Atomic Layer Deposition of TiO₂ for a High-Efficiency Hole-Blocking Layer in Hole-Conductor-Free Perovskite Solar Cells Processed in Ambient Air

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ABSTRACT: In this study we design and construct high-efficiency, low-cost, highly stable, hole-conductor-free, solid-state perovskite solar cells, with TiO₂ as the electron transport layer (ETL) and carbon as the hole collection layer, in ambient air. First, uniform, pinhole-free TiO₂ films of various thicknesses were deposited on fluorine-doped tin oxide (FTO) electrodes by atomic layer deposition (ALD) technology. Based on these TiO₂ films, a series of hole-conductor-free perovskite solar cells (PSCs) with carbon as the counter electrode were fabricated in ambient air, and the effect of thickness of TiO₂ compact film on the device performance was investigated in detail. It was found that the performance of PSCs depends on the thickness of the compact layer due to the difference in surface roughness, transmittance, charge transport resistance, electron–hole recombination rate, and the charge lifetime. The best-performance devices based on optimized TiO₂ compact film (by 2000 cycles ALD) can achieve power conversion efficiencies (PCEs) of as high as 7.82%. Furthermore, they can maintain over 96% of their initial PCE after 651 h (about 1 month) storage in ambient air, thus exhibiting excellent long-term stability.

KEYWORDS: atomic layer deposition, hole-conductor-free perovskite solar cells, hole-blocking layer, carbon counter electrode, long-term stability

1. INTRODUCTION

Since the introduction of organometal halide perovskite into liquid dye-sensitized solar cells (DSSCs) in 2009,¹ perovskite solar cells (PSCs) have boomed as a new-generation, promising photovoltaic device for clean energy conversion due to their low cost and high efficiency.² However, to realize commercial applications scientists still need to develop PSCs with higher efficiencies, enhanced stability, and lower manufacturing cost. Thus, efforts have been made to improve the performance of PSCs, such as improvements in device architecture,³–⁵ control of morphology and crystal growth,⁶–⁹ and optimizations of interface manipulation.¹⁰,¹¹ These efforts have improved PSC’s potential for use as cost-effective, high-efficiency solar cells.

Generally, in most cases, typical PSCs are fabricated with very expensive organic/polymeric hole-transporting materials (HTM) such as Spiro-OMeTAD or poly(3-hexylthiophene) (P3HT) and noble metals (usually Au or Ag) acting as counter electrodes.¹²,¹³ Besides, these PCSs require rigorous conditions (e.g., a high vacuum) for the deposition of Au or Ag to fabricate counter electrodes and for the assembly of PSC devices which significantly increase manufacturing costs. To reduce the overall cost of such devices, it is worth developing hole-conductor-free (HTM-free) PSCs assembled in normal conditions (ambient air) and replacing the noble metal with other available candidates. In hole-conductor-free PSCs, the use of an expensive hole-transporting layer (HTL) can be avoided.¹⁴,¹⁵ Recently due to its low cost, considerable stability, and abundance, carbon materials have emerged as promising alternatives to noble metals (Au or Ag) as highly efficient counter electrodes (CEs) in PSCs.¹⁶–²⁴

It is has been confirmed²⁵ that, in PSCs, the photogenerated charge carriers (electrons and holes) are both formed in the organometal halide perovskite layer which could also transport carriers with diffusion lengths exceeding 1 μm. It should be
mentioned that electron–hole recombination within the device is one of the major known loss factors decreasing the open-circuit potential. In typical mesoporous-structured PSCs, the photoanode comprises a compact layer and a mesoporous layer. The compact layer (or hole-blocking layer) is able to transport, and collect, photogenerated electrons and can also prevent holes formed in the perovskite or HTL layer from reaching the fluorine-doped tin oxide (FTO) electrode to avoid a short-circuit of the cell. Therefore, the compact layer (hole-blocking layer) plays a crucial role in PSCs. TiO2 film with a thickness of dozens of nanometers in a compact layer has been used to inhibit electron–hole recombination and avoid direct contact between the perovskite layer and the FTO electrode.26

In general the TiO2 compact layer was prepared by various conventional methods including spin coating,27 spray pyrolysis,28,29 electrochemical deposition,30 and thermal oxidation.31,32 Usually in these methods, high-temperature (>450 °C) thermal post-treatments are needed. Thus, on one hand, it greatly increases the fabrication cost and presents drawbacks in view of industrial-scale roll-to-roll fabrication due to a lack of compatibility with flexible substrates; on another hand it can increase the occurrence of pinholes in the TiO2 compact film,34 which impaired the performance of PSCs.35 In addition it is generally more challenging to precisely control the thickness of a compact layer film at the atomic to nanometric scale (e.g., from 10 nm down to 0.5 Å) when using the aforementioned methods. Compared with conventional techniques for preparation of the compact layer, the ALD technique has additional advantages of being a low-temperature process, offering precise thickness controllability, and having excellent film conformity and uniformity.36 Hence, ALD is capable of depositing a homogeneous pinhole-free TiO2 thin film on the photoanode of perovskite solar cells as it involves the chemical reactions of volatile, metal, and oxidizing precursors at two separate stages where no sintering is needed after the deposition of the blocking overlayer.

In this work TiO2 thin films, of different thickness, were deposited on an FTO-coated glass substrate by the ALD technique. Then we directly assembled them into a series of PSCs in ambient air with a mesoporous structure of glass-FTO/compact TiO2/mesoporous TiO2–CH3NH3PbI3/C and compared their photovoltaic performances. Based on these TiO2 compact films in the PSCs, a stable performance at over 96% of the initial PCE was accomplished in the devices after 651 h. It was found that the ALD-TiO2 film was sufficient to serve as a high-efficiency hole-blocking layer and electron transport layer in the PSC leading to a PCE of 7.82%.

2. EXPERIMENTAL WORK

The ALD-TiO2 coating process was carried out using a Savannah S100 ALD reactor (Savannah System, Cambridge NanoTech. Inc., USA) equipped with a gas-flow system. TiO2 was deposited at 150 °C using titanium(IV) isopropoxide (TTIP) and H2O as Ti and O precursors, respectively. High-purity nitrogen (N2, 99.999%) was used as both the purge gas and carrier gas for both precursors. A steady flow of N2 at 50 sccm (standard cubic centimeters per minute) was used in the ALD process. Before ALD processing, the FTO/Glass substrates (sheet resistance 14 Ω cm−1) were cleaned by ultrasonication in acetone, ethanol, and deionized water, successively. TTIP was pulsed into the chamber for 0.2 s, after which water vapor was pulsed into the chamber for 0.05 s. For two half-deposition processes, the FTO/glass substrates were exposed to vapor for 8 s, and the reactors were then purged with N2 for 3.5 s. The ALD cycling was repeated an appropriate number of times to obtain systematic variation in the coating thicknesses (as shown in Figure 1).

On the top surface of ALD-TiO2 film, the mesoporous TiO2 layer was deposited by spin coating at 7000 rpm for 60 s using a commercial TiO2 paste (average particle size, c. 20 nm) diluted in ethanol and then sintered in air at 550 °C for 60 min. After cooling to room temperature, the perovskite layer was then deposited by spin coating at 4000 rpm for 60 s using CH3NH3PbI3 liquid (dissolved in dimethylformamide (DMF), at about 40% solid content, Shanghai MaterWin New Materials Co., Ltd.). The monolithic cell fabrication is completed after a back-contact layer of carbon (JELCON CH-8 carbon ink, sheet resistance 10 Ω cm−1, JUJO Printing Supplies & Technology (Pinghu) Co., Ltd., China) forming the CE was fabricated by a blade-coating method on top of the device.

The cross-section of the devices, and the top views of ALD-TiO2 films, were imaged by a field-emission scanning electron microscope (FE-SEM, Jeol JEM 6510LV) and a atomic force microscope (AFM, Nanoscope-IIIa). The transmission spectra were obtained by a UV–vis spectrophotometer (UV-3600, Shimadzu). The X-ray diffraction (XRD) data of the ALD-TiO2 film, after annealing, were collected with a Bruker-AXS D8 Advance. Current–voltage (I–V) characteristics of the devices were measured in the dark and under simulated AM 1.5G (100 mW cm−2 irradiance), respectively, using a solar simulator (Oriel, model 91192–1000) and a source meter (Keithley 2400, USA). Electrochemical impedance spectroscopy (EIS) was performed using an electrochemical workstation (Zennium, IM6,
over the frequency range of 10 mHz to 2 MHz under simulated AM 1.5G (100 mW cm\(^{-2}\) irradiance).

3. RESULTS AND DISCUSSION

Figures 2(a) and 2(b) show the surface morphology of an examplatory compact TiO\(_2\) layer fabricated on FTO substrates using ALD with and without annealing, respectively. The film is highly compact and resembles the bumpiness of the underlying FTO substrate.\(^{37,38}\) This can be explained by the nature of ALD, which is a surface-sensitive process that creates self-limited layer-by-layer films. A similar morphological analysis for an atomic layer deposited TiO\(_2\) layer has been observed by Wu et al.\(^{37}\) Figures 2(a) and 2(b) reveal that the small TiO\(_2\) crystalline grains with size of tens of nanometers are closely conjoined: no nanoscale pinholes are observed. These signify that the surface coverage of the ALD-TiO\(_2\) compact layer was particularly high. For comparison, the film was exposed to a typical annealing treatment; as shown in Figure 2(b), the morphology and uniformity of ALD-TiO\(_2\) film were not disrupted, indicating the high thermal stability of the ALD-TiO\(_2\) compact layer. An XRD pattern of an ALD-TiO\(_2\) film after annealing treatment is shown in Figure 2(c). The (010), (004), (200), (015), (211), and (204) planes are included, confirming the anatase phase of the TiO\(_2\).

One focus of this work was to improve the cell efficiency and performance by finding the optimum thickness of the TiO\(_2\) compact films. Hence, we have used a different number of ALD cycles (ranging from 200 to 4000) to tune the thickness of the ALD-TiO\(_2\) film and measured the corresponding cross-section of each FE-SEM image to determine the thickness of various ALD-TiO\(_2\) layers. As shown statistically in Figure 2(d), the thickness of the ALD-TiO\(_2\) film linearly increases with the number of cycles. The corresponding thicknesses of each film prepared by 200, 800, 1200, 1600, 2000, and 4000 ALD cycles were 16, 68, 106, 145, 181, and 368 nm, respectively. We fitted an equation to the data in Figure 2(d) to show the relationship between the number of ALD cycles (X) and the thickness of ALD-TiO\(_2\) film (nm) (Y): Y = 0.091X − 2.41. From this equation, the thickness was calculated with a deposition rate of 0.9 Å per cycle.

Figures 3(a) to 3(l) show typical AFM images of the pure FTO substrate and the ALD-TiO\(_2\) films for the different ALD cycles. The root-mean-square roughnesses (R\(_{\text{rms}}\)) of pure FTO substrate and each ALD-TiO\(_2\) film were calculated with 11.93 nm (FTO), 20.74 nm (800 cycles), 31.82 nm (1200 cycles), 24.80 nm (1600 cycles), 25.09 nm (2000 cycles), and 23.80 nm (4000 cycles), respectively. Dependence of R\(_{\text{rms}}\) of the ALD-TiO\(_2\) compact layer on different ALD cycles was shown in Figure 4(a). The surface roughnesses of all the ALD-TiO\(_2\) films were thus slightly bumpier than that of bare FTO substrate and increase with TiO\(_2\) film thickness, due to the growing TiO\(_2\) grains, thus creating continuously denser films.
speaking, the filling of the bumpy surface by TiO₂ nanoparticles on the last layer could affect the surface roughness of the next layer. The ALD-TiO₂ films deposited at 1200 cycles (106 nm) reached a maximum value of Rₘₚ. The illuminated light would be scattered strongly by the ALD-TiO₂ films with rougher surface, resulting in a great loss of light energy when passing through to the perovskite layer. Another criterion for the cell efficiency is the transparency of the TiO₂ compact film. Figure 4(b) shows the transmittance spectra of the pure FTO and the ALD-TiO₂ films with varying thickness. The pure FTO had over 98% transmittance in the visible region (450–900 nm wavelength). For comparison, the transmittance decreased slightly with the introduction of the ALD-TiO₂ films in direct correlation with the film thickness, yet still retained values above 92%. Only the thickest film reduced the transmittance to about 88%. On one hand, for the device based on 1200 cycles of ALD-TiO₂ film, although the transmittance was high, the light scattering was also strong. On the other hand, the device based on 4000 cycles of ALD-TiO₂ film had the lowest transmittance. The above results indicated that the high transmittance and the weak light scattering of the ALD-TiO₂ films (800 cycles, 1600 cycles, 2000 cycles) sufficiently increased the utilization efficiency of illuminated light.38

Figure 3. (a) to (f) AFM 2D topography and (g) to (l) 3D views of the pure FTO substrate and the ALD-TiO₂ films for the different ALD cycles.

Figure 4. (a) Dependence of Rₘₚ of ALD-TiO₂ compact layer on different ALD cycles. (b) Corresponding transmittance of various thicknesses of the ALD-TiO₂ films on FTO/glass substrates.
allowing for increased absorbance of light by the perovskite layer.

Figure 5 shows the device structure and energy level diagram of the PSC. This PSC includes a conductive glass/FTO substrate, a compact layer, a perovskite-sensitized TiO₂ mesoporous layer, and a carbon counter electrode. The actual images of ALD-TiO₂ film on the top of an FTO/glass substrate and the whole device are shown in Figures 6(b) and 6(c), respectively. After TiO₂ was deposited by ALD on the bare FTO/glass substrates, the as-formed TiO₂/FTO/glass films still show excellent transmission of light. Without any HTL in the device, the TiO₂ compact film fabricated by ALD plays a crucial role in collecting and transporting the electrons and effectively inhibiting the electron–hole recombination. The energy levels for the conduction band edges of TiO₂ and CH₃NH₃PbI₃ are at −4.1 and −3.9 eV, and as for the valence band edges they are at 7.3 and −5.43 eV, respectively. Meanwhile the Fermi level of carbon is at −5.0 eV which is slightly higher than the energy levels of the valence band edge of CH₃NH₃PbI₃ (−5.43 eV). The good matching of band structure makes electron–hole separation available in the perovskite layer.

Furthermore, to reduce costs, we assembled a group of PSCs based on free HTL and a carbon counter electrode, which will lead to a relatively lower fill factor (FF). The cross-sectional SEM image of the device is shown in Figure 6(a). The total thickness of the TiO₂ mesoporous layer filled with the perovskite and capping layer is about 3 μm. The thicker top layer, with a thickness of about 10 μm, is the carbon counter electrode.

Photovoltaic performance of the corresponding PSC devices was tested under AM 1.5G irradiation (100 mW cm⁻²) and in the dark, respectively. All of the devices were fabricated under ambient air at a humidity of about 55% and then stored in a drying oven (dry air environment, no sealing) for about 12 h. The J–V characteristics of these PSCs based on various TiO₂ compact layers fabricated by different ALD cycles are shown in Figure 7(a), and the corresponding photovoltaic parameters are listed in Table 1. The devices based on the ALD-TiO₂ films at low ALD cycles (e.g., at 200 cycles and 750 cycles) had low PCEs (3.21% and 3.54%, respectively, as shown in Table S1). The device at 800 cycles with the ALD-TiO₂ compact layer had Vₜₙ, Jₙₑ, and FF, respectively, of 856 mV, 12.74 mA cm⁻², and 43.99%, leading to a PCE of 4.85%. With 1200 cycles applied to the ALD-TiO₂ compact layer, the PCE of the device increased to 6.06%. As the number of ALD cycles increased to 1600, PCE reached 7.03%. The improvement mainly came from the increase in Vₜₙ (by around 100 mV, i.e., from 856 to 955 mV) and Jₙₑ (from 12.74 to 18.30 mA cm⁻²). Furthermore, on increasing the number of ALD cycles to 2000, Vₜₙ and Jₙₑ slightly increased by 10 mV and 1.23 mA cm⁻², respectively, leading to a best-performance device with a PCE of as high as 7.82%. However, as the number of ALD cycles increased to 4000, PCE decreased to 5.61%, which was attributed to the decreases in Vₜₙ (by around 70 mV, i.e., from 960 to 895 mV) and Jₙₑ (by around 5.09 mA cm⁻², i.e., from 19.53 to 14.44 mA cm⁻²) compared to the best-performance device.

As shown in Figure 7(b), the onset of dark current emerges at about 600 mV in the J–V curve of PSC based on an 800 cycles ALD-TiO₂ compact layer measured in the dark. On increasing the thickness, the onset shifts to over 650 mV, and the current value decreases rapidly at the same applied bias in the dark, indicating a decrease in back electron–hole recombination from the conduction band of TiO₂ and FTO/glass to the HTL or perovskite layer.

To authenticate the performance reproducibility of the devices, 12 separate devices (the same batch of samples) based on an optimized TiO₂ compact film (2000 cycles ALD, 181 nm) were fabricated under the same experimental conditions. The distributions of photovoltaic parameters for them under simulated AM 1.5G (100 mW cm⁻²) irradiance are shown in Figure 8 and Table S2. It can be found that all of them had a PCE of over 6.5%, and 83.3% of the devices had a PCE greater than 7.0%, indicating their good reproducibility. Meanwhile, 83.3% of the devices had a Vₜₙ of over 900 mV, and 83.3% of them had a Jₙₑ of above 18 mA cm⁻²; however, their FF was poor, at less than 45%.

Importantly, the PCE decay measurements further revealed that the ALD-TiO₂ compact layer played a vital role in the stability of the devices assembled in ambient air. As shown in Figure 9, under the same testing conditions, the devices based on 1200 cycles of the ALD-TiO₂ compact layer were measured immediately and 651 h later, respectively. All the PSCs exhibited a PCE decay feature with parallel trends. To our surprise, Jₙₑ and FF reduced slightly leading to an approximately 3% drop in the PCE of the device even after 651 h (the PCE
still reached 5.87%), indicating the excellent long-term stability of the as-fabricated PSCs.

To investigate the charge transport in the as-fabricated hole-conductor-free PSC devices based on ALD-TiO$_2$ as the compact film, electrochemical impedance spectroscopy (EIS) measurements were performed over the frequency range of 10 mHz to 2 MHz at a 0.8 V bias under simulated AM 1.5G (100 mW cm$^{-2}$ irradiance). In a typical mesoporous PSC device, the device is constructed to an architecture of TiO$_2$/perovskite/HTM/CE, and thus there are three contact interfaces: TiO$_2$/perovskite, perovskite/HTM, and HTM/CE, respectively. In our study, due to the absence of HTM layer, the devices comprised a simplified structure of TiO$_2$/CH$_3$NH$_3$PbI$_3$/C. As a result, two interfaces, i.e., TiO$_2$/perovskite and perovskite/C, had to be taken into account. We used a circuit model (the inset of Figure 10(a)) consisting of two parallel resistive/capacitive (RC) elements connected in series with a series resistance ($R_s$) to obtain a good fit of the experimental data; the fitted parameters are listed in Table 2. It is well-known that the $R_s$ value has a deleterious influence on FF of the device. The devices based on 1200 cycles ALD-TiO$_2$ layer had the lowest $R_s$ of 49.46 $\Omega$, in good agreement with the highest value of FF (47.67%), and other devices had much higher $R_s$ with relatively lower FF.

![Figure 7. J–V characteristics of PSCs based on different thickness of ALD-TiO$_2$ compact layer under (a) simulated AM 1.5G (100 mW cm$^{-2}$ irradiance) and (b) in the dark.](image)

Table 1. Summarized Device Parameters of PSCs Based on 800 to 2000 Cycles of the ALD-TiO$_2$ Compact Layer$^a$

<table>
<thead>
<tr>
<th>samples</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>800 cycles TiO$_2$ (68 nm)</td>
<td>856</td>
<td>12.74</td>
<td>43.99</td>
<td>4.85</td>
</tr>
<tr>
<td>1200 cycles TiO$_2$ (106 nm)</td>
<td>895</td>
<td>14.19</td>
<td>47.67</td>
<td>6.06</td>
</tr>
<tr>
<td>1600 cycles TiO$_2$ (145 nm)</td>
<td>955</td>
<td>18.30</td>
<td>40.22</td>
<td>7.03</td>
</tr>
<tr>
<td>2000 cycles TiO$_2$ (181 nm)</td>
<td>965</td>
<td>19.53</td>
<td>41.47</td>
<td>7.82</td>
</tr>
<tr>
<td>4000 cycles TiO$_2$ (368 nm)</td>
<td>895</td>
<td>14.44</td>
<td>43.41</td>
<td>5.61</td>
</tr>
</tbody>
</table>

$^a$The corresponding parameters indicated are open-circuit voltage ($V_{oc}$), short-circuit current ($J_{sc}$), fill factor (FF), and power conversion efficiencies (PCEs).

![Figure 8. Histograms of photovoltaic parameters for 12 devices (the same batch of samples) based on 2000 cycles compact TiO$_2$ layer under simulated AM 1.5G (100 mW cm$^{-2}$ irradiance).](image)

![Figure 9. J–V characteristics of PSCs based on 1200 cycles of ALD-TiO$_2$ compact layer under simulated AM 1.5G (100 mW cm$^{-2}$ irradiance), which was measured immediately and 651 h later, respectively.](image)
cycles) had small values of $R_{tr}$ from 199.92 to 475.83 Ω. As the ALD-TiO$_2$ film became thicker (4000 cycles), the corresponding values of $R_{tr}$ increased to 1232.18 Ω. Probably, a thicker ALD-TiO$_2$ film could weaken the attachment of the perovskite to the C counter electrode interface, thus inhibiting injection or extraction of photogenerated holes at the perovskite/C interface. Furthermore, with the ALD-TiO$_2$ compact layer being thicker (from 800 cycles to 2000 cycles), the increase in $R_{rec}$ (from 161.64 to 736.40 Ω) can reduce the electron–hole recombination probability at the perovskite/TiO$_2$ interface, resulting in the increase in $V_{oc}$ of the PSCs from 856 to 965 mV (Figure 10(d)). However, the device based on 4000 cycles of the ALD-TiO$_2$ compact layer had a large $R_{rec}$ (3473.60 Ω) and a large $R_{tr}$ (1232.18 Ω), in which the $R_{tr}$ was dominant in the structure of TiO$_2$/$\text{CH}_3\text{NH}_3\text{PbI}_3$/C, thus resulting in comparatively lower $V_{oc}$ (Figure 10(b)).

Figure 10. (a) Nyquist curves, (b) Bode curves, (c) FF, $R_s$ plots, and (d) PCE, $V_{oc}$, $R_{rec}$ and $\tau$ plots of the PSCs based on different thickness of ALD-TiO$_2$ compact layers under simulated AM 1.5G (100 mW cm$^{-2}$ irradiance) with a bias of 0.8 V.

Table 2. Summary of Electrochemical Impedance Spectroscopy Parameters of PSCs Based on 800 to 2000 Cycles of the ALD-TiO$_2$ Compact Layer

<table>
<thead>
<tr>
<th>samples</th>
<th>$R_s$ (Ω)</th>
<th>$R_{tr}$ (Ω)</th>
<th>$R_{rec}$ (Ω)</th>
<th>$\tau$ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>800 cycles TiO$_2$ (68 nm)</td>
<td>93.62</td>
<td>199.92</td>
<td>161.64</td>
<td>685.66</td>
</tr>
<tr>
<td>1200 cycles TiO$_2$ (106 nm)</td>
<td>49.46</td>
<td>185.88</td>
<td>285.28</td>
<td>723.50</td>
</tr>
<tr>
<td>1600 cycles TiO$_2$ (145 nm)</td>
<td>154.53</td>
<td>374.23</td>
<td>386.91</td>
<td>732.53</td>
</tr>
<tr>
<td>2000 cycles TiO$_2$ (181 nm)</td>
<td>76.07</td>
<td>475.83</td>
<td>736.40</td>
<td>782.60</td>
</tr>
<tr>
<td>4000 cycles TiO$_2$ (368 nm)</td>
<td>79.32</td>
<td>1232.18</td>
<td>3473.60</td>
<td>372.72</td>
</tr>
</tbody>
</table>

The corresponding parameters indicated are series resistance ($R_s$), charge transfer resistance ($R_{tr}$), recombination resistance ($R_{rec}$), and electron lifetime ($\tau$).

4. CONCLUSIONS

In summary, we have developed HTM-free PSCs with high efficiency, low cost, and excellent long-term stability in an ambient atmosphere where thickness-controllable TiO$_2$ forms the compact layer and cheap carbon forms the counter electrode. Detailed investigations with EIS, $J$–$V$, AFM, UV–vis, and other techniques revealed that the performance of PSCs depends on the thickness of the compact layer due to the difference in surface roughness, transmittance, charge transport resistance, electron–hole recombination rate, and the charge lifetime. The method developed here paves the way for the fabrication of low-cost, high-stability PSCs for practical applications in the future.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b02701.
Table S1 and S2 showing summarized device parameters for PSCs and statistical data of photovoltaic parameters for 12 devices (PDF)

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**Notes**
The authors declare no competing financial interest.

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