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Sequential Dip-spin Coating Method: Fully Infiltration of MAPbI_{3-x}Cl_x into Mesoporous TiO₂ for Stable Hybrid Perovskite Solar Cells

Woochul Kim¹, Jiyeon Park¹, Hyeonhuh Kim¹, Yusin Pak², Heon Lee³, and Gun Young Jung^{1,*}

¹School of Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju 61005, Republic of Korea

²Division of Physical Science and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

³Department of Materials Science and Engineering, Korea University, Seoul 02841, Republic of Korea

*corresponding author: gyjung@gist.ac.kr

Highlights

- Sequential dip-spin coating method is developed to coat a uniform perovskite film without voids.
- The dip-spin coated perovskite film increases the recombination resistance owing to complete pore-filling, enhancing the J_{SC} and PCE.
- A void-free and pore-filled perovskite film with large grains (average 2.10 μm) is achieved by the dip-spin coating.
- The pore-filled and void-free perovskite film fabricated via dip-spin coating prevents the diffusion.
- The cell fabricated via the dip-spin coating maintains 99 % of their initial PCE after 35 days of storage.

Abstract

Organic-inorganic hybrid perovskite solar cells (PSCs) have reached a power conversion efficiency of 22.1 % in a short period (~7 years), which has been obtainable in silicon-based solar cells for decades. The high power conversion efficiency and simple fabrication process render perovskite solar cells as potential future power generators, after overcoming the lack of long-term stability, for which the deposition of void-free and pore-filled perovskite films on mesoporous TiO₂ layers is the key pursuit. In this research, we developed a sequential dip-spin coating method in which the perovskite solution can easily infiltrate the pores within the TiO₂ nanoparticulate layer, and the resultant film has large crystalline grains without voids between them. As a result, a higher short circuit current is achieved owing to the large interfacial area of TiO₂/perovskite, along with enhanced power conversion

efficiency, compared to the conventional spin coating method. The as-made pore-filled and void-free perovskite film avoids intrinsic moisture and air and can effectively protect the diffusion of degradation factors into the perovskite film, which is advantageous for the long-term stability of PSCs.

Keywords: Perovskite solar cell; Mesoporous TiO₂; Dipping; Hybrid perovskite; Stability

1. Introduction

Organic-inorganic hybrid perovskite solar cells (PSCs) have been spotlighted as a new third-generation photovoltaic devices due to their extremely low fabrication cost and skyrocketing power conversion efficiency (PCE) [1]. Kojima *et al.* pioneered particles of nanocrystal CH₃NH₃PbI₃ perovskite material as a dye material in dye-sensitized solar cells and achieved a PCE of 3.81 % in 2009 [2]. After that, Kim *et al.* firstly demonstrated solid-state PSCs utilizing a thin (CH₃NH₃)PbI₃ perovskite film itself as a light absorbing layer on a mesoporous TiO₂ electron-transporting layer and reported a high PCE of 9.7 % [3]. The hybrid perovskite has an ABX₃ structure, where the A site is occupied by an organic or inorganic cation, such as CH₃NH₃⁺ (methylammonium), HC(NH₂)₂⁺ (formamidinium), Cs⁺, or Ru⁺; the B site is filled with Pb²⁺, Sn²⁺, or Ge²⁺; and the X site is usually a halide anion, such as Cl⁻, Br⁻, or I⁻ [4]. Perovskite materials have several advantages as the active layer in photovoltaic devices, such as a suitable direct energy band gap of ~1.55 eV [2,5], small exciton binding energy [5,6], high extinction coefficient [7,8], long carrier life time, and long exciton diffusion length [9-11], which are essential for achieving a higher PCE. Many approaches have been explored to obtain a competitive PCE of 22.1 % over a short period [12], which has been obtainable in silicon-based solar cells for decades.

Despite the high efficiency, long-term stability is the major problem to resolve for the commercialization of PSCs because the hybrid perovskite materials are vulnerable to moisture, oxygen and UV exposure [13]. Recently, several strategies have been reported for improving the stability of PSCs by introducing a blocking layer against the UV and moisture [14], modifying the electron transport layer (ETL) [15], and increasing the perovskite grain size using a nanostructured TiO₂ scaffold layer [16].

Particularly, perovskite film is very sensitive to moisture. In order to enhance the stability against the water, a uniform and less defective perovskite film with large grains and thus fewer grain boundaries that can act as an air-protection patches to suppress the permeability of oxygen and moisture into the perovskite film is necessary. The grain boundaries between two grains are reported to be the routes of moisture infiltration into the film, which initiates the degradation of the perovskite material along the in-plane direction of the grains [17]. In addition, the perovskite film should overlay the underneath electron transport layer without any voids. Otherwise, the subsequently coated hole transport layer directly interfaces the electron transport layer through the voids, inducing primary recombination pathways at the interface and deteriorating the photovoltaic performance [18]. A 200-400 nm thick perovskite capping layer on top of the TiO_2 scaffold layer was also applied to eliminate the direct contact between the two charge transport layers [19-21].

Furthermore, the pores within the TiO_2 mesoporous nanoparticulate layer (mp- TiO_2) should be filled with the perovskite material during film fabrication, which is favorable to fast charge transfer and reduces the chance of recombination during exciton diffusion [22]. It has also been a persistent, but rarely researched, issue in perovskite solar cells to perfectly fill the pores with the active material during film deposition. Kim *et al.* applied a TiO_2 nanorod structure instead of a TiO_2 nanoparticulate layer for the easy flow of active material solution through the nanorods; however, the surface area of the TiO_2 nanorods was greatly reduced compared to that of the nanoparticulate film, in return inducing an inevitable loss in photocurrent [23]. Leijtens *et al.* reported that the fraction of pore-filling increased with decreasing thickness of the mp- TiO_2 layer, leading to improved photovoltaic performances despite the lower optical density of the photoanode film [18].

In the long run, a new deposition method, which is capable of high fraction of pore-filling together with high optical density, better coverage, and smooth perovskite film, should be developed regardless of the underlying scaffold layer at different thicknesses.

One-step spin coating is a widely used coating method to form a perovskite thin film on top of the mesoporous ETL [24-28]. The perovskite precursor solution is usually dropped on the ETL for spinning; however, there is a limit as to how much solution can infiltrate into and soak the mp-TiO₂ layer perfectly during the spin coating, leaving unwanted pores within the nanoparticulate layer. Other deposition methods have been used to coat the perovskite active film, such as spray coating [29], blade coating [30], vacuum-assisted deposition [31], and vapor deposition [32]. High vacuum is required for vacuum-assisted deposition and vapor deposition. Spray coating and blade coating are suitable for large-area device fabrication, but they are unsuitable for complete pore-filling. For the effective pore filling, dipping processes were applied to infiltrate the perovskite solution into the mesoporous TiO₂ layer [33,34]. However, these works did not show the degree of pore-filling within the mesoporous TiO₂ layer at different dipping conditions, but mainly focused on the enhancement of PCE.

In this study, we developed a new coating method to create a uniform perovskite film with large crystalline grains and complete pore-filling by sequentially performing dipping and spin coating on top of an mp-TiO₂ layer. Hereafter, this step is called dip-spin coating and is compared to the conventional spin coating method. The perovskite films made by the two methods were evaluated in terms of grain size, void density, and pore-filling. To probe the effect of the perovskite film, a set of photovoltaic cells were fabricated to compare their photovoltaic performances. In addition, long-term stability tests were performed to verify the effect of pore-filled and voids-free perovskite film via the dip-spin coating method.

2. Experimental Section

2.1. Device fabrication

An FTO glass was cleaned with acetone, isopropyl alcohol, and deionized water for 5 min each. After UV ozone cleaning, a compact TiO₂ blocking layer was deposited on the substrate by sequentially spin coating TiO₂ precursor solutions of 0.15 M and 0.3 M titanium butoxide in 1-butanol at 2000 rpm for 20 sec and annealing at 500 °C for 30 min. Then, the mp-TiO₂ layer was formed by spin coating a TiO₂ paste composed of 30 nm-sized nanoparticles in ethanol (1:5 weight ratio) at 4000 rpm for 15 sec on the TiO₂ blocking layer. The substrate was dried at 125 °C for 5 min to remove the residual solvent and then annealed at 500 °C for 1 hr. The perovskite precursor solution was prepared with 0.8 M PbI₂ (99 %, Sigma Aldrich), 0.8 M PbCl₂ (98 %, Sigma Aldrich), and 3.2 M methylammonium iodide (99.5 %, Lunatec) in dimethylformamide (DMF) (99%, Sigma Aldrich). In the dip-spin coating method, the substrate was vertically immersed slowly with a dipping speed of 1 mm/sec into the perovskite precursor solution and then soaked for 40 min. After removal, the sample was spin coated at 6000 rpm for 40 sec and annealed at 150 °C for 40 min. For the conventional spin coating method, 100 µL of the same precursor solution was dropped on the mesoporous TiO₂ layer, spin coated at 6000 rpm for 40 sec, and finally annealed 150 °C for 40 min. The hole transport material solution was prepared with 78.1 mg of Spiro-MeOTAD, 28.8 µL of tert-butylpyridine, and 17.5 µL of a solution of lithium bis(trifluoromethylsulfonyl)imide (Li-TFSI 520 mg in 1 mL of acetonitrile) in 1 mL of chlorobenzene. The solution was spin coated on the perovskite film at 2000 rpm for 20 sec. Finally, 80 nm thick gold electrodes were deposited through a shadow mask with a dumbbell aperture by thermal evaporation (0.7 Å/sec) under a vacuum pressure of 3.0×10^{-6} Torr. All processes for solar cell fabrication were performed in a glove box filled with N₂ gas.

2.2. Perovskite film analysis

Top views of the perovskite film and cross-sectional images of the perovskite solar cells were taken using a field-emission scanning electron microscope (FE-SEM, JEOL 2020F).

The crystallography of the perovskite film was measured by X-ray diffraction (XRD) using Cu K α X-ray radiation (40 kV, 100 mA, Rigaku D/max-2400)

2.3. Device performance characterization

The photocurrent density (J)-voltage (V) curves of the perovskite solar cells were measured over an active area of 4.64 mm² under AM 1.5G illumination at an intensity of 100 mW/cm² (SANEI solar simulator, Class A). Prior to the measurement, the light source was calibrated using a reference silicon photodiode (Ashahi Spectra Co., Ltd.). All the solar cells were measured using a Keithley 2400 source meter. The Nyquist plots were measured by electrochemical impedance spectroscopy (EIS) analysis (FRA2 μ AUTOLAB type III) over a frequency range of 1 Hz to 1 MHz at the open circuit voltage of each cell under dark condition. For the photocurrent decay measurements, the cells were kept in a gas chamber (Nextron Co., Ltd.) and measured while being irradiated with a white light-emitting diode at 20 mW/cm² at relative humidities (RHs) of 30, 50, 70, and 90 %. The air was flowed continuously into the gas chamber during measurement at a certain humidity, which was adjusted by controlling the flow rates of water vapor and high purity air.

3. Results and discussion

Dip-spin coating method was proposed to produce stable perovskite solar cells (PSCs) by depositing a pore-filling perovskite layer on the mp-TiO₂ layer. **Figure 1a** depicts the architecture of the PSC; a ~200 nm thick mp-TiO₂ layer was deposited on top of a TiO₂ blocking film, acting as a hole blocking layer, which was deposited on a fluorine-doped tin oxide (FTO) glass substrate, and used as an electron transport scaffold layer for a 400-500 nm thick CH₃NH₃PbI_{3-x}Cl_x (MAPbI_{3-x}Cl_x) active layer. Spiro-MeOTAD was used for the hole transport layer (HTL, ~200 nm thickness), and 80 nm thick gold was deposited as the top electrode. The dip-spin coating method for perovskite film formation is depicted in Figure 1b. First, the mp-TiO₂ anode substrate was immersed into a mixed solution of PbI₂, PbCl₂, methylammonium iodide (MAI), and dimethylformamide (DMF) with a slow dipping speed of 1 mm/sec to achieve enough capillary filling for efficient infiltration of the perovskite precursor solution into the pores of the TiO₂ nanoparticulate layer. Then, the substrate was soaked for 40 min in the solution. Second, the substrate was removed from the solution and then spin coated at 6000 rpm for 40 sec. The color of the perovskite film changed from bright yellow to dark brown after 20 sec of spin coating. Finally, the perovskite film was annealed not only to remove the residual solvent but also to form the crystalline perovskite film.

The optimized dipping time of the mp-TiO₂ layer into the perovskite solution was explored after annealing at 150 °C for 40 min. Different morphologies of the perovskite film with respect to the dipping time are shown in the supporting information [Supporting information (SI), **Figure S1**]. In less than 40 min of dipping, the perovskite film had many pores within the TiO₂ nanoparticulate film, and the perovskite film had small grains with voids, leading to the incomplete covering of the underneath mp-TiO₂ layer. After 40 min of dipping, large crystalline grains were generated without voids, and the pores within the mp-TiO₂ layer were completely filled. The average photovoltaic parameters from a set of 4 cells under each dipping time condition are compared in Figure S1c. It is notable that the

dipping time affected the short circuit current rather than the open circuit voltage and fill factor. The best solar cell performance was achieved from the cell dipped for 40 min.

The formed perovskite films were annealed at different temperatures for 40 min and showed different morphologies [SI, **Figure S2a**]. The grains of the perovskite film were enlarged with increasing temperature. At 150 °C, a compact and uniform perovskite film was formed with an average grain size of 2.10 μm with no voids between the crystalline grains. It is also notable that needle-like crystalline PbI_2 vaguely appeared at the perovskite surface, which was confirmed as a peak at 12.63° in the X-ray diffraction (XRD) pattern, as shown in Figure S2b. At above 150 °C, more voids between the perovskite crystalline grains appeared, and the needle-like crystalline PbI_2 were discernible with increasing annealing temperature. At this temperature, the perovskite film was decomposed, and the MAI species escaped to form PbI_2 [35]. The average PCE values from a set of 10 cells in each annealing temperature are compared in Figure S2c. A maximum PCE of 12.1 % at 150 °C was achieved, which then decreased with increasing annealing temperature due to excessive PbI_2 generation and the rough surface morphology of the perovskite film.

The effect of the annealing time on the film morphology was also investigated at 150 °C for 10-50 min. The top-view FE-SEM images of perovskite films annealed for various times are shown in **Figure S3a**, and their corresponding XRD patterns are shown in Figure S3b. After 10 min of annealing, the film had voids with many XRD peaks, demonstrating a metastable perovskite film [31]. Two dominant perovskite peaks appeared at 14.07° and 28.44°, which correspond to the (110) and (220) planes of $\text{MAPbI}_x\text{Cl}_{3-x}$, respectively [36]. In the sample annealed for 40 min, a peak of the nanocrystalline PbI_2 at 12.63° was newly appeared in the XRD pattern. The generated PbI_2 crystals were previously reported to act as a buffer layer for effectively blocking charge recombination at the interface between the perovskite film and the HTL, resulting in enhanced charge separation in perovskite solar cells [35]. However, the excessive amount of needle-like PbI_2 crystals generated when annealed for over 40 min had a negative effect on the photovoltaic performance [35]. Figure S3c shows

a statistical PCE box chart from a set of 10 cells in each annealing time condition. The perovskite film annealed for 40 min showed indistinct PbI_2 crystals on top of the film and revealed the best PCE. Hereafter, the dip-spin coated perovskite film was annealed at 150 °C for 40 min for further study.

Figure 2 compares top-view FE-SEM images of perovskite films deposited by the conventional spin coating and dip-spin coating methods before and after annealing. The amorphous perovskite film formed by the spin coating method initially had many voids (Figure 2a), which agglomerated and formed crystalline grains with an average grain size of 1.78 μm during the following annealing process (Figure 2b). As the perovskite film crystallized, the voids enlarged, through which the uncovered TiO_2 nanoparticulate layer could be directly exposed to the HTL layer. In contrast, the film formed via the dip-spin coating method was initially very compact with no voids, as shown in Figure 2d. After annealing, crystalline grains were formed with an average size of 2.10 μm (Figure 2e), which is larger than the previously reported ones, ranging from 500 nm to 1 μm [31, 37-40]. No voids were noticed in this case; as a result, the underneath mp- TiO_2 layer was perfectly covered and did not have direct contact with the HTL, eliminating the primary recombination pathways. We can confidently state that the perovskite film quality after annealing is heavily affected by the initial film morphology before crystallization. It was reported that the as-coated film should initially be homogeneous and free of voids to achieve a void-free film with large grains after annealing [41]. To probe the pore-filling fraction within the mp- TiO_2 layer, the cells were cut in half to obtain cross-sectional images. The SEM image (Figure 2c) of the mp- TiO_2 layer coated by the spin coating method shows relatively clear TiO_2 nanoparticles with many vacant pores, meaning that the precursor solution insufficiently infiltrated into the pores prior to spin coating. However, for the mp- TiO_2 layer coated by the dip-spin coating method, most of the pores were filled with the perovskite material, and the TiO_2 nanoparticles were embedded within the active material

(Figure 2f). The dipping speed at a slow rate of 1 mm/sec facilitated the soaking of the precursor solution into the pores within the mp-TiO₂ layer by capillary action, resulting in complete pore-filling. A 400 nm thick perovskite capping layer resided on top of the TiO₂ scaffold layer in both samples, which protected the ETL from direct contact with the HTL.

Figure 3a compares the best current density-voltage (J-V) plot of the perovskite solar cells based on the perovskite films deposited by the two coating methods. In each coating method, 26 cells were fabricated and measured. The average photovoltaic parameters, including short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF), and PCE, and their standard deviations are listed in **Table 1**. Figure 3b demonstrates the PCE value distribution among the samples. When using the spin coating method, the PCE values are less than 10 % and are mostly in the range of 9 % from 14 cells. In contrast, when using the dip-spin coating method, the PCE values are above 9 % and are mostly in the range of 10-11 % from 18 cells, with a best PCE value of 12.1 %. The perovskite solar cells produced via the dip-spin coating method revealed better device performance compared to their counterpart, having a J_{sc} of 25.43 mA/cm², a V_{oc} of 0.73 V, an FF of 58 % and an overall PCE of 10.83 %, which is 19 % higher than the reference cell produced via the spin coating method. The enhancement is mainly due to the increase in short circuit current, which was possible by both the enlarged contact area of the perovskite material to the TiO₂ nanoparticles through pore-free film formation and the elimination of primary recombination pathways owing to the void-free perovskite film composed of large grains.

Electrochemical impedance spectroscopy (EIS) was utilized to analyze the contact resistances at the mp-TiO₂/perovskite and perovskite/HTL interfaces over a frequency range from 1 Hz to 1 MHz at the open circuit voltage of each cell under dark condition. **Figure 4** shows the corresponding Nyquist plots, which are fitted with the equivalent circuit model, as shown in the inset, where R_s , R_1 , and R_2 represent the series resistance of the FTO electrode

and counter electrode, the charge transport resistance at the mp-TiO₂/perovskite/HTL interfaces, and the interfacial recombination resistance, respectively. The Nyquist plot is separated into two arcs at high and low frequencies; the first arc at high frequencies (left circle in the magnified plot of Figure 4b, frequency range > 10 kHz) corresponds to the charge transport resistance (R_1), and the second arc at low frequencies (right part in Figure 4a, frequency range < 10 kHz) is associated with the recombination resistance (R_2) [42,43]. The extent of electron transport can be decided by the impedance, which is defined as the diameter of the corresponding arc. The impedance values of the equivalent circuit are summarized in **Table 2**.

The solar cell fabricated via the dip-spin coating had a lower charge transport resistance of 50.3 Ω than that (53.3 Ω) from the cell produced via the conventional spin coating, indicating that the pore-free mp-TiO₂ photoanode increased the contact interface area between the ETL and perovskite material and thus facilitated charge carrier transport between them, minimizing energy losses of the charge carriers at the interface [44]. Moreover, the dip-spin coating cell had a much larger recombination resistance (26.4 k Ω) than its counterpart (774 Ω), which signifies that charge recombination was greatly suppressed at the mp-TiO₂/perovskite/spiro-MeOTAD interfaces owing to the superior film quality; the void-free perovskite film prevented the direct contact of the mp-TiO₂ layer to the spiro-MeOTAD, eliminating the primary recombination pathways [18]. In addition, the pores within the TiO₂ nanoparticulate film, which could also act as charge recombination sites during exciton diffusion, were perfectly filled with perovskite material by capillary flow during the slow dipping process. The EIS results explain the reasons for the enhanced photovoltaic performance of the cell fabricated via the dip-spin coating method. We can easily expect that the enhanced charge carrier transport and high recombination resistance increased the short circuit current and thus enhanced the PCE, as shown in Figure 3.

As mentioned in the introduction, the lack of long-term stability is the main barrier to the realization of perovskite solar cells. The effect of a void-free and pore-free perovskite film on the device stability was examined with perovskite solar cells fabricated via the two coating methods. The performance degradation induced by the ambient moisture and oxygen was minimized by storage in a nitrogen-filled glove box (~ 1 ppm moisture and oxygen level) in the dark. Then, 13 solar cells in each coating method were measured with respect to storage days, and the average open circuit voltage, short circuit current density, fill factor and PCE from the 13 cells in each coating method are plotted for comparison in **Figure 5**. For the cells produced via the spin coating method, the open circuit voltage dropped rapidly after 14 days, and the solar cell malfunctioned. The current density and fill factor decreased dramatically after 7 days. As a result, the PCE also decreased rapidly after 7 days. In contrast, for the cells with the dip-spin coated film, the open circuit voltage and fill factor increased slightly after 7 days and remained constant for 35 days. The initial current density of ~ 24 mA/cm² dropped to 21.2 mA/cm² after 15 days, but it recovered after 22 days. The PCE followed the same trend as the current density and almost maintained its initial value after 35 days, as shown in Figure 5d, but dropped to 5.81 % after 60 days [SI, **Figure S4**].

The degradation of perovskite solar cells kept under N₂ atmosphere is affected by the intrinsic degradation factors of oxygen and moisture, denoted intrinsic degradation [45]. Oxygen and moisture can be trapped in the pores within the mp-TiO₂ layer during the film formation, which degrades the perovskite film and thus deteriorates the photovoltaic performance. The rapid drop of photovoltaic properties of solar cells produced via the spin coating method may mainly be affected by intrinsic degradation factors, which could be more serious for TiO₂ nanoparticle-based perovskite solar cells because of the inherent large number of pores within the TiO₂ scaffold layer. The solar cells fabricated via the dip-spin coating method demonstrated greatly enhanced stability. The only difference during the cell fabrication

was the film coating process, which led to a different degree of voids and pores within the active layer. The pore-free perovskite film showed enhanced stability due to the absence of inherent oxygen and moisture within the film. In addition, the compact and uniform perovskite film with large grains and less grain boundaries may act as an air-protection patches and thus be less affected by attack from ambient oxygen and moisture [30].

In the presence of moisture, the photocurrent (short circuit current at 0 V) decreases because the perovskite film gradually degrades into $(\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot 2\text{H}_2\text{O}$ and PbI_2 , which is reported to be an electrical insulator [46-48]. To measure the photocurrent decay induced by moisture, the cells were kept in a gas chamber, where an air at relative humidities (RHs) of 30, 50, 70, and 90 % was continuously flowed while the cells were irradiated with a white light-emitting diode at 20 mW/cm^2 . At 30 % RH, the photocurrent linearly decreased up to 20000 sec for both coating methods (**Figure 6a**). On the other hand, at RHs of 50, 70, and 90 %, the current decreased exponentially, as shown in Figure 6b, c, and d. The times to decrease to 50 % of the initial photocurrent are compared in Table 3. Because the perovskite material is degraded by moisture, the photocurrent decay was greatly accelerated with increasing humidity level. The perovskite film fabricated via dip-spin coating underwent less degradation in all RH conditions, demonstrating a higher resistance to moisture attack.

4. Conclusions

Dip-spin coating of a perovskite film on a mp-TiO₂ scaffold layer was first demonstrated, and the photovoltaic performance was compared with the cells fabricated via the conventional spin coating method. The mp-TiO₂ scaffold layer was dipped into the perovskite precursor solution, and the solution soaked the mesoporous TiO₂ scaffold layer by capillary flow, resulting in a pore-free TiO₂ photoanode. Furthermore, the as-coated amorphous perovskite film was initially free from voids, leading to a void-free film with large grains (average size of $2.10 \mu\text{m}$) after annealing. The increased interfaces owing to the pore-free photoanode led to an enhanced short circuit current and thus a

higher PCE compared to the cells fabricated via the spin coating method. The best solar cell had a current density of 26 mA/cm² and a PCE of 12.1 %. Furthermore, the stability was also dramatically improved, owing to the reduced confinement of intrinsic oxygen and moisture within the active layer during the fabrication process. The PCE remained almost constant after 35 days of storage in nitrogen atmosphere. In contrast, solar cells produced via the spin coating method degraded rapidly due to the trapped degradation factors and malfunctioned after 14 days.

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<Figure captions>

Figure 1. (a) Schematic of the perovskite solar cell. (b) Procedure for perovskite film deposition on the mp-TiO₂ scaffold layer via the dip-spin coating method.

Figure 2. FE-SEM images of the perovskite film on the mp-TiO₂ layer: (a) as deposited and (b) after annealing at 150 °C for 40 min. (c) Cross-sectional view of the perovskite solar cell via the spin coating. (d), (e), and (f) are the corresponding images of the perovskite film via the dip-spin coating.

Figure 3. (a) Comparison of the best current density (J)-voltage (V) curves of the perovskite solar cells fabricated via the spin coating and dip-spin coating methods. (b) Histograms of the PCE values from 26 perovskite solar cells via the spin coating (black) and dip-spin coating methods (red).

Figure 4. Nyquist plots of the perovskite solar cells fabricated via the two different coating methods measured at open circuit voltage under dark condition. (a) The main arc in the low-frequency region represents the charge recombination resistance at the mp-TiO₂/perovskite/HTL interfaces. (b) Magnified plots in the high-frequency region represents the charge transport resistance at the mp-TiO₂/perovskite/HTL interfaces. The inset shows the equivalent circuit model used for fitting the Nyquist plots.

Figure 5. Stability test to check the variation of (a) V_{oc}, (b) J_{sc}, (c) FF, and (d) PCE as a function of storage days in N₂ atmosphere. The values are averaged from 13 cells in each coating method.

Figure 6. Photocurrent decay of the perovskite solar cells over time during exposure to air at an RH of (a) 30, (b) 50, (c) 70, and (d) 90 % under white-light irradiation at an intensity of 20 mW/cm².

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Table 1. Average photovoltaic performance parameters of V_{oc} , J_{sc} , FF and PCE from 26 perovskite solar cells in each coating method.

	Voltage (V)	Current density (mA/cm ²)	Fill factor	PCE (%)
Spin coating	0.69	22.05	0.58	9.10
method	(± 0.03)	(± 2.4)	(± 0.03)	(± 1.60)
Dip-spin coating	0.73	25.43	0.58	10.83
method	(± 0.04)	(± 1.54)	(± 0.04)	(± 1.29)

Table 2. Analyzed resistance values of the perovskite solar cells by fitting the Nyquist plots to the equivalent circuit model.

	Spin coating	Dip-spin coating
Series resistance R_s (Ω)	34.6	43.0
Charge transport resistance R_1 (Ω)	53.3	50.3
Recombination resistance R_2 (Ω)	774	26400

Table 3. The time to decrease to 50 % of the initial photocurrent.

Relative humidity (%)	Time to maintain 50 % of the initial photocurrent (sec)	
	Spin coating	Dip-spin coating
30	40000*	62000*
50	3250.2	6232.0
70	188.3	426.1
90	107.1	373.9

*These values were obtained by extrapolating the curves.