A Novel Approach for the Development of Moisture Encapsulation Poly(vinyl alcohol-co-ethylene) for Perovskite Solar Cells

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Supporting Information

ABSTRACT: In this study, we developed the universal encapsulation method using poly(vinyl alcohol-co-ethylene) (EVOH) to improve the water stability of perovskite solar cells. In order to enhance the moisture barrier property, we utilized SiO2 and graphene oxide (GO) fillers in the EVOH matrix. First, UV-treated SiO2 increased the dispersibility in the EVOH matrix and made the penetrating path more complicated, which led to a better moisture barrier property. The water vapor transmission ratio (WVTR) is enhanced from 4.72 × 10−2 (EVOH only) to 1.55 × 10−2 (EVOH with SiO2 filler) g/m² day. Second, we found that GO reduce the unreacted hydroxyl groups that could attract water molecules at the surface of EVOH. The addition of GO increased the WVTR up to 3.34 × 10−3 g/m² day. Finally, our EVOH-based film successfully encapsulated without the efficiency drop. The encapsulated devices surprisingly maintained 86% of their performance even under direct contact with water for 5 h.

INTRODUCTION

Perovskite solar cells (PSCs) have attracted tremendous attention owing to their excellent photovoltaic properties, such as their high optical absorption coefficients and carrier diffusion lengths.1–3 Since the first reported power conversion efficiency (PCE) value of 3.8%, tremendous progress has been accomplished. Accordingly, the PCE values reported in 2018 have reached 23.7%, which allows them to serve as alternatives to Si solar cells.4,5 However, halide perovskite materials have low moisture stability that limits their potential industrial applications.6,7

One of the most promising approaches used to solve the moisture instability issue is the adoption of large cations into perovskite structures that leads to the low dimensionality (2D or quasi-2D) of perovskite materials. Zhang et al. reported that unsealed (PEA)2(MA)4Pb5I16 retained 78.5% of its original PCE for 160 h in an air atmosphere with 55 ± 5% humidity, while Yan et al. claimed that (BA)2(FA)2Pb3I10 retained 80% efficiency for 25 days in ambient air with 25 ± 5% humidity without any device encapsulation.8,9 However, these materials cannot endure adverse conditions, such as direct contact with water, which occurs in rainy days. Therefore, the encapsulation is still essential to guarantee the long-term stability of PSCs.

The use of polymer films is a well-known strategy for device encapsulation owing to their low-cost benefits, ease of process, and chemical stabilities. Han and co-workers fabricated a device using a PMMA/reduced graphene oxide composite as the encapsulant. It was stable for 1000 h at 35 °C and 40% humidity.10 Liu and co-workers used poly(dimethylsiloxane) (PDMS) for encapsulation. It retained its performances during a testing period of 3000 h in ambient air with a humidity of ~20%.11 However, these polymers showed poor thermal, mechanical, and moisture barrier properties and were considered inadequate for practical applications and use in various devices. Recently, poly(vinyl alcohol-co-ethylene) (EVOH) has received worldwide attention as an alternative...
because its good barrier properties can inhibit the permeation of gases, such as oxygen, carbon dioxide, and moisture. Specifically, its outstanding barrier properties from oxygen render it applicable to various industrial fields.\textsuperscript{12−15} The excellent barrier properties of EVOH are attributed to the establishment of strong bonds between polymer chains due to the hydrogen bonding of hydroxyl groups present in vinyl alcohol units.\textsuperscript{14−16} However, water also can be absorbed to hydroxyl groups owing to their reactivity to water. When additional water molecules are absorbed by EVOH, it will be plasticized, and its barrier properties will diminish.\textsuperscript{14} This is why EVOH is necessary to be modified by methods such as the addition of fillers and multilayer structures.\textsuperscript{17−19} For instance, Liu and co-workers added SiO\textsubscript{2} in EVOH to improve its properties.\textsuperscript{20} They claimed that SiO\textsubscript{2} makes the permeation path of gases more tortuous and leads to an improvement of its barrier properties.\textsuperscript{20} The addition of 5 wt % SiO\textsubscript{2} nanoparticles in EVOH reduced the permeation of oxygen and water to 64.4 and 54.2\%, respectively. Conversely, Li and co-workers utilized boric acid and graphene oxide (GO) to form hydrogen bonds with the unreactive hydroxyl groups of EVOH. Their water vapor transmission ratio (WVTR) was reduced by 80.2\% compared to that for the pure film.\textsuperscript{21} Despite the techniques reported in these studies, it is difficult to apply them to PSCs using simple processes, such as spin-coating, because PSCs are soluble in hydrophilic solvents, such as DMSO, DMF, and water, which are common solvents for EVOH. Therefore, it is challenging to achieve the encapsulation of PSCs using EVOH.

In this study, we apply EVOH as the encapsulant of PSCs to improve their water stabilities. Dispersibility changed SiO\textsubscript{2} and GO fillers were added to increase the barrier properties of EVOH. The properties and performance of our EVOH compositions were characterized using SEM, zeta potential, surface contact angle, and WVTR. We successfully incorporated our EVOH compositions onto the PSCs that led to their good stability even under the direct contact of water.

### RESULTS AND DISCUSSION

#### Effects of Incorporating UV-Treated SiO\textsubscript{2}

To investigate the effects of SiO\textsubscript{2} on the quality of the EVOH film, samples (EVOH/SS:EVOH film with nontreated SiO\textsubscript{2}, EVOH/SS/UV:EVOH film with UV-treated SiO\textsubscript{2}) were prepared using the method described in the \textit{Experimental Section}. It is worth noting that 5 wt % SiO\textsubscript{2} in EVOH is the optimized condition for obtaining the best moisture barrier property as shown in Figure S1. Figure 1a,b shows the surface morphology of EVOH/SS and EVOH/SS/UV. As shown in Figure 1a, SiO\textsubscript{2} nanoparticles in EVOH/SS were aggregated (red circles) that may lead to poor moisture barrier properties owing to the excessive presence of a nonblocked moisture

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**Figure 1.** SEM images of EVOH films after the incorporation of SiO\textsubscript{2} fillers for (a) EVOH/SS and (b) EVOH/SS/UV. Corresponding EDS mapping analysis for (c) EVOH/SS and (d) EVOH/SS/UV with the UV/ozone treatment. (e) Schematic of the dispersion of SiO\textsubscript{2} fillers in the EVOH solution and film with and without UV/ozone treatments.
permeation path. Conversely, SiO₂ nanoparticles in EVOH/S5/UV were well dispersed in the form of relatively small particles as described in Figure 1b. SiO₂ was confirmed by EDS for EVOH/S5 (Figure 1c) and EVOH/S5/UV (Figure 1d). The uniformly dispersed SiO₂ fillers in EVOH/S5/UV help form a more complicated penetration path of moisture, which improves their moisture barrier properties. This result was attributed to the homogeneous dispersion of nanoparticles into the EVOH matrix caused by the reduction of organic compounds. UV treatment cleans the surface of SiO₂ and reduces the aggregation of particles.²² Figure 1e shows a schematic of the effect owing to the UV treatment. Contaminants, such as organic compounds, are being absorbed on the surface of SiO₂ nanoparticles, which induces aggregation of particles and adversely affects the homogeneous dispersion of SiO₂ nanoparticles in the EVOH matrix.²³ UV treatment allows them to be dispersed uniformly by removing organic compounds that may help improve their barrier properties. To verify the improved dispersibility of the UV-treated SiO₂, a zeta potential analysis was conducted for EVOH/S5 and EVOH/S5/UV. Accordingly, a potential of −88.12 mV was obtained for the EVOH/S5/UV solution, which had more negative charges on the surface compared to the evoked potential of −70.21 mV for the EVOH/S5 solution, as shown in Figure S2. This means that SiO₂ in EVOH/S5/UV is well dispersed as a stable colloid in the solvent compared to EVOH/S5.²⁶,²⁷ Furthermore, the improved optical properties for EVOH/S5/UV also dictate the homogeneous dispersion of SiO₂ compared to EVOH/S5 films (see Figure S3).

The Ca cell was fabricated to evaluate the barrier properties of EVOH according to the addition of SiO₂ nanoparticles, as shown in Figure 2a. The Ca test was carried out at 25 °C/85%, and the conductance was calculated by the time Ca was fully oxidized. Calculation of the WVTR was performed using the following equation that was originally proposed by Paetzold et al.²⁸

\[
\text{WVTR} = -2 \times \left( \frac{M_{\text{H}_2\text{O}}}{M_{\text{Ca}}} \right) \times \rho_{\text{Ca}} \sigma \left( \frac{d(G)}{d(t)} \right) \times \left( \frac{A_{\text{Ca}}}{A} \right)
\]

where the factor “2” is the molar equivalent of the Ca corrosion reaction, \(M_{\text{H}_2\text{O}}\) (18 g/mol) and \(M_{\text{Ca}}\) (40.1 g/mol) are the molecular weights of water and Ca, respectively, \(\rho_{\text{Ca}}\) (1.55 g/cm³) is the density of Ca, \(\sigma\) (3.4 \(10^{-8}\) Ω m) is the resistivity of Ca, \(d(G)/d(t)\) is the rate of change of conductance (G), \(A_{\text{Ca}}\) is the area of deposited Ca, and \(A\) is the barrier film area on Ca.

As shown in Figure S4, the conductance decreases consistently in a linear manner in the interval known as the lag region during a time interval described as the lag time interval or alternatively known as the breakthrough time.³⁰ The WVTR was calculated by substituting the slope during the lag region in the above equation.³¹ The conductance changes of the Ca test by the addition of fillers and its calculated WVTR are shown in Figure 2b and Table 1.

| Sample (in wt %) | WVTR (g/m² day) | Lag time (h) |
|-----------------|-----------------|--------------|
| EVOH            | 4.72 \(10^{-2}\) | 0.74         |
| EVOH/S5         | 2.87 \(10^{-2}\) | 2.21         |
| EVOH/S5/UV      | 1.55 \(10^{-2}\) | 4.40         |

respectively. According to the results of the WVTR, it is obvious that the incorporation of SiO₂ into the EVOH yields better moisture barrier properties, thereby improving the WVTR from 4.72 \(10^{-3}\) to 1.55 \(10^{-3}\) g/m² day and increasing the lag time from 0.74 to 4.40 h. The WVTR result was also confirmed by MOCON test, which shows a similar result (4.66 \(10^{-3}\) g/m² day) on the EVOH sample, which means our WVTR calculation is reliable to use (see Figure S5). It should be noted that the barrier properties of EVOH/S5/UV were enhanced compared to the results of EVOH/S5.

This finding is expected given our SEM and zeta potential results in the previous section. Therefore, increased dispersibility of SiO₂ in the EVOH matrix by the UV treatment made the penetration path more complicated, which led to better moisture barrier properties.²⁹,³⁰

Effects of Incorporating Graphene Oxide. Although we successfully demonstrated UV-treated SiO₂ as a moisture barrier in EVOH, the encapsulation property could be enhanced by passivating the hydroxyl groups of EVOH. GO was added into the EVOH solution to increase the hydrogen bonding with the unreacted hydroxyl groups of EVOH. When 1 wt% GO (G1) was added, the highest barrier properties were evoked, and a tendency was observed whereby the barrier properties diminished as the concentration of GO increased (see Figure S6 and Table S1). This is why the addition of GO decreases the crystallinity of EVOH that
turn adversely affects its barrier properties. Therefore, it is expected that the barrier properties could be maximized by the addition of 1% GO into our EVOH/S5/UV sample, as discussed in the previous section. The images of the Ca test for each sample are shown in Figure 3a. As water penetrated, Ca was gradually oxidized and changed to transparent, thereby resulting in a decreased conductance.

As shown in Figure 3b and Table 2, the WVTR of EVOH/S5/UV/G1 surprisingly increased by more than 10 times compared to EVOH. The conductivity reached $3.34 \times 10^{-3}$, and the lag time was 6.92 h. The results of the EVOH/G1 sample also showed a similar trend with EVOH/S5/UV/G1. These results indicate that the increase of hydrogen bonding among the unreacted hydroxyl groups and GO lead to better barrier properties owing to the reduction of the reactive sites for water.

Table 2. Barrier Properties of Composite Films after the Incorporation of Fillers

| sample (in wt %) | WVTR (g/m² day) | lag time (h) |
|-----------------|----------------|--------------|
| EVOH            | $4.72 \times 10^{-2}$ | 0.74         |
| EVOH/S5/UV      | $1.55 \times 10^{-2}$ | 4.40         |
| EVOH/G1         | $3.66 \times 10^{-3}$ | 6.65         |
| EVOH/S5/UV/G1   | $3.34 \times 10^{-3}$ | 6.92         |

As shown in Figure 3b and Table 2, the WVTR of EVOH/S5/UV/G1 surprisingly increased by more than 10 times compared to EVOH. The conductivity reached $3.34 \times 10^{-3}$, and the lag time was 6.92 h. The results of the EVOH/G1 sample also showed a similar trend with EVOH/S5/UV/G1. These results indicate that the increase of hydrogen bonding among the unreacted hydroxyl groups and GO lead to better barrier properties owing to the reduction of the reactive sites for water.

Stability Test with PSCs. To examine the stability of the encapsulated PSCs, a reservoir test (direct contact with water on the encapsulated surface) was performed. It is a harsh condition because the halide perovskite materials are immediately degraded when it is in contact with water. As shown in Figure 4a, we successfully developed the simple encapsulation process for the utilization of our EVOH-based film on PSCs that consisted of the following steps: (i) fabrication of PSCs on the glass substrate, (ii) placement of prepared EVOH-based films on top of PSCs, and (iii) sealing of the outer parts of PSCs using the adhesive followed by a UV curing process (see Experimental Section). It should be noted that the conventional spin-coating method for the deposition of EVOH is not applicable owing to the use of a polar solvent that can dissolve the perovskite. The encapsulation process does not damage the PSCs, as assessed by their power conversion efficiencies of 17.86% (before) and 17.28% (after), as shown in Figure 4b. The distribution of efficiency for our PSCs in this study is shown in Figure S7. The reservoir test had already been performed by the time the cell was breaking. To maintain the temperature, the samples were maintained on the hot plate at 25 °C. Figure 4c shows the evaluation results of PSCs with and without encapsulation. PSCs without encapsulation were rapidly decomposed as soon as water was dropped, which resulted in the destruction of the PSCs. In the case of the PSCs with encapsulation, water penetration was successfully blocked. Approximately 86 and 61% of the PCEs were still retained compared to their initial values after 5 and 10 h from the onset of the reservoir test, respectively. It is worth noting that the results exhibited by the encapsulated PSCs, which retained their efficiency of 86% of their initial performance for 5 h, were much better than those where the efficiency was maintained at 95% of their initial performance for 60 s, as reported by Idigoras et al. This indicates the

![Figure 3](image-url)

Figure 3. (a) Oxidation of Ca samples encapsulated with composite films as a function of time. (b) Normalized conductance of EVOH after the incorporation of SiO2 and GO fillers. (c) Surface contact angle of composite films.
potential as the encapsulant of EVOH/S5/UV/G1 to protect the perovskite device requiring excellent barrier properties to moisture.

**CONCLUSIONS**

This study demonstrated the encapsulation of PSCs using EVOH with SiO₂ and GO fillers. We found that UV-treated SiO₂ increases the dispersibility in the precursor solution and the film of EVOH, which is caused by removing organic compounds on the surface of SiO₂. The well-dispersed SiO₂ in the EVOH matrix made the moisture-penetrating path more complicated, which leads to an enhanced WVTR result of $1.55 \times 10^{-2}$ g/m² day compared to the result without SiO₂. We further improved the moisture barrier property up to $3.34 \times 10^{-3}$ g/m² day of WVTR by the addition of GO in the EVOH matrix. It was found that GO decreases the unreacted hydroxyl groups in the EVOH matrix that reduces the attraction of water molecules. It is confirmed by the surface contact angle measurements of both EVOH/G1 and EVOH/S5/UV/G1 samples. Using the optimized EVOH film with fillers, perovskite solar cells were successfully encapsulated. The encapsulant process utilized the UV curing adhesive to attach our EVOH film on the device, and it did not show any damage to the performance of PSCs. To examine the moisture stability of encapsulated PSCs, we made the reservoir that is in direct contact with water on our encapsulated device. Surprisingly, the performance of our device retained 86% of the initial performance even after 5 h in the reservoir test, which is the harsh condition for PSCs. The unencapsulated device was immediately degraded after contacting with water. To the best of our knowledge, this is the first report that applies EVOH as the encapsulant on PSCs. We consider that it has the potential to pave the way toward a universal encapsulation method.

**EXPERIMENTAL SECTION**

**EVOH Precursor Fabrication.** The EVOH precursor solution was prepared to synthesize the thin films with spin-coating. EVOH (32% ethylene), SiO₂ (5–20 nm particle size), GO (sheets), and dimethylsulfoxide (DMSO) were purchased from Sigma-Aldrich Ltd. Specifically, EVOH (1.5 g) was dissolved in 10 mL of DMSO at 100 °C for 2 h with stirring. For the synthesis of EVOH/S5 samples, 5 wt % SiO₂ was dispersed in 10 mL of DMSO with stirring for 2 h and was subsequently sonicated for 2 h. Other concentrations of SiO₂ samples were prepared in the same method. Subsequently, EVOH/S5/UV sample, the same procedure was used as that used for EVOH/S5 with the exception that the UV treatment of SiO₂ lasted for 2 h with the use of a UV/ozone cleaner (ProCleaner, BIOFORCE) before usage. GO was prepared with the same method as that used for EVOH/S5 with the exception that the UV treatment of SiO₂ lasted for 2 h with the use of a UV/ozone cleaner (ProCleaner, BIOFORCE) before usage. GO was prepared with the same method as that used for EVOH/S5 at the concentrations of 1 (G1), 3 (G3), and 5 wt % (G5). The mixed solution of UV-treated SiO₂ and GO (EVOH/S5/UV/G1) was prepared by dispersing the GO first in DMSO followed by the execution of the same procedure used for EVOH/S5/UV. All solutions were prepared in a nitrogen-filled glovebox and were cooled to room temperature.

**Ca Detector Test.** The 200 nm Al electrode was deposited on a glass substrate (2.5 cm × 2.5 cm) using a thermal evaporator. After the Al deposition, the 300 nm Ca electrode
was deposited onto the glass via an evaporator. The EVOH precursor solution was spin-coated at 2000 rpm for 30 s onto the Ca cell. The deposited substrates were heated at 70 °C for 1 h. These processes were carried out three times after the precursor solution was cooled to room temperature for 30 min. The thickness of the thin films was ~100 nm. To evaluate the WVTR, the Ca detector coating EVOH was exposed at 25 °C at an 85% relative humidity (RH) (PR-1, ESPEC, Japan). The resistance changes of the Ca detector were measured with the use of a data acquisition system (DAQ, 2680A, FLUKE).

### Perovskite Solar Cell Fabrication. Materials.**

For the perovskite absorber material, 15 g formamidine acetate and 30 mL of H1 (57 wt % in water) were dissolved in 100 mL of ethanol at 0 °C for 2 h with stirring to obtain HC(NH2)2I. The HC(NH2)2I solution was dried using a rotary evaporator at 50 °C for 1 h. Following recrystallization from ethanol, white crystals were washed with diethyl ether. To synthesize CH3NH2Br, 11 mL of methylamine (33 wt % in water) and 10 mL of HBr (48 wt % in water) were mixed in 100 mL of ethanol at 0 °C for 2 h with stirring. The prepared HC(NH2)2I (or CH3NH2Br) and PbI2 (or PbBr2) solutions were dissolved at room temperature in a dimethylformamide (DMF)/dimethyl sulfoxide (DMSO) mixed solvent (1:0.25 (v/v)) to obtain a 1.2 M HC(NH2)2PbI3 (or CH3NH3PbBr3) solution. To prepare the absorption layer precursor solution, HC(NH2)2I and CH3NH2Br3 solutions were mixed with the specific volume ratio for (HC(NH2)2PbI3)0.85(CH3NH3PbBr3)0.15. Additionally, extra PbI2 (5 mol % to HC(NH2)2PbI3) was then dissolved in the synthesized (HC(NH2)2PbI3)0.85(CH3NH3PbBr3)0.15 solution by heating it at 60 °C for 30 min. The materials used in this work were purchased from Alfa Aesar, Lumtect, or Sigma-Aldrich and were not purified.

### Cell Fabrication.

To fabricate mesoporous solar cells for the experimental work, a compact TiO2 layer (c-TiO2) was deposited by spray pyrolysis (~50 nm) using 20 mM titanium disopropoxide bis(acetylacetonate) solution at 450 °C on the clean FTO glass (TEC8). After the deposition of the c-TiO2 layer, 150 mg/mL mesoporous TiO2 paste (m-TiO2, Dyesol 30 NR-D) in ethanol was spin-coated at 5000 rpm (acceleration of 2000 rpm/s) for 10 s. The deposited substrates were heated at 100 °C for 10 min followed by sintering at 500 °C for 30 min. The prepared perovskite solution was spun at 2000 rpm (acceleration of 200 rpm/s) and 6000 rpm (acceleration of 2000 rpm/s) for 10 and 30 s, respectively. The antisolvent chlorobenzene was drop-cast (110 mL) during the last 20 s of the second spin-coating step. The coated perovskite film was dried on a hot plate at 100 °C for 20 min. For the deposition of the hole transport layer, a solution containing 41.6 mg of spiro-OMeTAD, 7.5 μL of a 500 mg/mL lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) in acetonitrile, and 16.9 μL of 4-tert-butylpyridine (4-BP) in 0.5 mL of chlorobenzene was spin-coated on the perovskite/m-TiO2/FTO substrate at 2000 rpm (acceleration of 1200 rpm). All films on m-TiO2 were prepared in a nitrogen-filled glove box. Finally, 100 nm of gold was deposited by thermal evaporation.

### Stability Test.

The EVOH precursor solution without or with fillers was poured into the Si mold and was heated at 70 °C on the hot plate overnight. The residue solvents of the fabricated film were removed using a vacuum pump. The EVOH film was then attached to the top of the PSCs using the Norland optical adhesive (NOA, NOA 63, Norland). It was cured with UV light for 60 s. Water was dropped onto the encapsulated PSCs, and it was placed on the hot plate at 25 °C by the time the PSCs were breaking.

### Characterization.

The morphology of the EVOH films was measured with the use of a field emission scanning electron microscope (FESEM, JEM-2100F, JEOL Ltd.). The dispersion of the fillers was measured using energy-dispersive X-ray spectroscopy (EDS, Quanta 3D FEG, FEI) and a zeta potential analyzer (ELS-1000ZS, Otsuka Electronics Ltd.). The water contact angle was measured using the dynamic contact angle equipment (DCA, Phoenix 300, SEO). The analysis of transmittance was performed with the use of the UV–vis spectrophotometer (V-570, JASCO). The current density–voltage measurements were measured with a solar cell testing system (LAB 200, McScience, Korea), which used simulated solar light (AM 1.5 G) with an intensity of 100 mW cm–2. Light was generated with a K3000 model (McScience) and was recorded using an ADCMT 6244 source measurement unit. After masking them with a 0.02 cm2 aperture, the solar cells were measured at a scan rate of 1.2 V/s. All the results were obtained under ambient conditions. The illumination intensity was calibrated using a standard Si reference cell (K801S-K067, McScience, Korea).

### ASSOCIATED CONTENT

 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00350.

Zeta potential analysis of EVOH precursor solution after the dispersion of SiO2 fillers, transmittance analysis of EVOH after the incorporation of SiO2 fillers, normalized conductance based on the calculated values of WVTR, conductance changes of EVOH manifested following the addition of GO, WVTR calculation outcomes for GO as a function of concentration, and efficiency distribution histogram of perovskite solar cells (PDF)

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**Notes**

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

This research was supported by the Technology Development Program to Solve Climate Changes of the National Research Foundation (NRF) funded by the Ministry of Science and ICT(no. 2017M1A2A2048905) and the New & Renewable Energy of the Korea Institute of Energy Technology Evaluation and Planning (KETEP). Grant funded by the Ministry of Trade, Industry and Energy (MOTIE) (grant number 20173010012970).
ABBREVIATIONS

DMF, dimethylformamide; DMSO, dimethylsulfoxide; EVOH, poly(vinyl alcohol-co-ethylene); FTO, fluorine-doped tin oxide; GO, graphene oxide; HI, hydroiodic acid; PDMS, poly(dimethylsiloxane); PSCs, perovskite solar cells; PMMA, poly(methyl methacrylate); SEM, scanning electron microscopy; SiO₂, silicon dioxide; TiO₂, titanium dioxide; UV, ultraviolet; rpm, revolutions per minute; WVTR, water vapor transmission ratio

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