (1486.6 eV) with a resolution of 0.5 eV and an unfiltered HeI excitation line (21.22 eV) from a Helium discharge lamp with a resolution of 0.1 eV were used for XPS and UPS, respectively. Optical properties were measured using a UV-vis-near-IR spectrometer (Perkin Elmer Lambda 750) with an integrating sphere. Surface morphology of the samples was characterized by scanning electron microscopy (SEM) (FEI, Quanta 200FEG) and AFM (Veeco MultiMode V) in tapping mode. The refractive index (*n*) and layer thickness of the films were determined by the alpha-SE Spectroscopic Ellipsometer (J. A. Woollam Co., Inc). The crystal structure of samples was characterized by XRD (a PANalytical diffractometer) with Cu K α radiation (λ = 0.15406 nm). The photovoltaic characteristics of PSCs were examined in air at room temperature using a programmable Keithley 2612 source measurement unit under 100 mW cm⁻² AM 1.5G illumination generated by a solar simulator (Oriel model 91160). The illumination intensity of the solar simulator was calibrated using a standard Si photodiode with a known spectral response. To avoid the shadow effect on the area derivation of the devices during the electrode deposition, a shadow mask with an area of 0.0725 cm² was used to determine the actual illumination area of the devices during the current-voltage measurements. The EQE measurement was carried out with a photomodulation spectroscopic setup (Newport monochromator), including a xenon lamp, an optical chopper, a monochromator, and a lock-in amplifier operated by a computer, whose power-density calibration was performed by a traceable silicon photodiode. For EQE measurement, monochromatic light with profile area much smaller than the device area was chose to illuminate the device without any mask.

Optical Modeling: The in-plane waveguide modes in PSCs were simulated through FDTD approach by Lumerical FDTD Solutions. The optical properties, i.e., polarized incident light, reflection, absorption, and surface plasmonic resonance were fully taken into account in the device modeling. For simplicity, the DAN pattern was constructed by using hexagonal closely packed nanostructures with sinusoidal tapered profile. The wavelength-dependent refractive index (*n*) and extinction coefficient (*k*) of ITO, ZnO, ZnO:Al₂O₃, and PTB7:PC₇₁BM films were experimentally determined by the ellipsometer. All the films were constructed on precleaned silicon wafer except for ITO. The recorded ellipsometric data and fitting results were shown in Figure S8 (Supporting Information). Cauchy model was employed to fit the recorded Psi and Delta of ITO, ZnO, and ZnO:Al₂O₃, while basis spline model was used to fit PTB7:PC₇₁BM data.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

charge extraction, external quantum efficiency, light manipulation, polymer solar cells

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