

CAN ENDOW HIGH PURITY PEROVSKITE PHASE IN AMBIENT AIR? TOWARD LOW-COST, SCALABLE, AND VACUUM FREE PEROVSKITE SOLAR CELLS*

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Abstract

In recent years, lead halide perovskite solar cell efficiency has tremendously reached up to 22.7% due to excellent optoelectronics properties with various fabrication methods. However, stability in ambient air for perovskite solar cells is a lack of effective solution to the problem until now. On the other hand, fabrication processes in a glovebox are strictly limited for large scale production due to high operational costs. Hence, perovskite films are fabricated by two-step deposition method in ambient air relative humidity (RH) of $45 \pm 5\%$ to acquire high quality films and good crystallization. For the first step, 1 M of lead iodide/N, N-dimethylformamide (PbI₂/DMF) solution is deposited on the glass substrate. In a second step, separated amount of 10 to 25 mg of methylammonium iodide (MAI) in 1 ml of isopropanol (IPA) solution is deposited on the PbI₂ film. To optimize the high-purity phase, 1% of N, N-dimethylformamide (DMF) is added to MAI/IPA solution. Meanwhile, residual PbI₂ peaks transform in the final perovskite films indicate that DMF additive increases the full reaction state of perovskite film. Furthermore, three different annealing times (10, 15 and 30 min) are investigated at 110 °C in air. The highest purity phase achieved for 25 mg/ml (MAI/IPA) increases crystalline size up to 51.8 nm from 35.2 nm (10 mg/ml) analyzed by X-ray diffraction (XRD) and ultraviolet–visible (UV–vis) spectrum exhibits higher absorbance intensity in the longer wavelength as well. Thus, solvent additive method facilitates mass production fabricated in an ambient environment due to increase crystalline growth of perovskite films.

Keywords: Perovskite, N, N-dimethylformamide, isopropanol, crystallization, additive

Introduction

Perovskite solar cells (PSCs) are promising candidate in the future photovoltaic power generation due to their outstanding optoelectronics properties and low cost fabrication techniques. The power conversion efficiency of PSCs have greatly achieved from barely 3.8% to 22.7% in 2021 (Jeong et al., 2021). However, stability issues of PSCs are crucial to repair the point defects as vacancies, interstitials, and substitutions as well as degradation of perovskite films occur due to easily decomposed under high temperature or moisture (Kim et al., 2017; Wang et al., 2018). One critical drawback of PSCs is sensitivity to moisture due to organic cation dissolved by water.

In addition, the device performance of PSCs films depend on deposition methods to improve high quality film such as grain size, high phase purity, good crystallization, surface coverage etc (Ansari et al., 2018). Several deposition methods including single-step or sequential deposition, thermal evaporation and vapor processing have been reported (Chen et al., 2020). Among them, one-step and two-step sequential processes are low cost and easiest way to enhance films quality, especially in two-step solution method is essential for morphology of desire outcome film in pinhole free to achieve high efficiencies (Burschka et al., 2013; Im et al., 2014; Ko et al., 2015). To achieve the high quality films, purity phase MAPbI₃ has been prepared in the N₂ filled glove box which increases the equipment costs and limits mass production in the industrial points of views. This barrier may financially prohibit in large-scale manufacture of PSCs. Thus,

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fabrication method for perovskite are required in ambient air even under high humidity condition using solvent additive method to achieve the high performance of PSCs.

In this work, we prepared the perovskite films by two-step process using the solvent additive method in ambient relative humidity (RH) of $40 \pm 5\%$. It was found that 1% DMF additive in the optimum solution 25 mg/ml (MAI/IPA) improved the crystallization and absorbance of perovskite film. Our work provides a simple and low cost fabrication approach to achieve high-quality perovskite film under ambient air.

Experimental Section

Materials

lead (II) iodide (PbI_2 , 99.5%), N, N-dimethylformamide (DMF, 99.8%), dimethylsulfoxide (DMSO, 99.8%), methylammonium iodide, $\text{CH}_3\text{NH}_3\text{I}$ (MAI), chlorobenzene (anhydrous, 99.8%) and isopropanol (IPA, ACS reagent, $\geq 99.5\%$) were purchased from Sigma-Aldrich. All purchased chemicals were used without further purification.

Perovskite Preparation Methods

Pure glass ($25 \times 25 \text{ mm}^2$) substrates were ultrasonically cleaned with diluted detergent, deionized water, acetone, ethanol and isopropyl alcohol for 15 min each, then dried in air stream. After being further treated by UV-ozone cleaning at 60°C for 15 min to remove the organic residues and increase the wettability. For perovskite precursor solution, 1M PbI_2 was dissolved in N, N-dimethylformamide (DMF) and then kept at 70°C for 2 h under laboratory type constant magnetic stirrer. And then methylammonium iodide, $\text{CH}_3\text{NH}_3\text{I}$ (MAI) was prepared in 2 propanol solvents with the different concentration ($10\text{--}25 \text{ mg ml}^{-1}$) separately, and then kept for 1 h under magnetic stir. Before perovskite layer deposition, PbI_2 solutions was filtered with $0.45\text{-}\mu\text{m}$ PTEE filters before use. The perovskite films were deposited using two-step in following steps. First, PbI_2 precursor solution was spun on the substrate at 5000 rpm for 20s, and then it was immediately moved to hotplate and dried at 100°C for 30 min. After cooling down at room temperature (RT), MAI/IPA solution was dropped on the PbI_2 substrate and kept for 20 s and spin coated at 3000 rpm for 30s for the final step. Finally, it was transferred on a hotplate and annealed at 110°C for 30 min. For the additive device, 1% DMF is added to MAI concentration varied from 10 to 25 mg in 1ml of IPA. For anti-solvent method, perovskite precursor was prepared by dissolving 1.2 M of PbI_2 and MAI in DMF/DMSO (9/1, v/v) via one step method and deposited at 3000 rpm for 30s. 200 μL chlorobenzene (CB) was dropped on the center of spinning substrate before 10 s prior to the end. All processes were carried out in lab ambient environment.

Characterizations and Measurements

Perovskite films were characterized by X-ray diffractometer (XRD, Shimadzu, Japan) with $\text{Cu K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation at 40 kV and 30 mA with a range from 10 to 55° scanning parameter in 0.6 s/step at 0.02° (2θ) step size. To analyze the absorption spectra of perovskite films, Ultraviolet-visible (UV-vis) spectrum was recorded on a Hitachi U-4100 spectrophotometer in the wavelength of $250 \text{ nm} - 900 \text{ nm}$.

Results and Discussion

Figure 1 shows the schematic diagram of experimental produces using two step deposition method. In second step, solvent additive method was applied in the sequential deposition which can increase the crystallization of MAPbI₃ perovskite films. Fabrication processes were carried out in the ambient atmosphere.

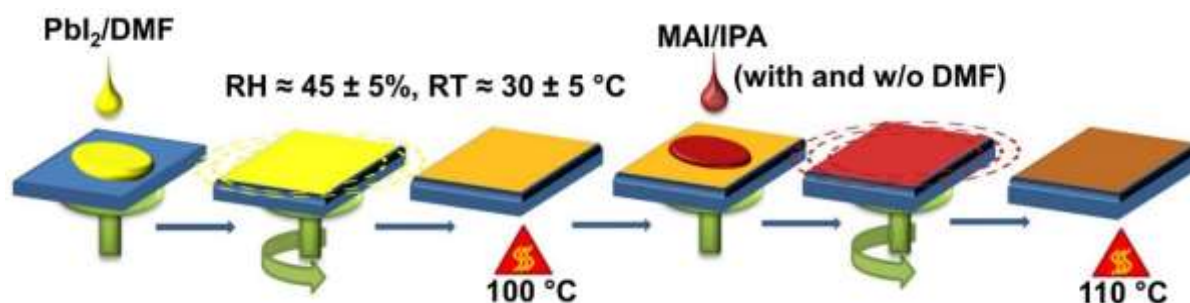


Figure 1 Schematic illustration of prepared with and w/o additive perovskite film by two step deposition method.

Figure 2 shows different PbI₂ molar (M) concentration with and without (w/o) additive films corresponding to the different MAI concentration as shown in Figure 2. In our study, 1% DMF was added into the different amount of MAI/IPA concentration. Comparison results at a PbI₂ concentration, w/o additive film (1M PbI₂) showed high roughness and many pinholes than PbI₂ additive films (1.2 M PbI₂) which increased the films quality likely smooth surface. However, it significantly changed to pale yellow color due to increased PbI₂ concentration. As an alternative, MAI concentrations were varied from 10 mg to 25 mg additive in IPA solution by solvent exchange method. As a result, dark brown and dense perovskite films were achieved when 20 mg and 25 mg/IPA solution were deposited on the 1M PbI₂ films. To confirm the films quality, Ultraviolet-visible (UV-vis) spectrophotometer and X-ray diffractometer (XRD) are further performed to be analyzed.

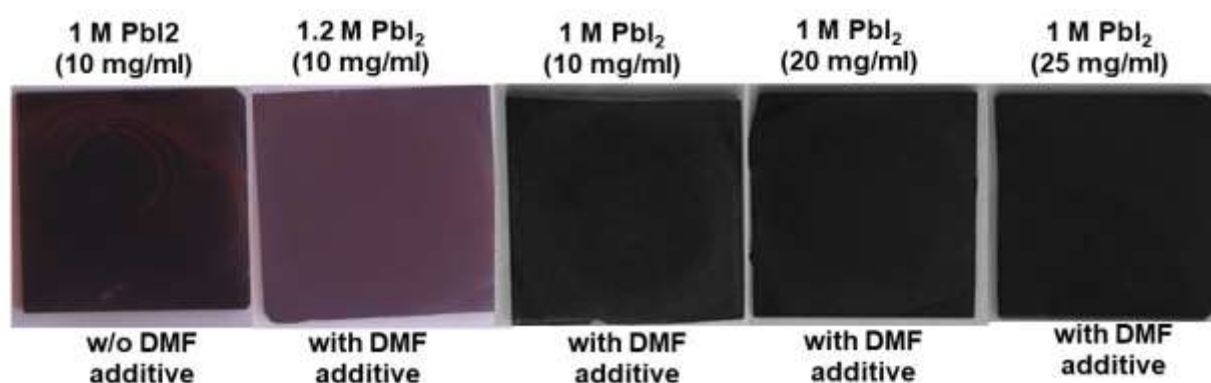


Figure 2 Photographs of different PbI₂ molar concentration with and w/o DMF additive films.

The absorption spectra of w/o additive perovskite films are measured with different annealing time for the concentration of 1M PbI₂ and 10 mg/ml (MAI/IPA) in Figure 3a. Obviously, absorbance spectra of perovskite films were increased during prolonged annealing. Strongest absorption spectrum (25 mg/ml) was observed in the visible region range between 350 nm and 650 nm by annealing at 110 °C for 30 min. Furthermore, UV-vis absorptions of additive films were measured for different MAI concentration plotted in Figure 3b. The film (25 mg/ml) exhibited highest absorption intensity in the range of 500 nm – 850 nm. It is noted that 30 mg/ml (MAI/IPA)

are not taken into further XRD characterization due to lower absorption spectrum than that of 25 mg/ml. Energy gaps were calculated from absorbance spectra using Tauc plot following this equation (Makula et al., 2018): $(\alpha h\nu)^2 = C(h\nu - E_g)$ where α = the absorption coefficient, h = Planck's constant, ν = the frequency of light, E_g = the band gap and C = the proportionality constant. Tauc plot showed the 1.54 eV (10, 25 mg/ml) and 1.56 eV (15, 20, 30 mg/ml) attributed to the similar energy values in Figure 3c. To compare with anti-solvent method (one step), absorption spectra of two step method was higher visible range compared than that of one step method in Figure 3d.

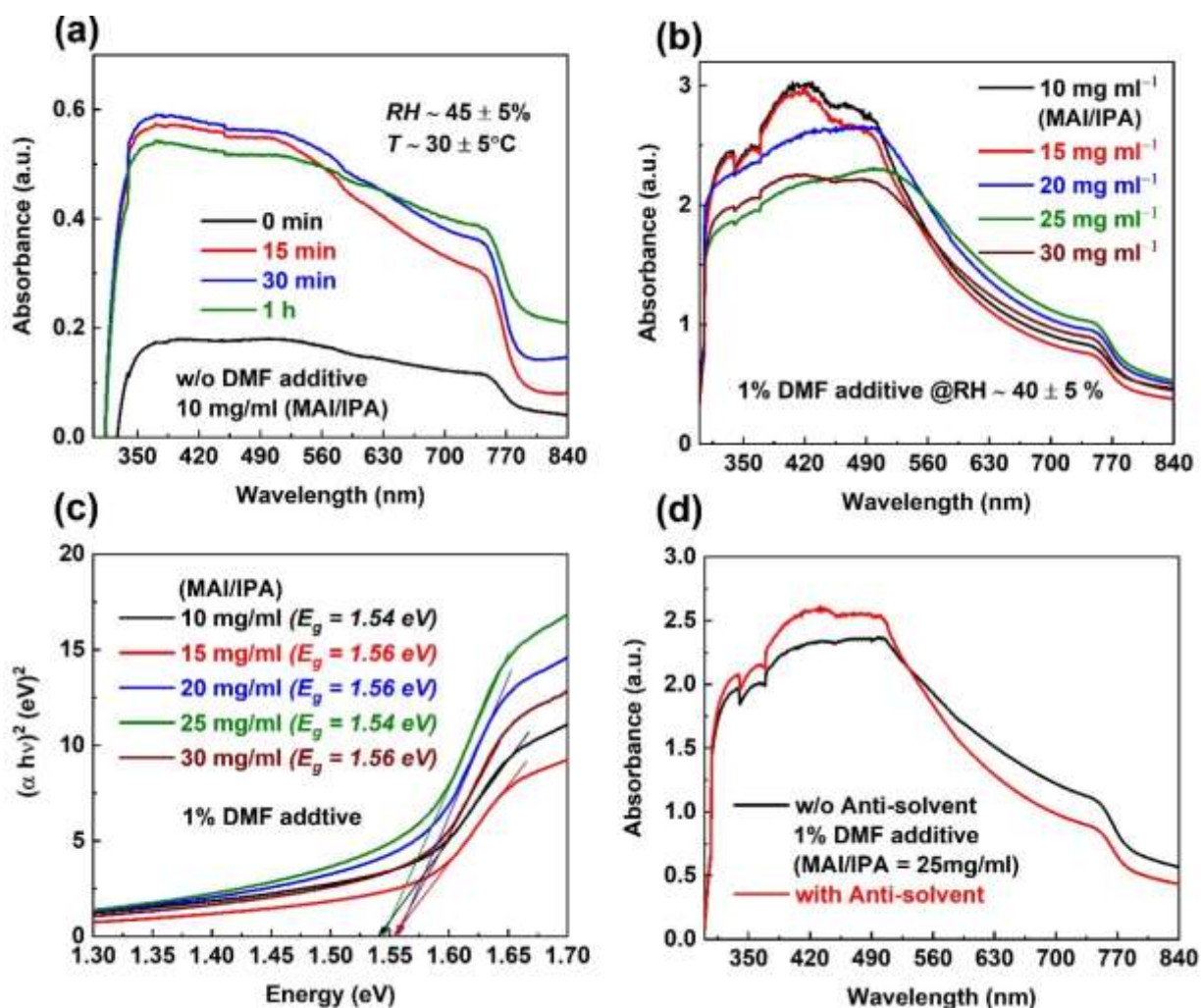


Figure 3 UV-Vis absorption spectra of perovskite films (a) w/o additive films under different annealing time (b) with 1% DMF additive films with different MAI concentration for 30 min each (c) Tauc plots calculated from absorbance spectra of different MAI concentration and (d) two different techniques between one step and two step deposition with and w/o anti-solvent.

First, we compared the X-ray diffraction (XRD) patterns of perovskite films (w/o DMF additive) on different annealing time and ambient atmosphere (Figure 4a-b). Strong diffraction peak (2θ) was 12.56° (PbI_2), corresponding to (001) crystal plane under ambient atmosphere (Guo et al., 2016). Perovskite crystal plane intensity (110) annealed for 30 min was slightly higher than that of 10 min and 15 min indication as an impurity of perovskite (Figure 4a). Similar results were received due to low purity of perovskite (110) crystal plane (figure 4b) after increased

MAI (w/o DMF additive) from 10 mg to 20 mg under $RH \sim 60 \pm 5\%$. Compared with crystal planes of PbI_2 (001) and perovskite (110), it can be seen that the content of perovskite decreases, whereas the residual PbI_2 increases. Unreacted PbI_2 was not completely transformed into perovskite film due to leaving a large portion of PbI_2 . Hence, low humidity environment ($RH \sim 45 \pm 5\%$) is for further optimization. Figure 4c shows the XRD patterns of perovskite additive (1% DMF) films with different amount of MAI/IPA solution. The perovskite peaks at $2\theta = 14.02^\circ$, 28.36° and 50.27° are corresponding to the (110), (220) and (404) planes of the tetragonal phase (I4/mcm space group) (Chen et al., 2016; Guo et al., 2016). A fraction of PbI_2 (12.56°) was decreased with increasing MAI concentration. As a result, strongest perovskite peak at 2θ (14.02°) was observed when MAI value was increased to in 25 mg. At last, least portion of PbI_2 peak remained in the final perovskite film. We suppose that residual PbI_2 could be beneficial to improve the grain boundaries and defect passivation. This result is good agreement with UV-Vis absorption spectrum corresponding to the higher absorbance in the visible region. The crystallite size of additive perovskite films can be calculated according to the Scherrer's equation: $D = k \lambda / (\beta_{hkl} \cos \theta_{hkl})$, where $k = 0.89$ (shape factor), $\lambda = 0.15406$ nm, β_{hkl} = half-width of the diffraction band (FWHM) θ_{hkl} = Bragg-diffraction angle. As shown in Figure 4d, the full width at half maximum (FWHM) of additive perovskite (110) peaks was highly reduced from 0.228° to 0.155° after increasing the MAI/IPA concentration. The crystallite sizes of perovskite films were increased from 35.18 nm (10 mg), 37.67 (15 mg), 40.17 nm (20 mg) up to 51.77 (25 mg). It is noted that crystallite size was easily controlled for perovskite fabrication in ambient atmosphere.

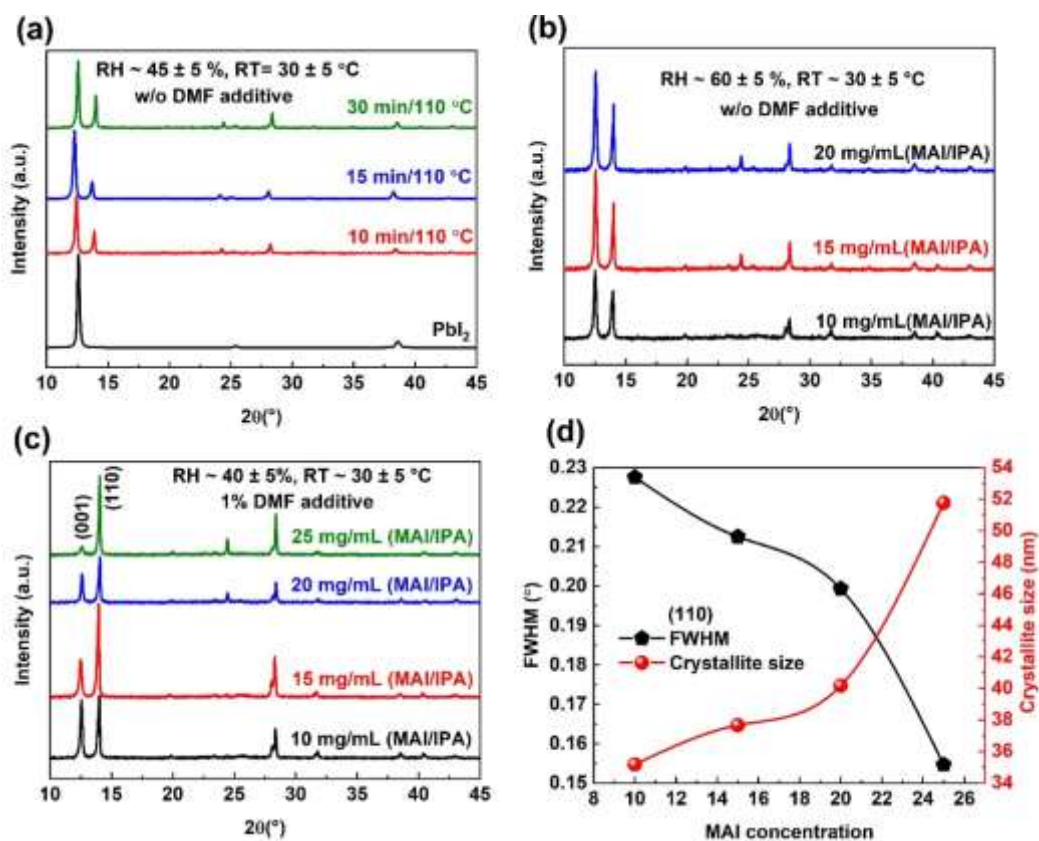


Figure 4 XRD of perovskite films fabricated on different annealing time in relative humidity of (a) $RH \sim 45 \pm 5\%$ (b) $RH \sim 60 \pm 5\%$ (c) different MAI concentration (d) Full-width at half maximum (FWHM) and crystallite size of (110) peak of all the samples.

Conclusion

We successfully fabricated that additive solvent method increases the perovskite formation by two-step deposition method in ambient air. Transformation kinetics between PbI_2 and perovskite peak intensities were confirmed by XRD analysis. Moreover, optimum concentration of 25 mg/ml (MAI/IPA) solution correlates to higher absorbance in the visible region confirmed by UV-vis spectroscopy. Both solvent additive and two step methods are essential improving high quality film. This work paves simple, low cost and vacuum free fabrication processes in air for potential application in perovskite solar cells.

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