Article category: Full Paper

Subcategory: Organic Solar Cells

Improved Efficiency and Stability of Organic Solar Cells by Interface Modification Using Atomic Layer Deposition of Ultrathin Aluminum Oxide

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Keywords: Organic Solar Cells; Interface Modification; Atomic Layer Deposition; Stability

The interfacial contacts between the electron transporting layers (ETLs) and the photoactive layers are crucial to device performance and stability for OSCs with inverted architecture. Herein, atomic layer deposition (ALD) fabricated ultrathin Al2O3 layers are applied to modify the ETLs/active blends (PM6:BTP-BO-4F) interfaces of OSCs, thus improving device performance. The ALD-Al2O3 thin layers on ZnO significantly improved its surface morphology, which led to the decreased work function of ZnO and reduced recombination losses in devices. The simultaneous increase in open-circuit voltage (), short-circuit current density () and fill factor (FF) were achieved for the OSCs incorporated with ALD-Al2O3 interlayers of a certain thickness, which produced a maximum PCE of 16.61%. Moreover, the ALD-Al2O3 interlayers had significantly enhanced device stability by suppressing degradation of the photoactive layers induced by the photocatalytic activity of ZnO and passivating surface defects of ZnO that may play the role of active sites for the adsorption of oxygen and moisture.

1. Introduction

Organic solar cells (OSCs) have gained intensive research attention due to the priorities of lightweight, flexibility and solution processability, thus showing great potential in commercialization.[1] Single junction OSCs have achieved great improvement in power conversion efficiency (PCE), which has reached 18% accompanied by the rapid development of high-performance polymer donors and non-fullerene acceptors (NFAs) over the last decades.[2-4] However, materials stability and device lifetime have received far less attention by far,[5] which has been a crucial issue to be addressed so that OSCs could be applicable in the marketplace.[6] The conventional OSCs normally employ poly (3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) as the hole transporting layer (HTL), which usually present lower stability due to the inherent hygroscopicity and acidity of PEDOT:PSS, that can corrode the indium-tin oxide (ITO) substrates, thus leading to diffusion of indium and tin into the HTL.[7, 8] OSCs with an inverted structure were then developed, which can facilitate the devices with better stability than the conventional OSCs, thus are more favorable to the practical application of OSCs.[9, 10] Zinc oxide (ZnO) is the most commonly employed ETL material in inverted OSCs due to its sufficient transmittance, low work function, high electron conductivity and readily film formation with solution-processing approaches.[11-13]

However，solution-processed ZnO-incorporated OSCs face quite a few challenges in achieving good performance. Firstly, surface defects of ZnO act as not only recombination centers for charge carriers but also the adsorption sites for environmental water and oxygen, which induce adverse effects on device stability and strongly degrade device performance.[14-16] Secondly, ZnO usually presents high photocatalytic activity under UV light irradiation, as the photoinduced charge carriers in the ZnO films would oxidate the dangling hydroxyl groups of NFA molecules and form hydroxyl radicals, which would lead to decomposition of NFA molecules.[17, 18] For instance, the C=C bonds can be broken by the photogenerated hydroxyl radicals, thus causing the decomposition of IT-4F on the ZnO surface, which would lead to poor stability of IT-4F based OSCs.[19, 20] Some strategies were utilized to address this issue, such as surface treatment with polar solvents[21], Lewis acid or gas plasma[22, 23], introducing dopants, i.e., aluminum (Al),[24] zirconium (Zr),[25] indium and lithium cations (Li+),[26, 27] into ZnO layers, surface defects passivation of ZnO via insertion of appropriate interlayers, i.e., self-assembled monolayers (SAMs),[28] functionalized fullerenes,[29] ionic liquid and high-molar-mass polymers[30, 31], which have been demonstrated effective to improve the stability and efficiency of OSCs. Amongst them, the insertion of interlayers could also reduce device leakage current, as they could improve charge extraction.[32] An effective approach for depositing the interlayers is atomic layer deposition (ALD),[33] which has been employed in silicon, dye-sensitized and perovskite solar cells to reduce undesirable surface recombination and to improve device performance.[34-36] Recently, there have been some reports on the utilization of the ALD technique for OSCs. Duan *et al.* inserted an ultrathin ALD-TiOx interlayer in OSCs to improve the efficiency and stability of the devices.[37] Polydorou *et al.* applied an ultrathin ALD-HfO2 film as a passivation interlayer on the ZnO ETL to improve device performance.[18] Vasilopoulou *et al.* introduced ultrathin ALD-Al2O3 and ZrO2 layers to passivate surface defects of TiO2 ETL for performance improvement of the inverted OSCs.[38] These works have proved that ALD fabricated interlayers have been successfull in further improving the performance of OSCs. Whilst most of them focused on the passivation of defects on the metal-oxide surface, the effects of the interlayers on the photocatalytic activity of ZnO were rarely reported.

In this work, we report on the utilization of an ultrathin ALD-Al2O3 film to form an interlayer in an inverted PM6:BTP-BO-4F based OSCs for improving device performance. The best device performance was achieved from OSCs introduced with 3 deposition cycles of ALD-Al2O3 interlayer. Accompanying with synergistically increased open-circuit voltage (), short circuit current density () and fill factor (FF), the PCE realized an absolute 1% enhancement compared to the control devices with pristine ZnO ETL, which was also comparable with that of the conventional devices we fabricated previously.[39] We found that synergistic effects of (ⅰ) ZnO surface defects passivation, (ⅱ) improved active layer nanomorphology, (ⅲ) decreased work function (WF) of ZnO, (ⅳ) reduced recombination loss, and (ⅴ) more balanced charge transport induced by the ALD-Al2O3 interlayer led to further improved efficiency. Moreover, the devices modified with ALD interlayers exhibited significantly improved stability, resulting from the reduced photocatalytic activity of ZnO and the passivation of surface defects on ZnO.

2. Results and discussion

To verify the feasibility of the strategy, the passivation effect of Al2O3 on the ZnOx (0002) surface was first evaluated with density functional theory calculation. In our model, oxygen vacancies were incorporated due to their lowest formation energy among all of the ZnO surface defects. In the beginning, we created and optimized the ZnOx (0002) surface, where x=0.87. **Figure 1a** (left) shows a quarter of oxygen atoms on the surface were removed from the slab, resulting in an O-vacancy coverage density of ρ=2.73×1014 cm-2. The Al2O3/ZnOx interfaces were then created and optimized (**Figure 1a (**right)). This process would release an energy of 8.05 eV per Al2O3 adsorbent unit according to our calculation results. **Figure 1b** exhibited the density of states (DOS) of the O-terminated ZnOx (0002) surface. The states located in the range of -1.5 eV to -0.27 eV under the Fermi levels were contributed from O states. The calculated DOS of ZnOx/Al2O3 interfaces is illustrated in **Figure 1c**, which demonstrates the suppression of surface oxygen states around the Fermi levels compared to the pristine ZnOx (0002) (**Figure 1b**). Bader charge analysis indicates that there existed charge transfer from Al2O3 to ZnOx (0002) surface oxygen atoms at a maximum of ≈1.39 |e|. These calculation results suggest that passivation of the ZnOx surface may be realized by charge transfer from Al2O3 to oxygen atoms.

2.1. The Effects of Al2O3 ALD Layers coated on ZnO

X-ray photoelectron spectroscopy (XPS) was used to analyze the elemental details to confirm the existence of ALD-Al2O3 layers on ZnO. Only the elements zinc (Zn), oxygen (O) and aluminum (Al) were detected. Shirley background method was adopted to fit the spectra in Avantage software. As shown in **Figure S1**, the Zn 2p3/2 and Zn 2p1/2 appeared at a binding energy of 1020.9 eV and 1044.1 eV, respectively.[37] No variation of the binding energy at the Zn 2p peaks has been observed before and after ALD-Al2O3 deposition. Only the peak intensities decreased significantly along with the increased number of ALD-Al2O3 cycles. The O 1s spectra were also recorded from samples with ALD-Al2O3 layers of different thicknesses. Three peaks were observed from deconvoluted O 1s XPS spectra(**Figure 2a-c**). The peak at the lowest binding energy (530.0 eV±0.1 eV) was correlated with the Zn-O bonds,[40, 41] the peak at a higher binding energy (531.1±0.1 eV) originated from Al-O bonds,[42] while the peak at around 532 eV was associated with the surface oxygen in the form of hydroxyl groups, which were formed from the reaction of oxygen with environmental air.[43] Furthermore, the atomic percentage of the deconvoluted O 1s peak associated with a different bond is presented in **Table S1**. We observed that both the Zn-O and Zn-OH peak intensities decreased while the Al-O peak intensity increased along with increased ALD-Al2O3 thickness, indicating that Al had consumed oxygen on the ZnO layer and strong Al-O bonds had formed. As a result, the reduction of -OH concentration can effectively suppress the recombination centers and realize passivation at the ZnO/Al2O3 interface.[37, 44] The Al 2p peaks at a binding energy of 73.9±0.01 eV were also observed (**Figure 2e-f)**, and the peak intensity was enhanced along with more ALD-Al2O3 deposition cycles, indicating the formation of Al-O bonds. Accordingly, we conclude that more ALD-Al2O3 cycles would lead to better passivation.

The surface morphology of the ETL influences the device performance of OSCs significantly. We used scanning electron microscope (SEM) and atomic force microscopy (AFM) to investigate the surface morphology of ZnO modified with ALD-Al2O3 of various thicknesses. Fiber-like surface nanomorphology patterns can be observed from the pristine ZnO films (**Figure 3a**). The patterns became blurring after being modified with 3 cycles of ALD-Al2O3, and almost disappeared when 10 cycles ALD-Al2O3 were deposited, which indicates that ALD-Al2O3 layers can smooth the surface morphology of ZnO effectively, and that may passivate surface defects of ZnO successfully. Moreover, the pristine ZnO layer delivered a root-mean-square (RMS) roughness of 3.97 nm (**Figure 3b**), while for ZnO modified with 3 and 10 cycles of ALD-Al2O3, the RMS decreased to 2.32 nm and 1.58 nm, respectively, which means that ALD-Al2O3 treatment had effectively reduced surface roughness of ZnO. We then conclude that a more conformal interface between the ZnO ETL and photoactive layer could be created by several cycles of ALD-Al2O3. AFM and transmission electron microscopy (TEM) were also utilized to explore the surface topography of the active layers PM6:BTP-BO-4F on ALD-Al2O3 modified ZnO substrates. As shown in **Figure S2a**, the PM6:BTP-BO-4F films showed smoother surface, while the RMS of the active layers also reduced with increased ALD-Al2O3 thickness. These results have demonstrated that ALD-Al2O3 modified ETLs also improved the surface morphology of the photoactive layers.

The work function (WF) of ZnO is also essential to the charge extraction process, which affects the overall performance of the devices. We performed Kelvin Probe Force Microscopy (KPFM) measurements to estimate the WF of ZnO layers deposited with ALD-Al2O3. As presented in **Figure S3**, the bare ZnO films presented a WF of 4.64 eV, whilst it reduced when ALD-Al2O3 was performed. The ETL ZnO modified with 3 cycles of ALD-Al2O3 showed the lowest WF of 4.55 eV. Consequently, the reduced WF would lead to lower electron extraction barrier, thus facilitating effective electron extraction from the active layer to ZnO films, as well as allowing better ohmic contact between ZnO films and BTP-BO-4F with the lowest unoccupied molecular orbital (LUMO) levels of -4.39 eV.[37, 45]

2.2. Solar Cell Performance Analysis

As addressed, the effects of ALD coatings on passivating ZnO layers had been demonstrated, and we then utilized the passivated ZnO films to fabricate OSCs with an inverted architecture of indium tin oxide (ITO)/ZnO/ALD-Al2O3/active layer/MoO3/Ag (**Figure 2a**). ZnO and MoO3 films were used as the ETL and HTL, respectively. The chemical structures and the corresponding energy levels of the materials in photoactive layers are shown in **Figure 2b**. To examine the impact of ALD-Al2O3 thickness on device performance, a series of PM6:BTP-BO-4F based OSCs were fabricated, with the ZnO layers unpassivated or treated with ALD-Al2O3 (Deposition cycles n=1, 3, 5 and 10). The current density-voltage curves of the devices modified with ALD-Al2O3 are presented in **Figure 2c**, and the corresponding photovoltaic parameters are listed in **Table 1** and exhibited as a box-plot diagram in **Figure S4**. We found that the devices incorporated with ALD-Al2O3 layers exhibited considerable enhancement in PCE compared with the control devices. Amongst them, the devices modified with 3 cycles of ALD-Al2O3 yielded the maximum PCE of 16.61%, along with a of 0.853 V, a of 25.94 mA cm-2 and an FF of 75.08%. When 10 cycles of ALD-Al2O3 deposition were completed, the device performance started to deteriorate, due to the insulating property of alumina that may start hindering electron transport when it reaches a certain thickness. In addition, the devices modified with 3 cycles of ALD-Al2O3 showed significantly higher than the control devices, attributing to the reduced WF of ZnO, thus a lower energy offset between ZnO and the photoactive layer.[46] Besides this, the decline in WF lowered the electron extraction barrier and elevated the built-in voltage, which facilitated electron extraction and transport, thus resulting in higher  of the 3 cycles ALD-Al2O3 modified devices finally.[45] **Figure S5** shows the dark *J-V* curves for the devices. The current density at -1.0 V is defined as leakage current density.[47] Obviously, the dark currents in devices with 3 cycles of ALD-Al2O3 exhibited lower reverse leakage currents compared with the control devices, which suggested effective passivation in the devices. **Figure 4d** shows the external quantum efficiency (EQE) measurement results. All of the integrated photocurrents obtained from the EQE spectra agreed well with the results achieved from the *J-V* curves (with less than 5% mismatch). We also found the incorporation of ALD-Al2O3 layers had not affected the spectral shape of EQE while improving the device efficiency.

2.3. Charge Separation, Transport and Recombination

To evaluate exciton dissociation and charge generation efficiency, the relation of photocurrent density() with respect to effective voltage () of the devices incorporated with ALD-Al2O3 layers was also analyzed. As shown in **Figure 5a**, can be estimated as , where and represent the current densities measured separately under light illumination at AM 1.5G and in dark.[48, 49] is determined by , where is the voltage when mAcm-2 and is the applied voltage. The saturation current density () is defined as the photocurrent when all of the photogenerated excitons are dissociated into free charges and collected by the electrodes at a high , i.e., when . The exciton dissociation possibility () can be calculated as , where is under short-circuit condition. **Table S2** summarizes the detailed exciton dissociation and charge collection efficiencies of the OSCs. Notably, the devices with 3 cycles of ALD-Al2O3 realized the highest exciton dissociation efficiency of 96.7%. They also achieved higher than that of the control devices. However, the devices with 10 cycles ALD-Al2O3 showed a reduced , which indicates that Al2O3 layers may impede charge transport when they reach a certain thickness. Light-dependent and were also measured to gain futher insights into the charge separation, transport and recombination properties of the devices. The relationship of versus can be expressed as: , where *k* denotes Boltzmann’s constant, *T* is the absolute temperature and is the elementary charge.[50] If *n* is close to 2, it means severe trap-assisted recombination would have been induced by morphology defects. As presented in **Figure 5b**, the fitted were 1.29, 1.16, 1.38 for devices with pristine ZnO, 3 cycles and 10 cycles ALD-Al2O3 treated ZnO, respectively. The 3 cycles ALD-Al2O3 incorporated devices presented the best performance in reducing trap-assisted recombination. The relationship between and is defined as:,[51] in which *α* represents the exponential factor and can be obtained from the slopes of fitting curves. An *α* of 0.959 was obtained for the control devices, which increased to 0.978 for 3 cycles ALD-Al2O3 inserted devices, indicating the biomolecular recombination in 3 cycles ALD-Al2O3 passivated devices had been effectively suppressed. To clarify the influence of ALD-Al2O3 interlayers on charge transport properties of the devices, the hole () and electron () mobilities of devices with Al2O3 layers were evaluated using the space charge limited current (SCLC) method. As summarized in **Figure 5d-e** and **Table S3**,the hole and electron mobilities of the control devices were 4.44×10-4 mA0.5cm-1 and 2.36×10-4 mA0.5cm-1, respectively. The mobilities marginally reduced after treatment with 3 cycles ALD-Al2O3, and continued to decrease along with the increased thickness of ALD-Al2O3. The ratio was utilized to evaluate the charge transport balance in the OSCs.[52] A ratio of 1.8 was obtained for the devices with 3 cycles ALD-Al2O3, which was closer to 1 compared with that of 1.89 for the control devices. These results manifest that the insulating property of alumina may affect charge mobility, whereas an ALD-Al2O3 interlayer of appropriate thickness can lead to more balanced charge transport in devices, which agrees well with the photovoltaic measurement results.

In order to further explore charge separation and recombination dynamics at the ZnO/PM6 interfaces, steady state photoluminescence (PL) measurements were carried out on neat PM6 films on top of ZnO layers with and without ALD-Al2O3 modification. All of the films were spin coated at a same spin speed with 5 mg ml-1 PM6 solution in order to obtain constant film thickness. Enhanced PL intensity was observed from PM6 films on ZnO/ALD-Al2O3 (3 cycles)surfaces, compared with that from PM6 films on pristine ZnO, which was attributed to effective passivation of traps on ZnO surfaces by the ALD-Al2O3 layers.[45] Next, time-resolved photoluminescence (TRPL) measurements were performed in order to investigate interfacial charge transfer from PM6 to ZnO (**Figure S6b**). The fluorescence lifetime (τ) was calculated by fitting the TRPL semilog decay curves using a two-exponential function, and the extracted parameters are presented in **Table S4**. As a result, the exciton lifetime of PM6 films on top of ZnO deposited with 3 cycles ALD-Al2O3achieved an apparent increase. The increased exciton lifetime resulted from the effective passivation of deep surface defect states on ZnO, which served as recombination centers for holes, thereby reducing hole trapping.[38] Referring to the above discussions, we concluded that effective passivation of traps on ZnO had been realized by introducing ALD-Al2O3,which is consistent with the better performance of ALD-Al2O3 incorporated devices.

2.4. Energy Loss Analysis

To further understand the origins for improvement of the ALD-Al2O3 treated devices, we analyzed energy loss () in both control devices and ALD-Al2O3 modified devices based on Marcus theory.[53] The total energy loss of an OSC includes three parts: radiative recombination loss (, charge generation , and non-radiative recombination (, which can be described as the following equation: [54, 55]

where is the optical bandgap of the device, is the charge transfer (CT) energy state. Firstly, we estimated of the two kinds of devices from the crossing points of the normalized electroluminescence (EL) and EQE spectra (**Figure S7**).[56] were 1.403 eV for the control devices and 1.400 eV for the devices with 3 cycles ALD-Al2O3. Next, can be estimated by simultaneously fitting the lower energy regions of highly sensitive EQE (s-EQE) and EL spectra.[57] can then be determined by the formula , which is related to the energetic difference between singlet excited states and charge transfer states.[58] As seen, the devices modified with 3 cycles ALD-Al2O3 exhibited similar with the control devices, resulting in comparable **(Figures 6a and 6b)**. is induced by radiative recombination, which is unavoidable for all kinds of OSCs. is the energy loss originating from non radiative resomibanition, which is the main cause for the large energy loss of OSCs, it can be quantified by the equation: , where *k* is Boltzmann constant, *T* is temperature and is external quantum efficiency of EL. As displayed in **Figure 6c**, of the control devices and ALD-Al2O3 treated devices are 0.61×10-4, 1.12 ×10-4, respectively. Correspondingly, are 0.251 eV for the control devices and 0.235 eV for the 3 cycles ALD-Al2O3 introduced devices. The suppressed of ALD-Al2O3 treated devices indicates that the ALD-Al2O3 passivation interlayer can inhibit charge recombination loss in devices, which coincides with the results from and versus light intensity measurements (**Figure 5b** and **5c**). **Table 2** summarizes the detailed parameters extracted from the measurements, the energy losses for the devices are compared in **Figure 6d**.

2.4. Device Stability

Besides device efficiency, stability is also a crucial parameter for OSCs. As known, photodegradation of the photoactive materials mainly causes deterioration of device performance, which is a complex process. To evaluate the ambient stability of our devices, we measured 12 hours evolution of *J-V* curves for unencapsulated devices with and without ALD-Al2O3 under UV light in ambient conditions. As shown in **Figure 7a-b** and **Table S5**, the PCE of 15.63% for the control devices decreased to 5.94% after 12 hours of constant UV illumination, only retaining 38% of the initial PCE. However, for the devices with 3 cycles ALD-Al2O3, the PCE decreased from16.61% to 14.05%, which retained ~85% of the initial PCE. These results manifested that ALD-Al2O3 interlayers can effectively lower the photocatalytic activity of ZnO, thus reducing the hydroxyl radicals that could react with NFA, thereby preventing the photoactive molecules from degradation.[20] Moreover, we investigated the influence of ALD-Al2O3 interlayer on the long time device stability. We stored the unencapsulated devices in a nitrogen-filled glove box and monitored the steady power output (SPO) stability for a certain period. **Figure 7c** shows the operational SPO stability performance of the corresponding devices under persistent one sun irradiation. We found that the devices with 3 cycles ALD-Al2O3 retained 95% of the initial PCE. The performance degradation was negligible as the light intensity decreased from 1 sun to 0.98 sun during 75 hours, while the PCE of the control devices dropped to 79.5% of the initial PCE. The significant improvement on the stability of the ALD-Al2O3 treated devices can be explained by the fact that ALD-Al2O3 interlayers had effectively passivated surface defects of ZnO that may act as active sites for the adsorption of oxygen and water molecules. Additionally, during the ALD process, the initially adsorbed water molecules on the ZnO surface participate in reactions with trimethylaluminum (TMA) to form the first monolayer of Al2O3, which means they are unable to act as corrosion agents.[45] The stability of devices stored in air (RH~40%) was also investigated (**Figure 7d**). Inverted devices are inherently more stable than normal devices due to the acidic environment created by PEDOT:PSS. When Al2O3 interface layers were introduced, the inverted devices’ stability was further improved, maintaining over 88% of its initial efficiency after 500 hours of degradation.

3. Conclusion

In summary, we systematically investigated the application of an ultrathin ALD-Al2O3 interlayer on ZnO as the ETLs in OSCs with inverted structures. It was found that the incorporation of ALD-Al2O3 thin layers led to effective passivation of surface defects on ZnO, which thus resulted in lowered electron extraction barrier and reduced surface recombination. In contrast to the control devices that used pristine ZnO as ETLs, the devices modified with 3 cycles ALD-Al2O3 showed optimal characteristics with improved , and FF, which delivered an absolute 1% increase in efficiency. Furthermore, the unencapsulated ALD-Al2O3 modified devices exhibited exceptional stability either under ultraviolet light in ambient conditions or under operational conditions. This work has explicitly shown the potential of ALD modification strategy in manipulating ETLs’ properties and suppressing defect trap states and also demonstrated the importance of ALD-dominated interface engineering in photovoltaic applications.

图表

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**Figure 1.** (a) The atomic structures of ZnOx (left) and ZnOx/Al2O3 (right) interfaces. (b) The density of states of ZnOx and (c) ZnOx/ Al2O3 interfaces.

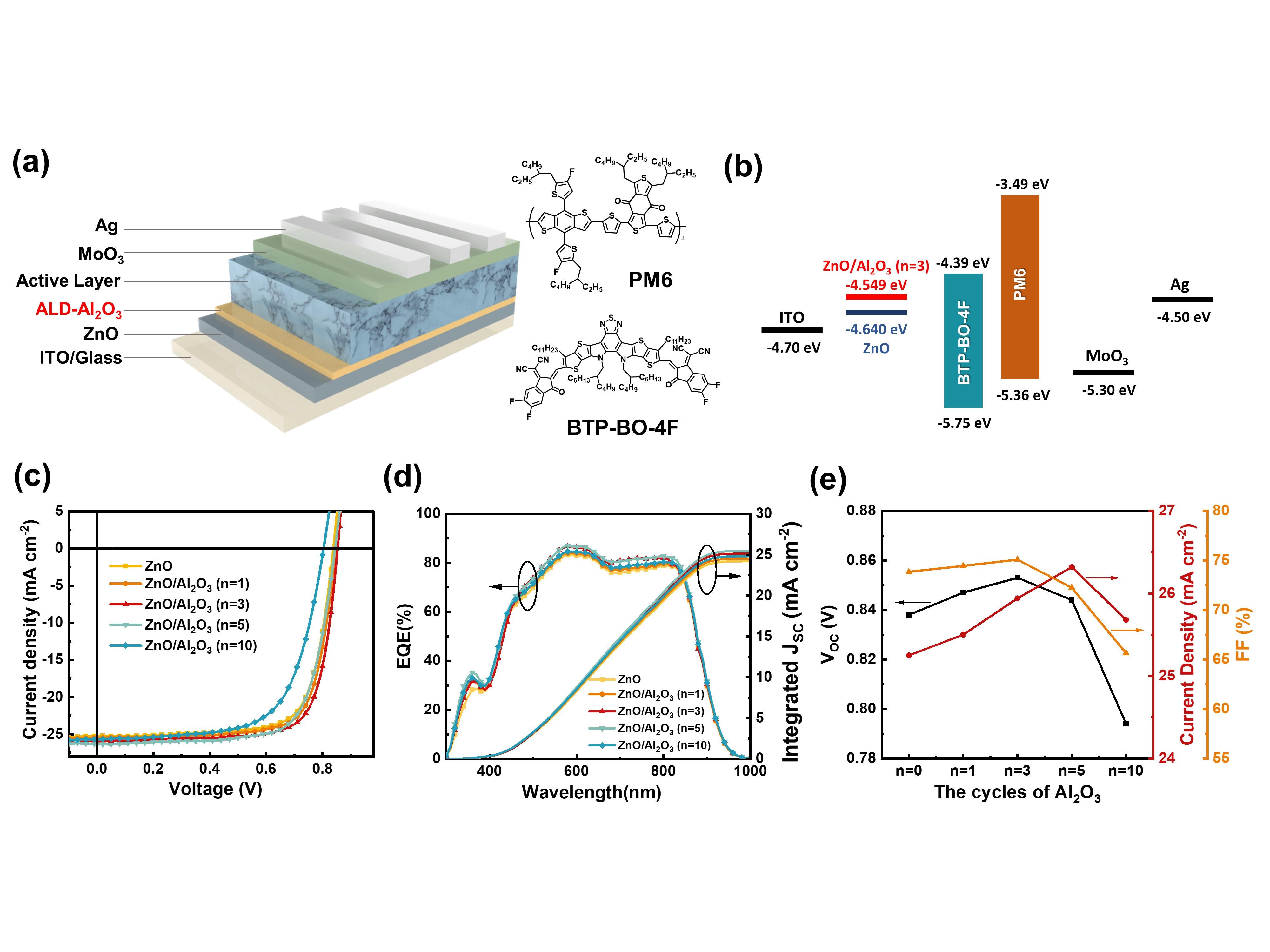
**图表

描述已自动生成Figure 2.** Deconvoluted XPS O 1s spectra of (a) 0 cycle, (b) 3 cycles and (c) 10 cycles of ALD-Al2O3 deposited onto the ZnO/ITO substrates. XPS spectra of Al 2p of (e) 0 cycle, (f) 3 cycles and (g) 10 cycles of ALD-Al2O3 on ZnO/ITO substrates.

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**Figure 3.** (a) SEM images and (b) AFM images of ZnO/ITO with ALD-Al2O3 layers (Deposition cycle: n=0, 3 and 10).

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**Figure 4.** (a) The device architecture; (b) The energy levels of devices modified with ALD-Al2O3 layers; (c) The current-voltage (*J-V*) measurements; (d) The EQE spectra and integrated curves; and (e) , and FF of the devices modified with ALD-Al2O3 layers (Deposition cycle: n=0, 1, 3, 5 and 10).

**Table 1.** Photovoltaic parameters of devices with different cycles of ALD-Al2O3.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Devices | [V] | [mA cm-2] | Cal.  [mA cm-2] | [*%*] | [%] |
| ZnO | 0.838  (0.834±0.003) | 25.25  (24.93±0.38) | 24.20 | 73.85  (73.14±0.83) | 15.63  (15.20±0.31) |
| ZnO/Al2O3 (n=1) | 0.847  (0.843±0.003) | 25.50  (25.20±0.32) | 24.52 | 74.45  (73.55±0.92) | 16.08  (15.75±0.36) |
| ZnO/Al2O3 (n=3) | 0.853  (0.850±0.002) | 25.94  (25.67±0.31) | 25.15 | 75.08  (74.36±0.73) | 16.61  (16.23±0.28) |
| ZnO/Al2O3 (n=5) | 0.844  (0.839±0.003) | 26.32  (25.88±0.42) | 25.45 | 72.24  (71.20±1.02) | 16.05  (15.63±0.40) |
| ZnO/Al2O3 (n=10) | 0.804  (0.799±0.004) | 25.68  (25.16±0.48) | 24.82 | 65.64  (64.97±1.04) | 13.55  (13.06±0.44) |

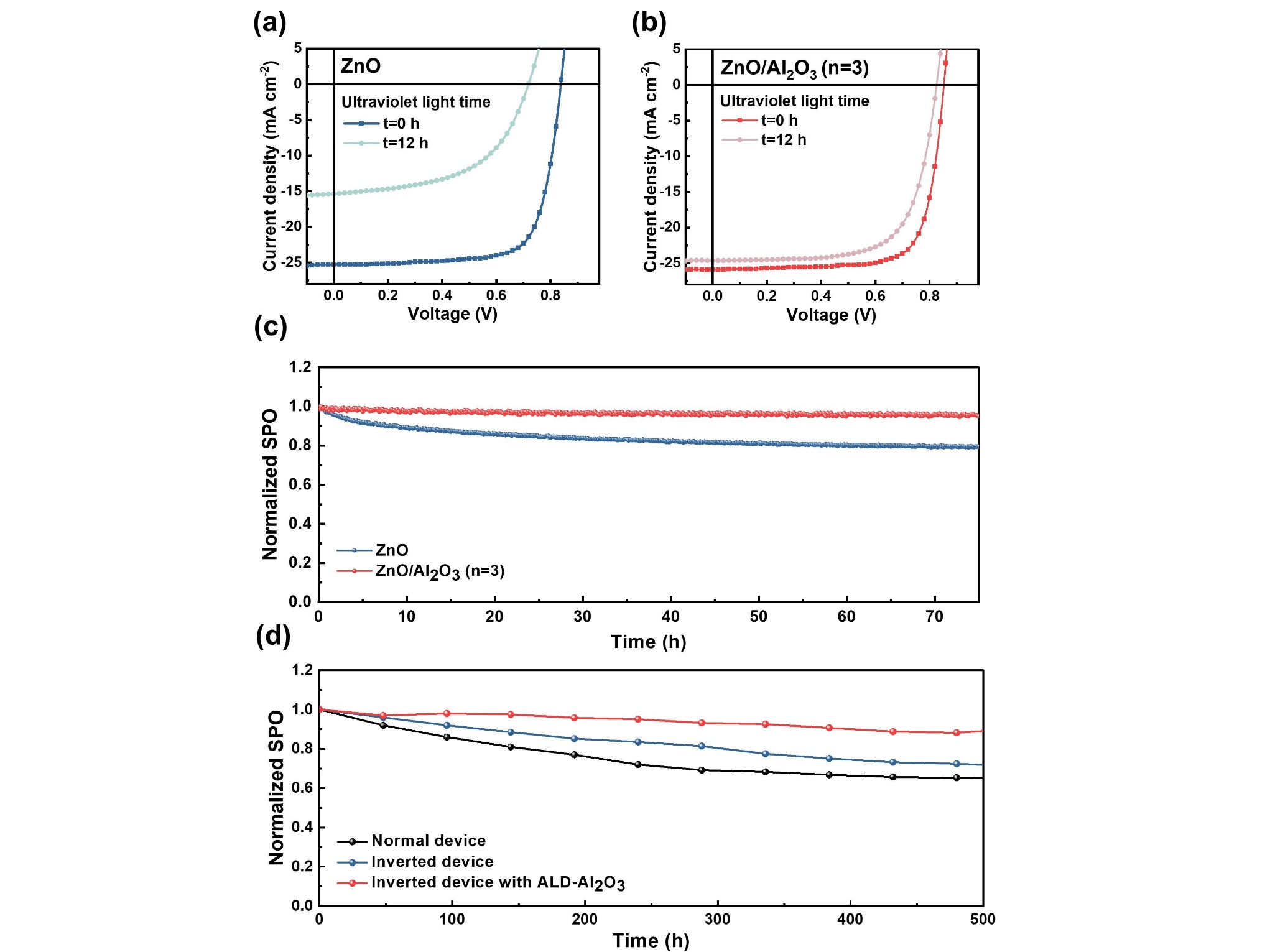
The standard deviations of PCEs were calculated from those of 12 independent cells.

图示

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描述已自动生成Figure 5.** (a) The - curves, (b) -light intensity fitting lines, (c) -light intensity fitting lines, the -V curves of (d) hole-only and (e) electron-only devices with ALD-Al2O3 layers (Deposition cycles: n=0, 3 and 10).

**Figure 6.** S-EQE and EL spectra of (a) devices with pristine ZnO and (b) devices with ALD-Al2O3 (Deposition cycle: n=3). (c) of the corresponding OSCs. (d) Schematic diagram of energy loss.

**Table 2.** Energy losses of the control devices and devices modified with 3 cycles ALD-Al2O3

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Devices | [eV] | [eV] | [eV] | [eV] | △[eV] | △[eV] | △[eV] |
| ZnO | 1.403 | 1.334 | 0.838 | 0.565 | 0.245 | 0.069 | 0.251 |
| ZnO/Al2O3 | 1.400 | 1.334 | 0.853 | 0.547 | 0.246 | 0.066 | 0.235 |

**Supporting Information**

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

Acknowledgements

The authors acknowledge financial support from National Natural Science Foundation of China (No. 21875106, 21850410456, 21875052, 51972172), the Strategic Priority Research Program of Chinese Academy of Sciences (Grant No. XDB36000000) and Jiangsu Excellent Postdoctoral Program.

Received: (will be filled in by the editorial staff)  
Revised: (will be filled in by the editorial staff)  
Published online: (will be filled in by the editorial staff)

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ToC figure

图示, 示意图

描述已自动生成Atomic layer deposition (ALD) fabricated ultrathin Al2O3 layers are applied to modify the ETLs/active blends (PM6:BTP-BO-4F) interfaces of organic solar cells, thus improving the efficiency and stability of devices.