Pinhole-Free Perovskite Films by Methylamine Iodide Solution-Assisted Repair for High-Efficiency Photovoltaics under Ambient Conditions

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ABSTRACT: In this study, we demonstrate a simple strategy for obtaining pinhole-free, homogeneous, well-crystallized perovskite films under ambient conditions. The preparation of perovskite film with high light-harvesting efficiency and long carrier lifetime is verified. By applying this film in TiO2-based perovskite solar cells (PVSCs), we achieved a high power-conversion efficiency (PCE) of 13.07%, which is doubled with respect to that of the PVSC not subjected to the same improvement procedure (6.54%). High open-circuit photovoltage, photocurrent density, and fill factor are the main contributions to the high PCE that results from low trap density and high recombination resistance of the resultant perovskite films. This work paves a new means for fabricating high-performance perovskite films and PVSC devices in an ambient atmosphere.

KEYWORDS: perovskite solar cell, methylamine iodide, pinhole free, homogeneous, ambient conditions

1. INTRODUCTION

Perovskite solar cells (PVSCs) with organic/inorganic hybrid perovskite materials as highly efficient light absorption layers have been reported and have attracted wide interest because of the device’s high-power conversion efficiency (PCE), simple solution process, flexibility, and low-cost. As such, PVSCs are considered a promising alternative for future energy supply. To date, the PCE of PVSCs has been boosted from an initial 3.8%1 to more than 20%.2–25 The typical structure of the PVSC is comprised of a conductive substrate, electron transfer layer, perovskite absorption layer, hole transfer layer, and metal electrode and is named as the “inverted” structure (conductive substrate/hole transfer layer/perovskite layer/electron transfer layer/mental electrode).3,5 The perovskite layer is mainly responsible for absorbing sunlight and generating electron–hole pairs. Some advantages of the perovskite materials in PVSCs have been reported and identified. These benefits include a superior optical property derived from a suitable and tunable band gap, long electron–hole diffusion lengths, and ambipolar charge transport.3–11 Given these attributes, perovskite materials, as a critical component, play a decisive role in PVSC performance by controlling crystallization and morphology. Currently, various preparation methods have been developed for producing high-quality perovskite films such as the one-step deposition, two-step sequential deposition, vapor-assisted deposition, and various improved methods.1,12–25 Among these methods, the two-step sequential deposition easily controls film thickness, uniformity, and morphology by regulating the thickness of PbI2, methylammonium iodide (MAI) solution concentration, and dipping time.2,13 Therefore, the method is a kind of general approach for generating high-quality perovskite. A water-free environment is another key point in the production of high-quality perovskite films; in such conditions, the adverse effect of high humidity is avoided.1,26 To achieve industrialization of the process, a highly efficient PVSC manufacture technique must be established under ambient conditions to simplify the production process, reduce cost, and improve market competitiveness. Recently, some strategies have been proposed for obtaining high-quality perovskite films under ambient conditions. These methods include solution-based one-step microflowing antisolvent deposition, replacing I− with SCN− in MAI and adding polymer matrix in the perovskite precursor.27–30

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In this work, we propose a simple and effective means for assisting the repair of perovskite films prepared by a two-step solvent process under ambient conditions. The generated highly crystallized, pinhole-free perovskite films are observed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The photovoltaic parameters of PVSCs based on the repaired perovskite film show obvious improvement relative to those of the reference PVSC device. A PCE of 13.07% is achieved, which is doubled with respect to that of the PVSC not subjected to the same enhancement procedure (6.54%) under an ambient environment.

2. EXPERIMENTAL DETAILS

2.1. Preparation of PSCs. Briefly, patterned FTO substrates were coated with a TiO2 compact layer (C-TiO2) by spin-coating the TiO2 organic sol at 3000 rpm for 30 s, followed by sintering at 500 °C for 15 min. The mesoporous TiO2 layer (M-TiO2) was coated with a commercial TiO2 paste (Dyesol 18NRT, Dyesol) diluted in ethanol (2:8; weight ratio) by spin coating at 2500 rpm for 30 s, followed by gradual heating to 500 °C and sintering at this temperature for 30 min. The perovskite absorbers were prepared by a two-step method according to literature.13 PbI2 (462 mg) was dissolved in 1 mL of N,N-dimethylformamide (DMF) under stirring at 70 °C. The as-prepared PbI2 films were covered with PbI2 by spin coating at 6500 rpm for 5 s and dried at 70 °C for 30 min. After being cooled to room temperature, the films were dipped in a solution of MAI in 2-propanol (10 mg/mL) for 30 s, rinsed with 2-propanol, and dried at 70 °C for 30 min. The HTM was then deposited by spin coating at 2000 rpm for 30 s, which was composed of 72 mg/L (2,2',7,7'-tetakis(N,N-di-4-methoxyphenylamine)-9,9-spirobifluorene) (spiro-OMeTAD), 28.8 μL of 4-tort-butylpyridine, and 17.5 μL of 520 mg/mL lithium bis(trifluoromethanesulfonyl)imide in acetonitrile in 1 mL of chlorobenzene. Finally, 100 nm of gold was thermally evaporated on top of the device to form the metal back electrode. The active area of PVSC was fixed 0.08 cm2. Notably, the assisted evolution strategy by methylamine iodide solution was performed after the preparation stage of perovskite. A solution of MAI in 2-propanol (10 mg/mL) was dropped to the perovskite surface and deposited by spin-coating at 4000 rpm for 10 s. It is worth mentioning that adding MAI solution is conducted when the spin-coating speed of PVK substrate is up to 4000 rpm. The above procedure was repeated several times.

2.2. Characterization. The phase composition and crystal structure were studied via X-ray diffraction (Smart Lab, Japan). The top view and cross section of the devices were observed by field-emission scanning electron microscopy (Merlin, Germany). The current density–voltage curves of PSCs were measured by a Keithley digital source meter (Keithley 2400, United States) under a solar simulator simulating the AM 1.5 spectrum (100 mW cm−2, Class AAA, Oriel, United States). External quantum efficiency (EQE) measurements were carried out on an EQE measurement setup (Newport, Oriel IQE-200, United States). The electrochemical impedance spectroscopy (EIS) measurements were conducted on a computer-controlled electrochemical workstation (Zennium, Zahner, Germany) under dark conditions at Voc bias. The measured frequencies ranged from 100 mHz to 1 MHz. The surface morphology of the active layer was characterized by atomic force microscopy (AFM, Multimode 3D, Veeco, United States) in tapping mode. The steady-state photoluminescence (PL) was measured by Fluoromax-4 (HORIBA Jovin Yvon, Edison, NJ, United States). Time-resolved photoluminescence (TRPL) spectra of the samples were measured by a time-resolved fluorescence spectrometer (F900, Edinburgh Instruments, U.K.) excited wavelength at 660 nm by PDL 800-B pulsed diode laser (PicoQuant, GER) and emission wavelength at 780 nm.

3. RESULTS AND DISCUSSION

XRD patterns of the perovskite films deposited on FTO/C-TiO2/M-TiO2 and the perovskite films repaired by solvent in different times are presented in Figure 1a. For convenience, the samples prepared under different number of repair times were
designated S0, S1, S3, S5, S7, S10, and S20. The perovskite peaks were observed at 14.0°, 20.0°, 28.1°, and 32.1°, corresponding to the (110), (112), (220), and (312) planes, respectively. The introduction of MAI solution in the repair process enhanced the conversion of PbI2 film into MAPbI3. The characteristic PbI2 peak at 12.3° obviously decreased in intensity along with the increase in repair time number. Figure 1b displays the XRD intensity of the MAPbI3 perovskite films (S0, S5, and S20) for the 110 reflection, showing a clear increase after 5 repair times and a decrease after 20 repair times. This result suggests that the perovskite films were better aligned than before and overtreated than after the process. This phenomenon signifies the crystallographic enhancement of the MAPbI3 perovskite films, which is beneficial in achieving highly efficient PVSCs.

Figure 3. AFM images (a and c) and cross-sectional SEM images (b and d) of the perovskite films and PVSC devices based on S0 and S5.

Figure 4. (a) J–V curves of the PVSCs under 1 sun illumination (100 mW cm−2) based on S0–S20 and (b) their corresponding EQE spectra. (c) S5 at different scan rates. (d) S5 at different scan directions. (e) Stabilized electric power output and the photocurrent density for the best performing PVSC based on S5 with the J–V curve shown in panel a, and parameters are summarized in Table 1.

Table 1. J–V Parameters of the Perovskite Solar Cells Assembled with Samples S0, S1, S3, S5, S7, S10, and S20

<table>
<thead>
<tr>
<th>sample</th>
<th>Voc (V)</th>
<th>Jsc (mA cm−2)</th>
<th>FF</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S0</td>
<td>0.83 ± 0.02</td>
<td>16.14 ± 0.65</td>
<td>0.40 ± 0.03</td>
<td>5.90 ± 0.48</td>
</tr>
<tr>
<td>best</td>
<td>0.87</td>
<td>17.08</td>
<td>0.44</td>
<td>6.54</td>
</tr>
<tr>
<td>S1</td>
<td>0.87 ± 0.01</td>
<td>16.22 ± 0.73</td>
<td>0.43 ± 0.04</td>
<td>6.80 ± 0.67</td>
</tr>
<tr>
<td>best</td>
<td>0.89</td>
<td>17.38</td>
<td>0.50</td>
<td>7.33</td>
</tr>
<tr>
<td>S3</td>
<td>0.87 ± 0.01</td>
<td>17.39 ± 0.53</td>
<td>0.47 ± 0.33</td>
<td>7.67 ± 0.54</td>
</tr>
<tr>
<td>best</td>
<td>0.89</td>
<td>18.05</td>
<td>0.52</td>
<td>8.35</td>
</tr>
<tr>
<td>S5</td>
<td>0.96 ± 0.01</td>
<td>19.34 ± 0.78</td>
<td>0.62 ± 0.03</td>
<td>12.26 ± 0.78</td>
</tr>
<tr>
<td>best</td>
<td>0.98</td>
<td>20.20</td>
<td>0.66</td>
<td>13.07</td>
</tr>
<tr>
<td>S7</td>
<td>0.90 ± 0.02</td>
<td>18.84 ± 0.66</td>
<td>0.47 ± 0.04</td>
<td>9.15 ± 0.60</td>
</tr>
<tr>
<td>best</td>
<td>0.92</td>
<td>19.56</td>
<td>0.54</td>
<td>9.72</td>
</tr>
<tr>
<td>S10</td>
<td>0.86 ± 0.01</td>
<td>18.34 ± 0.77</td>
<td>0.47 ± 0.03</td>
<td>7.85 ± 0.67</td>
</tr>
<tr>
<td>best</td>
<td>0.88</td>
<td>19.23</td>
<td>0.51</td>
<td>8.63</td>
</tr>
<tr>
<td>S20</td>
<td>0.85 ± 0.02</td>
<td>14.53 ± 0.79</td>
<td>0.41 ± 0.03</td>
<td>5.55 ± 0.39</td>
</tr>
<tr>
<td>best</td>
<td>0.87</td>
<td>15.40</td>
<td>0.45</td>
<td>6.03</td>
</tr>
</tbody>
</table>

designated S0, S1, S3, S5, S7, S10, and S20. The perovskite peaks were observed at 14.0°, 20.0°, 28.1°, and 32.1°, corresponding to the (110), (112), (220), and (312) planes, respectively. The introduction of MAI solution in the repair process enhanced the conversion of PbI2 film into MAPbI3. The characteristic PbI2 peak at 12.3° obviously decreased in intensity along with the increase in repair time number. Figure 1b displays the XRD intensity of the MAPbI3 perovskite films (S0, S5, and S20) for the 110 reflection, showing a clear increase after 5 repair times and a decrease after 20 repair times. This result suggests that the perovskite films were better aligned than before and overtreated than after the process. This phenomenon signifies the crystallographic enhancement of the MAPbI3 perovskite films, which is beneficial in achieving highly efficient PVSCs.

Figure 2 presents the evolution process of the perovskite morphology under SEM images. In the unrepaired perovskite film, many isolated large grain and obviously bare M-TiO2 are notable. The large pinholes increase the risk of short circuits.

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With the increased number of repair times, the pinholes disappeared then reappeared gradually. Among these samples, a dense-grained uniform morphology was observed after five repair times (S5). The entire film was composed of a homogeneous, well-crystallized perovskite layer and comprehensive coverage for M-TiO2. These results agree with the XRD measurements.

Figure 3 illustrates the images obtained by atomic force microscopy (AFM) and the cross-sectional images of PVSC devices based on S0 and S5. The 3D AFM images reveal that the root-mean-square roughness values apparently decrease from 96.3 to 33.3 nm. The “high peaks” are scraped and the “low valley” is filled. The homogeneous and well-crystallized perovskite film morphology was similar to that in Figure 2c. The cross-sectional images of the PVSC devices based on S0 and S5 display a typical PVSC device structure. However, obvious differences between the two samples are directly visible. (1) In S0, the M-TiO2 layer is incompletely filled by MAPbI3 unlike that in S5, which achieved opposite results. (2) The pinholes in S0 were also more apparent than those in S5. This result suggests that the repair process did not merely refill pinholes but also refilled the M-TiO2 layer to achieve a homogeneous, continuous, and well-crystallized perovskite layer.

The photovoltaic performances of PVSCs based on different number of repair times were measured under 1 sun illumination (AM 1.5, 100 mW cm−2) and plotted in Figure 4a. The detailed parameters are summarized in Table 1. Obviously, the PCEs increased first then decreased along with increasing number of repair times. The pinholes derived from an unsatisfactory coverage of perovskite on TiO2 were observed before evolution (S0), which can increase the risk of recombination and resist the charge transfer. This phenomenon directly diminished the photovoltaic performance, followed by the open-circuit photovoltage (Voc), photocurrent density (Jsc), and fill factor (FF). With the increase in the number of repair times, a perovskite film of uniform and complete coverage on TiO2 was fabricated. Therefore, the highest PCE was obtained by S5. The parameters of Voc, Jsc, and FF were 0.979 V, 20.20 mA cm−2, and 0.663, respectively, yielding the highest PCE at 13.07%. Furthermore, to increase the number of repair times, the PCE of devices decreased rapidly because of thin perovskite and again exposed TiO2. Figure 4b shows the EQE of the above PVK devices. It is clear that the integrated Jsc from EQE measurement is in good agreement with the measured Jsc from J-V test. This result indicated the facticity of the Jsc from J-V measurement and the matching of the spectrum between different light sources. Hysteresis of PVSKs fabricated by solvent-assisted repair was examined by J-V measurement under different scan rates and scan directions (Figures 4c and d). The results show negligible hysteresis, which may be explained by the pinhole-free, homogeneous, and well-crystallized perovskite films reduced bulk defect density and suppressed charge recombination. A 12.9% stabilized PCE output with a photocurrent density of 19.8 mA cm−2 was detected for S5 in Figure 4e, indicating that the PCEs from our routine scanning conditions are near actual device performance.

To evaluate the effect of repair procedures on the properties of MAPbI3, we measured steady-state photoluminescence (PL) and time-resolved photoluminescence spectra (TRPL) of samples based on S0 and S5. Two samples show a similar PL emission peak around 780 nm, but S5 shows a much stronger PL intensity, indicating fewer traps and defects within the film (Figure 5a).32 The TRPL indicated the occurrence of charge transfer process in the MAPbI3 films (Figure 5b). By fitting the data, we obtained the average lifetime of the charge carriers in the two films. The S5 shows a 623 ns lifetime, which was longer than that of the S0 (240 ns), which was possibly due to the formation of pinhole-free, homogeneous, and well-crystallized perovskite film structures of lower trap concentration, as confirmed by steady-state PL. This finding denotes that the radiative recombination process was restricted, potentially contributing to the high Jsc in the PVSC device.
EIS measurement is an important method for revealing charge transfer process of PVSCCs. Figures 5c and d present the Nyquist plots and recombination resistance ($R_{rec}$) of the PVSC devices based on S0 and SS at different biases in the dark extracted from the EIS spectra. Typically, two arcs were noted in the Nyquist plot. The arc at high frequency was derived from the charge transport in the TiO$_2$ layer, HTM, and/or at the HTM/Ag interface. The second arc in the intermediate frequency was related to the charge recombination resistance ($R_{rec}$) at the active layer. The intersection of the arc at the active layer and the x-axis was defined as the series resistance ($R_s$). Two PVSC devices (S0 and SS) were measured for EIS at the $V_{oc}$ bias in the dark, and the Nyquist spectra are plotted in Figure 5c. The relevant parameters were fitted on the basis of equivalent circuit (illustration in Figure 5c). Two devices show similar $R_s$ and $R_{HTM}$ because of identical substrates, interfaces, and parallel device construction. The differences mainly existed in the $R_{rec}$ $R_{rec}$ of 154 and 272 $\Omega$ cm$^{-2}$ were extracted from the Nyquist spectra. The higher $R_{rec}$ signifies that the charge recombination was effectively suppressed when MAPbI$_3$ films were repaired 5 times. The $R_{rec}$ of the two devices strongly depended on the bias voltage, which decreased with increasing voltage, similar to that in a previous report (Figure 5d). Notably, the SS-based PVSC device presented a higher $R_{rec}$ than that of the S0-based PVSC device at different biases, which reflects the former’s higher $V_{oc}$. The low values of $R_{rec}$ obtained at low applied voltage would adversely affect the FF, which shows the low FF of the S0-based PVSC accordingly.

4. CONCLUSIONS

In conclusion, pinhole-free, homogeneous, and well-crystallized perovskite films were prepared by a simple strategy using the MAI solution-assisted repair of perovskite films based on a two-step deposition method under ambient atmosphere. The resultant films were then applied to PVSC devices. A high PCE of 13.07% was achieved, which was doubled with respect to that of the PVSC not subjected to the repair procedure (6.54%). The mechanism study indicated that long carrier lifetime, low trap density, and high recombination resistance were likely responsible for the excellent photovoltaic parameters and PCE. This report paved a new way for developing high-performance perovskite films and PVSC devices in an ambient atmosphere.

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Notes
The authors declare no competing financial interest.

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REFERENCES


