Interface engineering of high efficiency perovskite solar cells based on ZnO nanorods using atomic layer deposition

Shibin Li1, *,(✉), Peng Zhang1, Yafei Wang1, Hojjatollah Sarvari2, Detao Liu1, Jiang Wu3, Yajie Yang1, Zhiming Wang4, Zhi David Chen1,2,* (✉)

1 School of Optoelectronic Information, University of Electronic Science and Technology of China (UESTC), Chengdu, 610054, China
2 Department of Electrical & Computer Engineering and Center for Nanoscale Science & Engineering, University of Kentucky, Lexington, Kentucky 40506, USA
3 Department of Electronic and Electrical Engineering, University College London, Torrington Place, London WC1E 7JE, United Kingdom
4 Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu, 610054, China

ABSTRACT

Despite dramatically improved efficiency of inorganic-organic metal hybrid perovskite solar cells (PSCs), electron transport is still a challenging issue. In this paper, we report the use of ZnO nanorods prepared by hydrothermal self-assembly as the electron transport layer in perovskite solar cells. The efficiency of perovskite solar cells is dramatically enhanced by passivating the interface defects via atomic layer deposition of Al2O3 monolayers on ZnO nanorods. By employing Al2O3 monolayers, the power conversion efficiency (PCE) of CH3NH3PbI3 (MAPbI3) PSCs is typically boosted from 10.33% to 15.06% on average, with the highest efficiency of 16.08%. We suggest that passivation of defects using atomic layer deposition of monolayers might provide a new pathway for improving all types of PSCs.

1 Instruction

Although sunlight is a clean, cheap, abundant, and renewable energy source, it is poorly utilized. The growing demand for cheap and renewable energy sources has led to substantial research effort to invent low-cost and highly-efficient photovoltaic materials and devices. Third generation solar cells, halide perovskite solar cells (PSCs) have a great
potential for highly efficient solar energy conversion. As ideal light harvesters, the family of perovskite materials are gifted with various attractive optoelectronic characteristics, including high absorption coefficient, tunable bandgap, long carrier diffusion length etc. Among various perovskite materials, methylammonium lead iodide (MAPbI₃), with a bandgap of about 1.5eV and an absorption spectrum up to 800 nm, has been extensively studied as a light harvester in solar cells. Following a rapid surge of development, solution processed MAPbI₃ has boosted the power conversion efficiency (PCE) of PSCs over 20% [1-18].

The state-of-the-art perovskite solar cells consist of a mesoporous TiO₂ electron transport material (ETM), a MAPbI₃ light-absorption layer and a spiro-OMeTAD hole transport layer. However, it is well known that the electron mobility of zinc oxide (ZnO) is substantially higher than that of TiO₂. ZnO is thus considered as an ideal alternative to TiO₂ for electron transport layer in perovskite solar cells. Large efforts have been devoted to developing the ZnO nanostructure based PSCs. Liu et al. reported PSCs with PCEs of 13.5% and 15.7% by using ZnO nanoparticles as ETM [19]. A perovskite solar cell using ZnO nanorods (NRs) as ETM has yielded a PCE of 11% [20]. With Al-doped ZnO interfacial modification, the PCE of ZnO NRs-based PSCs was impressively enhanced up to 10.7% [21]. Khalid and coworkers reported electron rich, nitrogen doped ZnO NRs-based PSCs with the highest PCE of 16.1% so far [22]. The above mentioned results have demonstrated that ZnO based nanostructures could be a competent candidate to replace TiO₂. However, why is the PCE of ZnO ETM based PSCs still inferior to the mesostructured TiO₂ based PSCs? It was reported that the efficiency losses originate from rapid carrier recombination at the interfaces, especially the interface between ZnO NRs and perovskite [23-25]. Therefore, it is of critical importance to find a way to passivate the defects at the interface between the oxide ETM and the perovskite material. In this paper, we report a new approach to passivate the interfacial defects between ZnO NRs and perovskite using atomic layer deposition (ALD). It was reported that the ALD-Al₂O₃ film was used for passivation of silicon solar cells [26]. Al₂O₃ films were deposited by ALD at the interfaces either between perovskite and HTM or between HTM and the Ag electrode for isolation of solar cells from moisture in air [27]. ALD-Al₂O₃ films were also used as encapsulation layers for protection of solar cells from moisture and oxygen [28]. ALD-Al₂O₃ and ALD-TiO₂ layers were deposited to passivate the surface defect of TiO₂ and ZnO ETM for PSCs [29,30]. In this work, we demonstrate ALD-Al₂O₃ monolayers can remarkably suppress the surface defects of ZnO NRs. The average PCE (PCE_avg) of ZnO NRs-based PSCs is impressively improved from 10.33% to 15.06%. The attained best efficiency of PSCs is 16.08%, which is the state-of-the-art efficiency of ZnO based PSCs [22]. The interface engineering proposed in this work can also be used to passivate defects in other types of perovskite solar cells.

2 Results and Discussion

2.1 Preparation and Optimization of ZnO NRs

Before ZnO NRs were synthesized, a ZnO seed layer (30nm) was prepared by magnetron sputtering at room temperature on the fluorine-doped tin oxide (FTO) glass substrate. It has been demonstrated that the photovoltaic performance and interfacial electronic behavior of the PSCs based on 1D nanostructured ETM with surface-decorated MAPbI₃ nanocrystals strongly depend on the length of the oxide arrays [20-22]. In this study, the ZnO NRs were synthesized by the hydrothermal method. We assume that the length of NRs depends directly on the growth time at a fixed precursor concentration. The influence of growth time on the length of ZnO NRs was
examined using a precursor solution (35mM) at a fixed concentration. ZnO NRs were grown at 90°C for 0.5h, 1h, 2h and 3h (correspondingly marked as A, B, C, D). The length was determined by cross-section SEM as shown in Figure 1 (a)-(d). Consequently, the average lengths of NRs for A, B, C, and D are 342, 910, 1730 and 2000 nm, respectively. It is worth to noting that the growth time only affects the lengths of NRs but their diameters [31,32]. The diameter of nanorods is controlled by the precursor concentration as suggested in the SEM images shown in Figure S1 (Supporting Information). In this study, it is difficult to produce the same thickness of perovskite capping layer on the ZnO NRs with different lengths. For NRs with the average lengths of 342, 910, 1730 and 2000 nm, we used PbI2 solutions with doses of 10, 20, 30 and 40μl to prepare perovskite capping layers on ZnO NRs as shown in the cross-section SEM images of Figure 1 (A)-(D). As shown in Figure 2S, the passivation of ALD-Al2O3 monolayers shows negligible effects on the grains size, and good quality of perovskite films are prepared by using mixture solution of DMF: DMSO=7:3. After synthesis of nanorods, the samples were annealed in O2 at 500 °C for 30 minutes to improve the quality of the seed layer and nanorods. The results of XRD measurements shown in Figure S3 confirm that the seed layer and nanorods are completely crystallized after annealing. Only one strong peak ascribed to the diffraction from (0002) facet of wurtzite ZnO is observed. The (0002) diffraction peak indicates that the ZnO seed layer and nanorods are crystallized in wurtzite structure with c-axis preferred orientation, which favors high electron mobility. Our previous

![Figure 1](attachment:image.png)

**Figure 1** SEM cross section view of ZnO nanorods fabricated for different reaction time: (a) 0.5 h, (b) 1 h, (c) 2 h, (d) 3 h; SEM cross section view of perovskite solar cells (Marked as Sample A, B, C, and D corresponding to the lengths of ZnO NRs) fabricated using ZnO nanorods with different lengths.
work demonstrated that electrons generated in the bulk perovskite are easily conducted to the FTO electrode through the ZnO NRs electron transport layer because high c-axis preferred-orientation ZnO NRs are perpendicular to the FTO substrate [33]. However, the XRD results obtained from the unannealed ZnO showed different crystal orientations, for instance, (100), (103), (112) and (201). Furthermore, the dense and completely crystallized ZnO seed layer also plays a significant role as a blocking layer that prevents direct contact between FTO and perovskite, which dramatically suppresses carrier recombination.

2.2 Effect of Length of ZnO NRs on PCE

Figure 2 exhibits fabrication processes of ALD interface engineering of PSCs based on ZnO NRs. As we have verified that the perovskite capping layer plays a crucial role as a protection layer to prevent direct contact between the ZnO NRs and the spiro-MeOTAD hole transporting material [34,35]. The configuration of a ZnO NRs-based PSC and energy bands/levels of the layers in the cell are shown in Figure 3 (a) and (b), respectively. The diagrams were drawn with the assumption of vacuum level alignment [17]. Meanwhile, the individual energy levels of various device components are relative to the vacuum level. Additionally, the perovskite capping layer captures photons efficiently and thus results in a superior light harvesting efficiency. A similar concern in mesoporous TiO$_2$ based PSCs has also been extensively addressed. The remaining PbI$_2$ is always an issue for the reproducible performance of PSCs. The performance of PSCs is irreproducible because the ratio of MAPbI$_3$ to PbI$_2$ is not the same from batch to batch. As shown in the XRD patterns of Figure 3 (c), no residual PbI$_2$ is observed in both Samples A and B, which suggests a full conversion of PbI$_2$ to MAPbI$_3$. More perovskite is loaded on longer nanorods, and the XRD results of Sample B indicate stronger perovskite peaks of (110), (112), (220), (310) and (312). Sample D shows much stronger diffraction peak of PbI$_2$ than that of Sample C. The result demonstrates that the amorphous and uniform PbI$_2$ can be fully converted to perovskite crystals for samples A and B with shorter ZnO NRs. For Samples C and D, the remaining PbI$_2$ cannot be fully converted to perovskite crystals even prolonging the dipping time to 1 hour.

![Figure 2 Flow chart of the experiment processes.](image-url)
Figure 3 (a) Device architecture; (b) Energy-level diagram; (c) XRD patterns of perovskite prepared with different lengths of ZnONRs, Samples A, B, C, and D are corresponding to the lengths of 342, 910, 1730, and 2000 nm; (d) J-V curves of PSCs based on different lengths of ZnO NRs. Samples A, B, C, and D are corresponding to lengths of 342, 910, 1730, and 2000 nm.

As shown in Figure S4 (a), the perovskite film was peeled off after 1-hour dipping time. In Figure S4 (b), we also observed strong absorption peak around 775 nm ascribed to perovskite, indicating completed conversion of PbI$_2$ to MAPbI$_3$ with dipping time of 1 minute with the optimized length of ZnO NRs. The result is consistent with the sequential deposition of perovskite reported by Grätzel et al [4]. The capping layer of crystallized perovskite on the top of ZnO NRs prevents the PbI$_2$ that is left among nanorods from conversion to MAPbI$_3$, resulting in more remaining PbI$_2$ in Samples C and D with longer nanorods that are able to load more PbI$_2$. The partial conversion of PbI$_2$ leads to a MAPbI$_3$-PbI$_2$ mixture as well as a hardly controllable amount of remaining PbI$_2$[36]. As shown in Figure 3 (d) and Table 1, the performance of PSCs based on as-grown ZnO NRs obviously depends on the length of NRs. The PSC (Sample A) based on ZnO NRs with a length of 342 nm exhibits PCE of 7.70%, Jsc of 13.11 mA/cm$^2$, FF of 58.67 % and Voc of 1.00V. As the length of nanorods increases, the PCE and Jsc increase to 10.38% and 17.85 mA/cm$^2$. For perovskite capping layers with similar thicknesses, the length-related improvement of performance is owing to the longer ZnO NRs, which allows loading more perovskite, resulting in more light absorption. It is reasonable that both the light harvesting and charge generation efficiency increase with the increase of ZnO NRs length. However, the performance of Samples C and D degraded as the lengths of ZnO NRs were increased to 1730 and 2000 nm. The increased length raises the transport distance and resistance of photo-generated carriers, leading to more recombination of carriers. Furthermore, for the PSCs with long ZnO NRs, the capping layers make main contribution to light harvest. Therefore, the increment of perovskite among ZnO NRs hardly enhances the performance further.

The above results demonstrate that the PSC based on ZnO NRs with the length of 910 nm (Sample B) exhibits the best performance among the PSCs with different lengths nanorods. The following studies therefore are focused on the performance of PSCs based on ZnO NRs with the length of 910 nm. As shown in Figure S5, the annealing process
The improved quality of ZnO NRs through annealing is essential for fabrication of high efficiency PSCs [37]. Additionally, the perovskite material may make direct contact on FTO through a thin seed layer, leading to a large leakage current and hence reduced Voc. The Voc increases with the thickness of the seed layer owing to the suppressed leakage current. Therefore, all the PSCs with seed layers of similar thicknesses exhibit similar Voc, because the open circuit voltage is mainly dependent on the thickness of ZnO seed layer. The single crystalline ZnO ETM obtained by annealing is c-axis orientation as well as perpendicular to the FTO substrate, providing a direct carrier pathway. The PCE of devices is therefore significantly improved due to efficient electron collection by the Au electrode. Meanwhile, the as-grown ZnO NRs are polycrystalline, which may disturb the transport of free electrons in ZnO ETM. The disturbing effect increases scattering of free electrons in ZnO ETM, leading to performance deterioration of PSCs [38-41].

2.3 Interface Engineering of PSCs Using ALD

As indicated above, the enhancement of performance is possible for the PSCs based on single crystal ZnO NRs because the trap states are suppressed to a certain extent. To further investigate the influence of interface engineering on the performance of PSCs, ALD-deposited Al2O3 monolayers were coated on the surface of the annealed ZnO NRs to suppress the defects, resulting in enhanced PCE of solar cells. As displayed in Figure S6, the linear increment of thickness with the number of ALD cycles ensures high-quality passivation of ZnO NRs by ALD-Al2O3. In addition, Al element is chemically active, and thus can be easily oxidized in the water cycle. The linear growth demonstrates that it is a conformal deposition of one-atomic-layer by one-atomic-layer. On considering both fully oxidation and conformal deposition, the Al2O3 film quality is assured. This is also suggested in References [42-44]. The energy levels of the interface engineered solar devices include the bandgap of ALD-Al2O3 monolayers as shown in the inset of Figure 4 (a). As the number of ALD-Al2O3 monolayers increases, the wide bandgap of Al2O3 could block tunneling of free electrons from MAPbI3 to ZnO, which degrades the PCE of solar devices. As a result, there is a trade-off between the PCE enhancement and degradation induced by ALD-Al2O3 passivation. Figure 4 (a) shows that the performance of ZnO NRs based PSCs is not only significantly enhanced by the ALD-Al2O3 coating but also depending on ALD cycles. As summarized in Table 2, one cycle ALD-Al2O3 coating on the ZnO NRs causes the PCE improvement from 10.38% to 11.72%, the Jsc from 19.65 mA/cm² to 20.90 mA/cm², the FF from 58.46% to 59.13%, and the Voc from 1.020V to 1.021V. To investigate the influence of ALD-Al2O3 on the surface electron trap density of ZnO, we measured the I-V curves of ZnO with contacts, as shown in Figure 4 (b). The log-log plot of I-V curves demonstrate that the current increases linearly with voltage at the lower bias voltage region. At the higher bias voltage region, the current increases at a much higher slope. The transition point is the ohmic to trap filled limit transition point (V_{TFL}) and related to the trap density (N_t) linearly[45].

Table 1 Performance parameters of PSCs prepared using ZnO NRs of different lengths.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Voc [V]</th>
<th>Jsc [mA/cm²]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>1.00</td>
<td>13.11</td>
<td>58.67</td>
<td>7.70</td>
</tr>
<tr>
<td>Sample B</td>
<td>1.01</td>
<td>17.85</td>
<td>57.70</td>
<td>10.38</td>
</tr>
<tr>
<td>Sample C</td>
<td>1.01</td>
<td>15.29</td>
<td>53.34</td>
<td>8.22</td>
</tr>
<tr>
<td>Sample D</td>
<td>1.00</td>
<td>12.17</td>
<td>60.56</td>
<td>7.38</td>
</tr>
</tbody>
</table>
Figure 4  (a) Dependent of J-V curves on cycles of ALD-Al₂O₃. Inset: Energy-level diagram of PSCs based on Al₂O₃ coating; (b) Log-log plot curves of ZnO ETM; (c) Schematic diagram of ALD-Al₂O₃ on ZnO NRs showing suppression of recombination on the surface; (d) EQE spectra of the best device fabricated without ALD cycle and that with two ALD cycle treatment; (e) J-V curves both in forward (dash line) and reverse (solid line) scanning directions of PSCs fabricated using 910 nm length of as-grown ZnO NRs, annealed ZnO NRs, and annealed ZnO NRs with ALD-Al₂O₃; (f) Reproducibility of annealed ZnO NRs-based PSCs fabricated with two ALD cycles and without ALD cycles.

Table 2 Dependence of performance of PSCs on ALD-Al₂O₃ cycles. The PSCs based on ZnO NRs with length of 910 nm.

<table>
<thead>
<tr>
<th>ALD cycles</th>
<th>Voc[V]</th>
<th>Jsc[mA/cm²]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 cycle</td>
<td>1.020</td>
<td>19.65</td>
<td>58.46</td>
<td>11.72</td>
</tr>
<tr>
<td>1 cycle</td>
<td>1.021</td>
<td>20.90</td>
<td>59.13</td>
<td>12.62</td>
</tr>
<tr>
<td>2 cycle</td>
<td>1.023</td>
<td>22.42</td>
<td>71.43</td>
<td>16.08</td>
</tr>
<tr>
<td>3 circle</td>
<td>1.018</td>
<td>20.05</td>
<td>58.69</td>
<td>11.98</td>
</tr>
</tbody>
</table>

The value of V_TFL increases as electron traps. The values of V_TFL can be estimated from the I-V curves. The V_TFL of devices based on ZnO (1.20 V) is higher than that based on ZnO with two cycles of ALD-Al₂O₃ (1.00V). According to the relation between surface traps and V_TFL, the density of surface electron traps in the ZnO is much higher than that of the in the ALD-Al₂O₃ coated ZnO. The results show evidence of the reduction of surface defects of ZnO by the passivation of ALD-Al₂O₃ monolayers. As shown in Figure 4 (c), the inferior performance of ZnO NRs based PSCs is due mainly to trap states derived from defects on the surface of ZnO NRs. In perovskite solar cells, the generated free carriers from MAPbI₃ dissociate mainly at the interface of ETM/MAPbI₃. The photogenerated holes may be captured easily by the defect induced trap on the surface of ZnO NRs. The ALD-Al₂O₃
coating functions not only as a defect passivation layer, but also as a blocking layer to obstruct the photogenerated holes into the ETM. Furthermore, the ALD-Al₂O₃ coating leads to surface band bending and accelerates the separation of photogenerated carriers, which enhances the internal quantum efficiency (IQE) and results in the performance improvement. As a result, after two cycles of ALD-Al₂O₃ being deposited at the interface of ZnO NRs and the perovskite light harvester, the performance of PSCs is further enhanced. ALD-Al₂O₃ coating of two cycles on the ZnO NRs improves the PCE from 12.62 % to 16.08%, the Jsc from 20.90 mA/cm² to 22.42 mA/cm², the FF from 59.13% to 71.43%, and the Voc from 1.021V to 1.023V. It is confirmed that the implemented annealing process remarkably reduces the surface defects on ZnO. As a result, only two cycles of ALD-Al₂O₃ are enough to heal the defects on the surface of ZnO ETM in PSCs. The performance of PSCs based on annealed ZnO NRs deteriorates because the photogenerated electrons are blocked by ALD-Al₂O₃ deposited over two cycles as mentioned above. The external quantum efficiency (EQE) spectrum shown in Figure 4 (d) indicates the onset of photocurrent at 800nm, which is consistent with the reported bandgap of MAPbI₃ (1.55eV) [11, 46]. Although both EQE spectra show similar shapes, the two-cycle ALD-Al₂O₃ coating on annealed ZnO NRs attains obviously higher EQE than that without ALD-Al₂O₃ coating on ZnO NRs. Especially, without ALD-Al₂O₃ coating, in the wavelength from 500 to 750nm, surface defects on ZnO NRs lead to efficiency loss. The performance of PSCs based on the ALD interface engineering is dramatically improved by suppressing the surface defects. As suggested by previous reports, the poor interface between the perovskite and the oxide ETM contributes majorly to the J-V hysteresis in MAPbI₃ perovskite solar cell [47, 48]. The J-V characteristics in both forward and reverse scanning directions, shown in Figure 4 (e), demonstrate the best performance of PSCs based on as-grown, annealed and 2-cycle ALD-Al₂O₃ monolayer coated ZnO NRs (910nm). The J-V curves of PSCs based on as-grown ZnO NRs show that the PCE from forward scanning direction (PCE_{fwd}) is 10.38%, which is lower than that (10.60%) from reverse scanning direction (PCE_{rev}). The PCE_{fwd} of 11.72% obtained from the PSC based on annealed ZnO NRs is slightly lower than the PCE_{rev} of 11.90% as well. After 2-cycle ALD-Al₂O₃ monolayers applied on the annealed ZnO NRs, the J-V curves of devices exhibit negligible hysteresis with the best PCE_{fwd} of 16.08%. Because of ZnO thermal annealing and ALD-Al₂O₃ coating ZnO NRs, the best solar cell exhibits negligible hysteresis nature due to less interface defects between MAPbI₃ and ZnO ETM. Reproducibility is essential for commercial production of large area PSCs, and we fabricated 100 solar cell devices based on annealed ZnO NRs and annealed ZnO NRs passivated by two-cycle ALD-Al₂O₃, respectively. The histogram shown in Figure 4 (f) exhibits the distribution of efficiencies of the devices fabricated with/without ALD-Al₂O₃ interface engineering. The statistical data shown in Table 3 suggests that the PSCs fabricated using ALD-Al₂O₃ yield lower standard deviations (±0.49) and higher average PCEavg of 15.06%. However, the PSCs fabricated without ALD-Al₂O₃

<table>
<thead>
<tr>
<th>Device Number</th>
<th>Standard Deviation</th>
<th>PCE_{fwd}[%]</th>
<th>PCE_{avg}[%]</th>
<th>PCE_{rev}[%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 cycles ALD</td>
<td>100</td>
<td>0.49</td>
<td>14.20</td>
<td>15.06</td>
</tr>
<tr>
<td>Without ALD</td>
<td>100</td>
<td>0.69</td>
<td>9.06</td>
<td>10.33</td>
</tr>
</tbody>
</table>

Table 3 Standard deviation of efficiency of ZnO NRs-based PSCs, 100 devices were fabricated for each group.
exhibit higher standard deviations (±0.69) and lower PCE_{avg} of 10.33%. The results demonstrate that ALD-Al₂O₃ on ZnO NRs also results in high reproducibility of PSCs.

To further confirm that the PCE improvement of PSCs is ascribed to the ALD-Al₂O₃ interface engineering, the full-scan XPS spectra of ZnO NRs were obtained. As shown in Fig. 5 (a), the existence of Zn, O, C elements are confirmed in both ZnO NRs. The XPS peak of Zn 2p 3/2 centered at 1022 eV is for ZnO NRs. The Zn 2p XPS peaks of two ZnO NRs samples are corresponding to crystal lattice zinc of ZnO [49]. Comparing the full-scan XPS spectra of the two samples, a weak, but distinct Al 2s peak at 125 eV is ascribed to ALD-Al₂O₃. The C 1s peak at 285 eV is ascribed to the carbon contamination from the organics used to prepare ZnO NRs [49]. As shown in Figure 5 (b) and (c), the O 1s XPS peaks of annealed ZnO NRs and annealed ZnO NRs with ALD-Al₂O₃ are decomposed into two components by fitting with the Gaussian function that centered at 530 and 531 eV, respectively. The peak at a lower binding energy is attributed to O²⁻ ions in ZnO crystal lattice, and the peak at a higher binding energy is associated with O²⁻ ions in oxygen-deficient regions within the matrix of ZnO [49,50]. The peak centered at 531 eV ascribed to oxygen vacancies generated by loosely bound oxygen on the surface of ZnO NRs. The atomic percentages of O²⁻ ions in oxygen-deficient regions are reduced from 42.1% to 28.4% owing to passivation of ALD-Al₂O₃ on ZnO NRs. The XPS results indicate that the ALD-Al₂O₃ coating on ZnO NRs apparently suppresses the peak intensity of O²⁻ ions because a certain amount of oxygen vacancies on the surface of ZnO NRs are repaired. Figure 5 (d) shows the photoluminescence property of ZnO NRs measured at the room temperature. The PL spectra clearly indicate that the ZnO NRs exhibit a near band emission around 380 nm and a broad visible emission (450-650 nm) that is usually associated with oxygen defects. Among the different defects proposed to explain the visible PL emission, oxygen vacancies are considered to be the most prominent one [51,52]. The intensity of UV emission is obviously enhanced and that of visible emission is suppressed to some extent by coating.

![Figure 5](image_url) (a) Full scan XPS of ZnO NRs (black) and ZnO NRs with ALD-Al₂O₃ (red); (b) O 1s XPS spectra of ZnO NRs; (c) O 1s XPS spectra of ZnO NRs with ALD-Al₂O₃; (d) PL spectra of ZnO NRs, inset: time-resolved PL of MAPbI₃ on ZnO NRs.
ZnO NRs with ALD-Al$_2$O$_3$. Furthermore, the time-resolved PL shown in the inset of Figure 5 (d) clearly shows an improvement in emission decay time, which supports that the ALD-Al$_2$O$_3$ monolayers on ZnO NRs suppresses the surface recombination of MAPbI$_3$, and thus the passivation enhances the PCE of PSCs. The obtained XPS and PL spectra are also consistent with the results from previous reports [29,45,51]. The enhancement of PCE of PSCs exhibited in Figure 4 (e) is confirmed by the results from XPS and PL measurements shown in Figure 5.

3 Conclusion

High performance PSCs based on interface engineering of ZnO NRs are successfully fabricated. The residual PbI$_2$ in MAPbI$_3$ crystals on ZnO NRs was eliminated by utilizing the mixture solvent of DMSO and DMF (VDMF: VDMSO =7:3) for PbI$_2$ to suppress the crystallization rate of PbI$_2$. The full conversion of PbI$_2$ to MAPbI$_3$ enables a uniform surface morphology of perovskite film, which ensures reproducibility of PSCs. The performance of PSCs was significantly improved by the ALD interface engineering for surface defect passivation of ZnO NRs. The PSCs based on annealed ZnO NRs passivated by ALD-Al$_2$O$_3$ exhibit the best PCE of 16.08% and the average PCE of 15.06%. We suggest that ALD-grown monolayers provide a new pathway for passivation of defects for PSCs.

4 Experimental

4.1 Growth of ZnO NRs and fabrication of PSCs

The ZnO NRs were grown based on a two-step method reported elsewhere [20, 21]. A thin ZnO film (30 nm) seed layer was prepared on a FTO coated glass. The well-arranged ZnO NRs were fabricated by immersing the preseeded samples into a solution of Zn(NO$_3$)$_2$ and hexamethylenetetramine(HMT) at 95 °C. The Al$_2$O$_3$ monolayers were deposited by ALD on the prepared ZnO NRs. The PSCs were fabricated using ZnO NRs by a two-step method in a nitrogen-filled glove box (<1 ppm O$_2$ and H$_2$O). The PbI$_2$ (460 mg/mL) was dissolved in a mixture solution of DMF: DMSO=7:3 at 70 °C. Following the spin-coating of the dissolved PbI$_2$ solution on ZnO NRs at 5000rpm for 30s, the sample was dipped into a MAI solution for 1min (MAI was dissolved in 2-propanol under stirring at a concentration of 10mg/mL). Consequently, the MAPbI$_3$ perovskite layer was produced by heating the sample at 100 °C for 5 min. The hole transporting layer was deposited by spin-coating the spiro-OMeTAD solution at 4000 rpm for 30 s. Finally, 80 nm of gold was prepared by e-beam evaporation on the top of the devices as a back contact.

4.2 Measurement and Characterization

The measurement of current-voltage curves was carried out under AM 1.5 simulated sunlight (Newport, Oriel Sol3A Class Simulator, calibrated using an NREL-calibrated Si solar cell) with a Keithley 2400. The EQE measurements were performed employing a 150 W Xe lamp coupled with a monochromator controlled by a computer. The photocurrent was measured using an optical power meter 70310 from Oriel Instruments, using a Si photodiode to calibrate the system. Surface morphology, cross-sectional scanning electron images of the NRs, and complete solar cell structures were obtained using field emission SEM (FEI-Inspect F50, Holland). X-ray diffraction measurements were performed using a Bede D1 system with Cu Kα radiation. The UV-vis absorption spectra of ZnO NRs/perovskite films were measured using an ultraviolet-visible (UV–vis) spectrophotometer (Schimadzu UV-3101 PC). XPS characterizations were carried out by using an instrument made by Thermo Scientific (Escalab 250Xi).
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Electronic Supplementary Material: Supplementary material (further details of top view of ZnO NRs via SEM; XRD patterns of as-grown and annealed ZnO NRs; Properties of perovskite material and devices, linear growth of Al2O3) is available in the online version of this article at xxxxxx

References


[51] Tam, K. H.; Cheung, C. K.; Leung, Y. H.; Djurišić, A.

Interface engineering of high efficiency perovskite solar cells based on ZnO nanorods using atomic layer deposition

Shibin Li¹, *,(✉), Peng Zhang¹, Yafei Wang¹, Hojjatollah Sarvari², Detao Liu¹, Jiang Wu³, Yajie Yang¹, Zhiming Wang⁴, Zhi David Chen¹,², *,(✉)

¹School of Optoelectronic Information, University of Electronic Science and Technology of China (UESTC), Chengdu, 610054, China
²Department of Electrical & Computer Engineering and Center for Nanoscale Science & Engineering, University of Kentucky, Lexington, Kentucky 40506, USA
³Department of Electronic and Electrical Engineering, University College London, Torrington Place, London WC1E 7JE, United Kingdom
⁴Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu, 610054, China

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Figure S1 Top view of ZnO NRs prepared at solutions of the same concentration for (a) 0.5 h, (b) 1 h, (c) 2 h, and (d) 3 h.

Figure S2 SEM view of perovskite film; (a) MAPbI$_3$/ZnO; (b) MAPbI$_3$/Al$_2$O$_3$/ZnO.
Figure S3 XRD patterns of as-grown ZnO NRs and ZnO NRs annealed at 500 °C for 30 min.

Figure S4 Perovskite film peeling-off as the dipping time exceeds 1 h; (b) UV-VIS absorption curves of perovskite prepared for 1 min and 1 h immersion time.
Figure S5 J-V curves of solar cell based on as-grown/annealed ZnO NRs (910 nm). The ZnO NRs used to prepare PSCs were annealed at 500 °C for 30 min.

<table>
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<tr>
<th></th>
<th>Voc[V]</th>
<th>Jsc[mA/cm²]</th>
<th>FF[%]</th>
<th>PCE[%]</th>
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<tr>
<td>As grown</td>
<td>1.01</td>
<td>17.85</td>
<td>57.70</td>
<td>10.38</td>
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<tr>
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<td>1.02</td>
<td>19.65</td>
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Figure S6 Atomic layer deposition of Al₂O₃ is evidenced by the linear increment of thickness with the ALD cycles.