Understanding the Effect of Delay Time of Solvent Washing on the Performances of Perovskite Solar Cells

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Abstract: Uniform and dense perovskite films were realized by the one-step solution-processing method combined with toluene washing. The influence of the delay time applied for toluene washing on the film quality of CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$) was investigated in a comprehensive manner. The optimal delay time was experimentally observed at the critical point when the color of the film changes from transparent to hazy. A detailed X-ray diffraction study suggested that such a color change was caused by the emergence of the MAPbI$_3$ crystal nucleus. This finding provides a convenient method to determine the optimal time accurately. With the optimal delay time, the most uniformly distributed MAPbI$_3$ grains with the largest average grain size and the smoothest surface were obtained. Owing to the realization of homogeneous MAPbI$_3$ films combined with full coverage of perovskite on the substrate achieved by toluene washing at the critical point, open-circuit voltage, short-circuit current, fill factor, and power conversion efficiency of 1.11 V, 18.24 mA/cm$^2$, 77.47, and 15.54% were obtained.

Introduction

Organometal halide perovskite solar cells (PSC) are settled as the most attractive topic in photovoltaic research area owing to its simple device fabrication technology and high power conversion efficiency (PCE). The highly efficient PSC benefited from the excellent properties of the perovskite light absorber, such as high light-absorption coefficient, high charge-carrier mobility, and appropriate direct bandgap. Since the first PSC with a PCE of 3.8% was reported by Miyasaka’s group in 2009, huge promotion has been achieved with a PCE exceeding 20%, which is close to the PCE of Si solar cells. These exhibited the feasibility of PSCs for commercial applications.

The film quality of the perovskite light-absorbing layer plays a crucial role in realizing highly efficient PSCs. During the past 8 years, technologies of vacuum thermal evaporation and solution processing have been developed to deposit perovskite films. Compared with the two-step sequential deposition process, the one-step solution method is simpler and takes shorter time. However, one-step solution-processed perovskite films generally demonstrate inhomogeneous surface morphology, irregular crystallinity, and poor reproducibility. To improve the film quality, the solvent washing method was developed, which has been proven to be effective in assisting the formation of uniform and dense perovskite films. Among the antisolvents for washing, toluene and chlorobenzene were commonly used. Except for the type of the solvent, the process conditions of solvent washing also play an important role in determining the film quality, such as the amount of solvent and the delay time from the beginning of perovskite solution spinning. Optimized the delay time of chlorobenzene washing during the spin coating of CH$_3$NH$_3$PbI$_3$ precursor solution, which was 6 s. However, as well-known, the optimal delay time for adding an antisolvent was usually different if the fabrication conditions changed, such as, the recipe of perovskite precursor solution and even the atmosphere around the spin coater. Therefore, it is necessary to identify the correlation between the optimal delay time and the morphology change of the perovskite film. In our manuscript, after elaborate investigation on the optimization of the delay time, we found a method to decide the optimal delay time simply by visual inspection, that is, the critical point when the color of the film starts to change from transparent to hazy. Hence, the optimal delay time can be adjusted conveniently and accurately.

Supporting Information

Supporting Information...
In this work, perovskite (CH₃NH₃PbI₃, MAPbI₃) films with uniform grain size distribution and smooth surface were realized by well-controlled delay time of solvent washing. Toluene washing was selected as an example because of its frequent use in the solvent washing method. The influences of delay time of solvent washing on the film morphology and device performance were studied in detail. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) images revealed the influence of delay time on the grain size distribution and surface morphology of MAPbI₃ films. The proper delay time had been proven to be the critical point when the film started to turn hazy owing to the emergence of MAPbI₃ crystal nucleus. Therefore, the optimal delay time of toluene washing can be visually determined from the color change of MAPbI₃ films. The realization of homogeneous MAPbI₃ films together with the greatly improved coverage on the substrate by toluene washing at optimal delay time led to the increase of open-circuit voltage ($V_{OC}$), short-circuit current ($J_{SC}$), fill factor (FF), and PCE of the device from 0.61 ± 0.04 V, 5.3 ± 0.2 mA/cm², 38.7 ± 0.6%, and 1.2 ± 0.1% of unwashed device to 0.90 ± 0.02 V, 19.7 ± 0.9 mA/cm², 68 ± 2%, and 12.1 ± 0.8%, respectively. To emphasize on the mechanism of the optimization of delay time of toluene washing, a basic device structure (without adding extra interlayer for improved carrier transport) was used although it displayed a moderate PCE of the solar cell. By applying this toluene washing method on the NiOₓ-based PSC with the device structure of ITO/NiOₓ/MAPbIₓ/phenyl-C₆₁-butyric acid methyl ester (PCBM)/Ag, a $V_{OC}$ of 1.1 V, $J_{SC}$ of 18.24 mA/cm², FF of 77.47%, and PCE of 15.54% were obtained.

### RESULTS AND DISCUSSION

Figure 1 presents the schematic diagram of the cell architecture and the corresponding energy levels, as well as the deposition processes of the MAPbI₃ film by means of spin coating. The inverted PSC had a structure of ITO/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS) (15 nm)/MAPbI₃ (380 nm)/PCBM (50 nm)/Ag (70 nm).

The detailed process procedures for preparing MAPbI₃ films are depicted in Figure 1c. Three steps were involved: MAPbI₃ precursor solution spinning, toluene washing, and thermal annealing. Step 1, the MAPbI₃ precursor solution was spin coated on PEDOT:PSS substrate. Step 2, toluene washing was applied during the spinning of MAPbI₃ precursor solution. Step 3, toluene washing was applied during the spinning of MAPbI₃ precursor solution. Three different delay times, 3, 8, and 15 s, from the beginning of MAPbI₃ precursor solution spinning were studied. Step 3, the resulting films were annealed at 100 °C for 10 min. The pictures taken from the films with different delay times are shown in Figure 2a–d. We noticed that a delay time of 8 s was the critical point in our case. Longer than 8 s, the film starts to turn hazy during the spinning, which can be observed visually.
Transparent films were formed immediately after toluene washing at delay times of 3 and 8 s (Figure 2b). A similar phenomenon has been observed when toluene washing was applied on the spinning of a mixture of PbBr$_2$, PbI$_2$, MABr, methyl ammonium iodide (MAI), γ-butyrolactone, and dimethylsulfoxide (DMSO) in N$_2$N-dimethylformamide (DMF).\textsuperscript{17} However, in the case of toluene washing at 15 s, similar to that without toluene washing treatment, the film did not become transparent any more; the resulting film was brown (Figure 2c). The color of all films turned to dark brown after thermal annealing (Figure 2d).

To understand the color change of the film caused by toluene washing during spin coating, XRD was carried out on the films with toluene washing at 8 s before and after thermal annealing, as shown in Figure 2e. Before thermal annealing, XRD peaks located at 6.74°, 7.29°, and 9.1° were observed, which were originated from the intermediate phase of PbI$_2$–MAI–DMSO, as suggested previously.\textsuperscript{17,22} Toluene selectively washed the DMF in MAPbI$_3$ precursor solution and froze the component as an intermediated phase of PbI$_2$–MAI–DMSO complex.\textsuperscript{17,22} After thermal annealing, the peaks of 6.74°, 7.29°, and 9.1° all disappeared, whereas the intensity of the peak at 14.1° increased greatly, which can be designated to the (110) diffraction of MAPbI$_3$. This indicated that the intermediate phase turned to MAPbI$_3$ completely after the evaporation of DMSO by thermal annealing.\textsuperscript{17} It had also been observed that thermal annealing turned the transparent film to dark brown, which represented the formation of MAPbI$_3$.\textsuperscript{23,24}

The XRD patterns of the films obtained with toluene washing at delay times of 3, 8, and 15 s as well as the film without toluene washing followed by annealing at 100 °C for 10 min are shown in Figure S1. All MAPbI$_3$ films showed intense diffraction peaks at 14.1° and moderate intensity at 27°, which can be, respectively, assigned to (110) and (220) diffractions of the MAPbI$_3$ phase.\textsuperscript{25} This indicated the preferred growth of grains along the (110) plane. After toluene washing at 3, 8, and 15 s, the intensities of peaks at 14.1° and 27° were similar to that of the unwashed MAPbI$_3$ film, illustrating similar crystallinity.

SEM images of the resulting MAPbI$_3$ films with different delay times of toluene washing, together with the film without toluene washing are depicted in Figure 3. Without toluene washing (Figure 3a), a number of bundles of MAPbI$_3$ with a length of over 10 μm were woven together in a network on the surface of the substrate. Numerous pinholes with irregular shapes distribute among them, indicating the bad coverage of MAPbI$_3$ on the substrate. With toluene washing at 3 or 8 s, uniform and dense MAPbI$_3$ films were formed after thermal annealing. Numerous polygonal grains were observed. In the case of dripping toluene at 15 s, MAPbI$_3$ had images similar to that without toluene washing, excepting the relative smaller size of the bundles. Numerous pinholes were also observed. Therefore, the SEM images revealed that the morphology of the MAPbI$_3$ film depended on the delay time of toluene washing.

The dense MAPbI$_3$ film with uniform grain size can be obtained simply by toluene washing at appropriate delay time. The distribution of grain size based on the SEM images was analyzed and summarized, as shown in Figure S2. The corresponding average grain sizes of unwashed and washed at 3, 8, and 15 s films were about 165.52, 158.79, 212.41, and 187.22 nm in diameter, respectively. This indicated that the average grain sizes of MAPbI$_3$ increased due to toluene washing. With toluene washing at the delay time of 8 s, the average size reached the maximum, indicating the most homogeneous-sized grains. However, with the washing delay time being further increased to 15 s, the average grain size decreased and nonuniform MAPbI$_3$ grains were formed.

AFM images shown in Figure 4 demonstrated that surface roughness of the MAPbI$_3$ film depended on the delay time of toluene washing. The root-mean-square roughness of the MAPbI$_3$ film by toluene washing at 3, 8, and 15 s were 11.9, 8.73, and 27.6 nm, respectively, confirming that the MAPbI$_3$ film resulting from toluene washing at 8 s had the smoothest surface.

The morphology of MAPbI$_3$ demonstrated by SEM and AFM showed that toluene washing led to better film quality. In addition, with the increase of delay time of toluene washing from 3 to 8 s, better MAPbI$_3$ morphology was obtained with the increased crystal size and decreased surface roughness; however, further extending the delay time led to bad morphology of the MAPbI$_3$ film. According to the morphology change of MAPbI$_3$, the delay times of toluene washing can be divided into three stages.\textsuperscript{26} At the early time of the spin coating of the MAPbI$_3$ precursor solution, for example, 3 s, the solution was far from supersaturation. The process was dominated by the removal of excess solution. Toluene washing at this stage was not so effective in regard to the formation of the intermediate phase. The grain sizes of MAPbI$_3$ were small and not so uniformly distributed. Stage 2, at about 8 s in our case, the solution was more concentrated and was about to form MAPbI$_3$ crystal nucleus. Toluene washing at this stage will freeze the components of MAPbI$_3$ precursor solution and form the intermediate phase. Therefore, the MAPbI$_3$ film had a uniform grain size. This stage can be determined by naked eyes since the film started to become hazy owing to the formation of MAPbI$_3$ crystal nucleus.\textsuperscript{26} Stage three, at about 15 s, the film had already became hazy before toluene washing, indicating the existence of MAPbI$_3$ crystal nucleus. The intermediate phase formed after toluene washing coexisted with MAPbI$_3$ crystal at this stage of toluene washing after 15 s. Therefore, the morphology of MAPbI$_3$ was similar to that without toluene washing.
PSCs with structures of ITO/PEDOT:PSS/MAPbI$_3$/PCBM/Ag based on MAPbI$_3$ films deposited with or without toluene washing were fabricated and measured. The current density−voltage ($J-V$) curves are shown in Figure 5, and the detailed performance parameters are summarized in Table 1.

The device without toluene washing had a $V_{OC}$ of 0.61 ± 0.04 V, $J_{SC}$ of 5.3 ± 0.2 mA/cm$^2$, FF of 38.7 ± 0.6%, and PCE of 1.2 ± 0.1%. After toluene washing, the device performances were improved with the increasing delay time from 3 to 8 s. That is to say, the optimal device was fabricated with toluene washing at the delay time of 8 s. It has a $V_{OC}$ of 0.90 ± 0.02 V, $J_{SC}$ of 19.7 ± 0.9 mA/cm$^2$, FF of 68 ± 2%, and PCE of 12.1 ± 0.8%.

The increase of $J_{SC}$ was further proven by the corresponding IPCE data, as shown in Figure S3. The integrated $J_{SC}$ values for devices without or with toluene washing (at 8 s) were 4.3 and 18 mA/cm$^2$, respectively. The moderate PCE of the optimal solar cell was attributed to the basic device configuration that was used. To further increase the PCE of the device, we fabricated the device with a configuration of ITO/NiO$_x$/MAPbI$_3$/PCBM/Ag. The MAPbI$_3$ film was deposited with toluene washing at 8 s, when the films became hazy. A $V_{OC}$ of 1.1 V, $J_{SC}$ of 18.24 mA/cm$^2$, FF of 77.47%, and PCE of 15.54% were obtained (Figure S4). We also applied this toluene washing method to n-i-p planar solar cells with the device configuration of FTO/TiO$_2$ (50 nm)/MAPbI$_3$ (380 nm)/spiro-OMeTAD (100 nm)/Ag (70 nm). A $V_{OC}$ of 1.08 V, $J_{SC}$ of 23.3 mA/cm$^2$, FF of 57.67%, and PCE of 14.49% were obtained by controlling the washing delay time at the point when the film color started to turn hazy. The corresponding $J-V$ curve is shown in Figure S5.

The performance enhancement of solar cells by toluene washing was attributed to the homogeneous MAPbI$_3$ grains, smooth surface, and improved coverage of MAPbI$_3$ films on the substrate. Uniform and dense MAPbI$_3$ films could benefit the charge transfer and depress the leakage current of devices. The dark current density−voltage plots in Figure 5b demonstrated that after washing at 8 s, the leakage current decreased.

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Table 1. Detailed Performance Parameters of Devices ITO/PEDOT:PSS/MAPbI$_3$/PCBM/Ag

| device          | $V_{OC}$ (V) | $J_{SC}$ (mA/cm$^2$) | FF (%) | efficiency (%) |
|-----------------|--------------|----------------------|--------|----------------|
| unwashed-forward| 0.61 ± 0.04  | 5.3 ± 0.2             | 38.7 ± 0.6 | 1.2 ± 0.1     |
| 3 s-forward     | 0.83 ± 0.02  | 15.0 ± 0.4            | 59.4 ± 0.5 | 7.4 ± 0.2      |
| 8 s-forward     | 0.90 ± 0.02  | 19.7 ± 0.9            | 68 ± 2 | 12.1 ± 0.8     |
| 8 s-reverse     | 0.90 ± 0.02  | 20 ± 1                | 65 ± 1 | 11.6 ± 0.8     |
| 15 s-forward    | 0.1 ± 0.1    | 6.1 ± 0.6             | 26 ± 3 | 0.2 ± 0.6      |

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significantly. The decrease of the surface roughness of the MAPbI3 film will improve its contact with the following PCBM layer and therefore enhance the collection of electrons. As a result, all performance parameters were increased greatly. The $J-V$ curves of 8 s in the reverse and forward scan direction well-overlapped to each other with only a slightly difference of FF and PCE, indicating there was no hysteresis effect. In addition, totally 72 devices with toluene washing at 8 s were fabricated from several batches, and the statics results of $V_{OC}$, $J_{SC}$, FF, and PCE are shown in Figure S6. It demonstrated that after toluene washing at optimal delay time, PSCs show good reproducibility.

## CONCLUSIONS

In conclusion, the morphology of MAPbI3 was controlled by toluene washing during the spinning of MAPbI3 precursor solution. Uniform and dense MAPbI3 films with improved coverage on the substrate were obtained after thermal annealing. The grain size distribution and surface roughness of MAPbI3 films depended on the delay time of toluene washing. The optimal delay time of 8 s was the critical point, which can be determined by visually observing the color change of MAPbI3 films. XRD, SEM, and AFM results showed that the crystal nucleus started to form at the critical point. With optimal toluene washing, a $V_{OC}$ of 1.1 V, $J_{SC}$ of 18.24 mA/cm², FF of 77.47%, and PCE of 15.54% were obtained.

## METHODS

### MAI Synthesis and Solution Preparation.

MAI was synthesized in our lab. Methylamine solution in alcohol (48 mL, 0 °C cooling) was added into hydroiodic acid (20 mL) and stirred for 3 h. To guarantee the complete reaction of hydroiodic acid, the amount of methylamine was excessive. During the reaction process, Na2 was continuously piped to the solution. The blended solution appeared pale yellow in color when the reaction was completed. By evaporating the solvents at 60 °C for 1 h with a rotary evaporator, the precipitated yellow-white crystal was collected. The products were purified with anhydrous diethyl ether and collected with a suction filter. Finally, the product, MAI, was dried in a vacuum oven at room temperature for 24 h. CH3NH3PbI3 solution (40 wt %) was prepared by adding the MAI powder, PbI2, and DMSO at a mole ratio of 1:1:1 in DMF and stirred for 1 h.

### Preparation of NiOx Nanoparticles and NiOx Films.

First, 12.885 g of NiCl2·6H2O was dissolved in 100 mL of deionized water under magnetic stirring. Then, 10 M NaOH solution was added into the solution drop by drop until the pH value reached 10. A turbid green solution was obtained and centrifuged. After being washed twice with deionized water, the obtained precipitation was dried at 80 °C overnight and then annealed at 270 °C for 2 h. NiOx nanoparticles (10 mg) were added into 1 mL of deionized water and then treated by ultrasonication for 8 h. Finally, NiOx films were deposited on ITO-coated glass substrates by spin coating at 4000 rpm for 20 s and then baked at 130 °C for 10 min in air.

### Device Fabrication and Measurements.

For PEDOT:PSS (P4083, Bayer)-based PSC devices, PEDOT:PSS was spin coated onto precleaned ITO-coated glass at 4000 rpm for 60 s and baked at 150 °C for 15 min. Following, a solution of PbI2/MAI/DMSO = 1:1:1 in DMF was spin coated at 1000 rpm for 10 s and then 6000 rpm for 20 s. Toluene (400 μL) was added dropwise during the spinning of MAPbI3 precursor solution. The delay times from the beginning of the spinning were changed from 3 s to 8 s to 15 s. Then, the sample was heated on a hot plate at 100 °C for 10 min. After that, PCBM solution in dichlorobenzene (40 mg/mL) was spin coated on top of the MAPbI3 layer at 1000 rpm for 20 s and then 6000 rpm for 20 s. Then, the sample was annealed at 70 °C for 1 h. Finally, Ag was evaporated as the top electrode in a vacuum chamber.

The NiOx-based PSC device with the structure of ITO/NiOx (40 nm)/CH3NH3PbI3 (380 nm)/PCBM (50 nm)/BCP (10 nm)/Ag (70 nm) was fabricated by sequentially depositing perovskite precursor solution, PCBM, BCP, and Ag. The method was the same as mentioned above. The n–i–p-type PSC used here was fabricated with a structure of FTO/TiO2 (50 nm)/MAPbI3 (380 nm)/2,2′,7,7′-tetrakis(N,N-di-p-methoxyphenylamine)9,9′-spirobi fluorene (spiro-OMeTAD, 100 nm)/Ag (70 nm). The TiO2 precursor solution was prepared by adding 369 μL of titanium isopropoxide (99.9%, Aldrich) in a mixed solvent of 2 mL of anhydrous ethanol and 35 μL of 2 M HCl. After spin coating TiO2 precursor solution at 2000 rpm for 30 s, a 50 nm thickness compact TiO2 film was formed on the FTO-coated glass substrate. Then, the sample was heated at 500 °C for 30 min. The perovskite film was deposited as mentioned above. Following, the spiro-OMeTAD solution (60 mM/mL in chlorobenzene) was spin-coated on top of the perovskite film at 4000 rpm for 20 s. The spiro-OMeTAD solution was prepared by adding 30 mM LiTFSI (lithium trifluoromethanesulfonate from a stock solution in acetonitrile) and 200 mM 4-tert-butylpyridine (TBP) in 1 mL spiro-OMeTAD solution (60 mM/mL in chlorobenzene). Spiro-OMeTAD and TBP were purchased from Borun New Material Technology Co., Ltd. and used as received. LiTFSI and chlorobenzene were purchased from Xi’an Polymer Light Technology Corp. and Sigma-Aldrich, respectively.

The current density–voltage ($J-V$) curves were measured by a Keithley 2602 sourceMeter under an illumination of 1 sun (100 mW/cm² AM 1.5G), which is calibrated with a standard Si photodiode. The device has an area of 0.096 cm² by using a shadow mask. SEM images were obtained with a Hitachi S4800 microscope. AFM images were measured by using Bruker’s Dimension Icon. XRD experiments were conducted by a Bruker D8 ADVANCE X-ray diffractometer.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01026.

Rutherford X-ray diffraction (XRD) patterns of the thermal annealed films, distribution of grain sizes of perovskite films, IPCE data and integrated JSC of devices, $J-V$ curves of NiOx-based PSC with toluene washing, $J-V$ curves of TiO2-based PSC with toluene washing, and statics of $V_{OC}$, $J_{SC}$, FF, and PCE of 72 devices (PDF).

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