Moisture-driven phase transition for improved perovskite solar cells with reduced trap-state density

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ABSTRACT

We report a mechanistic understanding of a moisture-driven intermediate-phase transition that improves the quality of perovskite thin films based on a lead-acetate precursor, improving the power-conversion efficiency. We clarify the composition of the intermediate phase and attribute the transition of this phase to the hygroscopic nature of the organic product, i.e., methylammonium acetate. Thermal annealing aids in the coarsening of the grains. These decoupled processes result in better crystal formation with a lower spatial and energetic distribution of traps. Thermal annealing of the films without exposure to air results in a faster intermediate-phase transition and grain coarsening, which occur simultaneously, leading to disorder in the films and a higher deep trap-state density. Our results indicate the need for a humid environment for the growth of high-quality perovskite films and provide insight into intermediate-phase dissociation and conversion kinetics. Thus, they are useful for the large-scale production of efficient solution-processed perovskite solar cells.

1 Introduction

Owing to their low cost and ease of processing, as well as the recent breakthroughs in their photovoltaic performance, organic–inorganic trihalide perovskite devices have attracted considerable attention [1, 2]. The facile formation and low-temperature crystallization of perovskite films have led to several different filmdeposition routes, growth techniques, and device architectures [3–6]. It is crucial to control the film growth and processing conditions, as they determine the phase composition and quality of the perovskite layer, which dictate the charge-carrier generation and transport in devices [7–10]. In a typical single-step coating process, precursors are dissolved in a solvent, and the formation of the precursor intermediate is followed by conversion and grain coarsening upon thermal annealing [11–14]. The solvent, lead salt, and

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annealing conditions determine the precursor intermediate structure, conversion, and growth kinetics [15, 16]. Among the different lead salts used, lead acetate (Pb(Ac)₂) is an effective precursor for forming smooth and uniform perovskite films [17, 18] and has potential for large-area solar cells and modules [19]. Hence, it is critical to investigate the formation of the intermediate phase and control its transition in Pb(Ac)₂-based precursors for realizing optimal growth conditions. Insights into the conversion and growth conditions are necessary for obtaining the desired film morphology with a low trap density for the lowcost and scalable production of perovskite solar cells.

Controlled moisture is beneficial for the growth of perovskite thin films [20-27]. Although film deposition requires an inert atmosphere, films annealed in a controlled-humidity environment have a superior optoelectronic quality to those annealed in an inert atmosphere. You et al. first reported the beneficial effects of moisture-induced growth for high-performance perovskite solar cells [20], observing improvements in the film morphology (large grain size, less pinholes) and carrier lifetime for films annealed under controlledhumidity conditions compared with films annealed in dry air or nitrogen. Snaith et al. also studied the role of air annealing and observed a higher photoluminescence quantum efficiency (PLQE) and carrier lifetime for films annealed in air compared with films annealed in nitrogen [28]. The enhanced PLQE and lifetime were attributed to the suppressed energetic disorder for the air-annealed films. The lower energetic disorder was attributed to the solvation of methylammonium iodide (MAI) in the moisture and the self-healing of the perovskite lattice [21]. While other studies have achieved similar improved optoelectronic properties by the ambient treatment of films, the effect of moisture on the growth mechanism is still not completely understood [29-31]. Therefore, for obtaining high-quality perovskite thin films with enhanced optoelectronic performance, it is important to understand the moisture-induced phase transitions.

Herein, we report a mechanistic understanding of the formation of perovskite films with a reduced trapstate density by the exposure of the deposited films to air before thermal annealing. Unlike previous reports, we show that the ambient-air exposure, rather than the annealing, plays a key role in the dissociation and the conversion of the intermediate phase to the perovskite phase. We clarify the composition of the intermediate phase and attribute the transition of this phase to the moisture-induced decomposition of the organic product, i.e., methylammonium acetate (MAAc). Upon thermal annealing, the ambient exposed films were transformed into compact perovskite films with large crystalline domains and a deep trap-state density one order of magnitude lower than those of films directly annealed in an inert atmosphere. Such moisture-assisted conversion of the active-layer films increased the photovoltaic efficiency by >50% and vielded power-conversion efficiencies (PCEs) of >13%. We propose the moisture-driven phase-transition mechanism as a new strategy for preparing efficient planar perovskite solar cells.

2 Experimental

2.1 Chemicals and reagents

MAI was purchased from Lumtec and used as-received. Lead acetate trihydrate $Pb(Ac)_2 \cdot 3H_2O$ and $PbCl_2$ were purchased from Sigma–Aldrich. $Pb(Ac)_2 \cdot 3H_2O$ was dehydrated for 48 h (at 80 °C) and stored in N₂ for further use. MAAc was synthesized by passing methyl amine gas through a NaOH column, followed by a reaction with 5 mM acetic acid in toluene. After the salt formation, the excess toluene was decanted, dried in vacuum, and stored in argon.

2.2 Device fabrication

Pb(Ac)₂ (0.8 M), PbCl₂ (0.1 M), and MAI (2.4 M) were mixed in a dimethylformamide solvent. The solution was stirred at 70 °C for 10 min and cooled to room temperature before use. Cleaned indium tin oxide (ITO) glass slides were treated with ultraviolet (UV)– ozone for 15 min and then coated with poly(3,4ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS) at 4,000 revolutions per minute (rpm) for 30 s. The PEDOT:PSS-coated substrates were annealed at 140 °C for 20 min and transferred into a dry box (H₂O and O₂ < 1 ppm). The perovskite precursor solution was spin-coated onto the substrates at different speeds to obtain the desired thicknesses. Samples 1 and 3 were left in the glove box, and Samples 2 and 4 were removed from the glove box and exposed to the ambient environment for 60 min. Samples 3 and 4 were annealed at 90 °C for 5 min in the glove box before $PC_{61}BM$ spin coating, followed by additional thermal annealing at 80 °C for 30 min. A rhodamine 101 (0.5 mg·mL⁻¹) solution in isopropyl alcohol was spincoated at 6,000 rpm for 30 s to form a 5-nm interlayer. The films were then loaded into a thermal evaporator for the evaporation of 80-nm silver at a base pressure of 10^{-6} mbar.

2.3 Device characterization

The current-voltage characteristics under illumination and in the dark were measured using a sourcemeter (Keithley 2400), and 100-mW·cm⁻² AM1.5G illumination was provided by a Newport solar simulator (Oriel LCS-100) calibrated with a silicon diode (KG-5 filter). A voltage sweep was performed in the reverse direction from 1.2 to -0.2 V with a scan rate of 0.2 V·s⁻¹ and a delay time of 50 ms. The external quantum efficiency (EQE) spectra were measured using an Enli Technology QE-R system. Mott–Schottky (C^{-2} vs. V) and capacitance-frequency measurements were performed using a potentiostat (VMP3, BioLogic) under dark conditions with an alternating-current amplitude of 30 mV. For the *C*–*f* measurements, frequency sweeps from 1 MHz to 0.1 Hz were performed with no external direct-current bias. The trap density of states (N_t) was calculated using the equation $N_{\rm t}(E_{\omega}) = \frac{V_{\rm bi} dC\omega}{qW d\omega kT}$,

where *C* is the measured capacitance, ω is the angular frequency, *q* is the elementary charge, *k* is the Boltzmann constant, and *T* is the temperature. *V*_{bi} and *W* are the built-in potential and depletion width, respectively, and were calculated according to the slope and intercept, respectively, of the linear region in the Mott–Schottky plot. The recombination lifetimes were plotted using transient photovoltage (TPV) spectroscopy. Here, the devices were kept at open circuit using the 1-M Ω input of an oscilloscope, and a small perturbation (~3.5-ns pulse) was applied to the device using a nanosecond laser (SRS NL-100). The open-circuit voltage was varied by placing neutral-density filters in front of a steady-state light source. The TPV was averaged for 20 pulses and recorded

using a Keysight MSOX4154A oscilloscope.

2.4 Film characterization

Films for X-ray diffraction (XRD), UV-visible (UV-vis) absorption, and Kelvin probe force microscopy (KPFM) were deposited on PEDOT:PSS-coated ITO glass slides using the same procedure that was used for the device fabrication. The XRD patterns were recorded using a diffractometer (Rigaku) with Cu K α radiation (1.5405 Å). The UV-vis absorption spectra were measured using a spectrophotometer (Cary 60, Agilent Technologies). The KPFM images were obtained using a scanning probe microscope (Keysight 5500) in the single-pass mode with a probe (PtSi-NCH, Nanosensors, 300 KHz). The photoluminescence (PL) spectra for the perovskite films were measured using a spectrometer (iHR320, HORIBA) equipped with a charge-coupled device (Synapse), and a 532-nm continuous-wave laser was used as the excitation source. For time-resolved PL (TRPL) measurements, the samples were excited with the second-harmonic generation of a femtosecond laser (Hurricane, Spectra-Physics; centered at 805 nm, 150-fs full width at half maximum (FWHM) pulse duration and 1-kHz repetition) after the laser passed through 400-nm bandpass and 750-nm short-pass optical filters. The PL signal was then spectrally filtered by 473- and 650-nm long-pass optical filters and detected using a Hamamatsu photomultiplier tube (H10721-20 photosensor) and a Tektronix oscilloscope (TDS 3052). The perovskite films for the PL measurements were coated directly on the glass, without a hole-transport layer, at 4,000 rpm for 60 s. The coating parameters and air-exposure times were the same as those used for the solar-cell fabrication. Fourier transform infrared (FTIR) spectra were recorded using an FTIR spectrometer (Nicolet iS50) in the single attenuated total reflection (Ge-sATR) mode.

3 Results and discussion

The chemical reaction between MAI and $Pb(Ac)_2$ is expressed as follows

$$3CH_{3}NH_{3}I + Pb(CH_{3}COO)_{2} \rightarrow CH_{3}NH_{3}PbI_{3}$$

+2CH_{3}NH_{3}(CH_{3}COO) (1)

The reaction product, MAAc, has a low sublimation temperature in a nitrogen environment (~88.5 °C) and can be removed by low-temperature annealing (≤ 100 °C). Perovskite films derived from Pb(Ac)₂ exhibit smooth and uniform film coverage, which is attributed to the facile removal of MAAc [17, 18]. The addition of non-stoichiometric lead-chloride salt to this mixture enhances the grain growth and yields films with fewer defects [19, 32]. An inverted planar device architecture was adopted to fabricate solar cells with a p-i-n architecture, as shown in the inset of Fig. 1(a). Care was taken to ensure that all the precursors were completely anhydrous. They were weighed, dissolved, and coated in an inert atmosphere to eliminate the effects of absorbed moisture. Prior to further discussion, we define the four samples investigated in this study: Sample 1, as-deposited films; Sample 2, films exposed to air (relative humidity $40\% \pm 5\%$) for 60 min; Sample 3, films annealed in glove box at 90 °C for 5 min; and Sample 4, film exposed to air for 60 min and then thermally annealed in a glove box at 90 °C for 5 min. Photographs of these four samples are shown in Fig. S1 (in the Electronic Supplementary Material (ESM)).

Figure 1(a) shows the current density–voltage (J-V)characteristics of Samples 3 and 4 under AM 1.5 illumination. The unannealed devices exhibited very low performance; thus, their *J*–*V* curves are not plotted. The distribution of the device performances was Gaussian, with mean efficiencies of ~7.5% and ~12.6% for the Sample 3 and 4 devices, respectively (Fig. S3 in the ESM). Different scan rates and directions resulted in a negligible variation in the *I–V* performance (Figs. S4 and S5 and Tables S2 and S3 in the ESM). Sample 3 exhibited a PCE of 8.66% with an open-circuit voltage (V_{oc}) of 0.84 V, a short-circuit current density (J_{sc}) of 17.56 mA·cm⁻², and fill factor (FF) of 58.87%. For Sample 4, the PCE increased to 13.09%, with $V_{\rm oc}$ of 0.95 V, J_{sc} of 18.68 mA·cm⁻², and FF of 73.74%. The stabilized *I-V* characteristics indicate a stable performance of 12.77% (Fig. S6 in the ESM). The enhanced efficiency of Sample 4 is attributed to the higher $V_{\rm oc}$ and FF. Figure 1(b) shows the EQEs of Samples 3 and 4. The $J_{\rm sc}$ obtained from the integration of the EQE spectra with the AM1.5G solar spectrum agrees with the J_{sc} obtained from the J-V curves, with less than 5% mismatch. Additional devices with different active-layer thicknesses were fabricated to evaluate



Figure 1 (a) J-V curves for Samples 3 and 4 under AM 1.5G illumination. Inset shows the device configuration. (b) EQE spectra for Samples 3 and 4. (c) Absorption and (d) XRD spectra for Samples 1 and 2 and the MAPbI₃ standard.

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the photovoltaic performance (Fig. S7 in the ESM). Regardless of the active-layer thickness, the PCE was always higher for Sample 4 owing to the higher FF and V_{∞} . Thus, we infer that the charge transport along the thickness of the device in Sample 4 was superior to that in Sample 3.

Figure 1(c) shows the absorption spectra for Samples 1 and 2 with reference to the perovskite film. Sample 1 shows the characteristic peak of the intermediate phase (vide infra) at 460 nm. After air exposure (Sample 2), the absorbance increased in the range of 400-700 nm, and a sharper onset of the absorption edge developed at 760 nm, indicating a partial phase transition to the perovskite phase. Figure 1(d) shows the XRD patterns for Samples 1 and 2. Because of the amorphous nature the intermediate phase of Sample 1, we only observed two weak peaks below 10°, which are attributed to the precursor intermediate phase. The sharp peaks at 13.94°, 14.24°, 27.78°, and 28.50° are attributed to the (002), (110), (004), and (220) peaks of perovskite, respectively. After the air exposure (Sample 2), the intermediate-phase peaks and the preferred orientation along the perovskite (110) direction were suppressed.

After analyzing the films before the thermal annealing (Samples 1 and 2), we investigated the annealed films (Samples 3 and 4). In Fig. 2(a), both films show a strong preferred orientation along the (110) direction, with second-, third-, and fourth-order reflections. While Sample 3 also exhibited peaks along the (310) and (224) directions at 32.30° and 41.08°, these reflections were substantially weaker for the Sample 4 films. The preferential texture towards the (110) and (220) directions is beneficial for enhanced charge transport, according to recent reports [8, 33]. In our study, the ratio of the intensity of (220) to (310) increased more than threefold for Sample 4 (7.09) compared with Sample 3 (2.27). The FWHM of the (110) peak decreased from 0.186° for Sample 3 to 0.167° for Sample 4, indicating the larger crystallite size for the annealed films exposed to air. TRPL and steady-state PL spectroscopy were performed to evaluate the charge-carrier density and lifetime of the Samples 3 and 4 films, as shown in Fig. 2(b). The short carrier lifetimes measured from the bi-exponential fit of the TRPL spectra for Samples 3 and 4 were 31.41 and 80.33 ns, respectively. The longer lifetime and higher PL intensity of Sample 4 indicate that the air



Figure 2 (a) XRD and (b) TRPL spectra for Samples 3 and 4. Inset shows steady state PL. (c) N_t vs. E_{ω} of Samples 3 and 4 devices. (d) KPFM images of Samples 3 and 4 (scale bar: 1 µm). (e) Line profiles and (f) counts vs. surface potential obtained from KPFM images of Sample 3 and 4.

exposure yielded perovskite films with a lower trap density and enhanced band-to-band radiative recombination, which are possibly the reasons for the higher V_{oc} of solar cells processed with air exposure [34].

Impedance spectroscopy is used to investigate the distribution and density of trap states in perovskite solar cells [35, 36]. In the plot of N_t vs. E_{ω} shown in Fig. 2(c), at a low E_{ω} (<0.35 eV), the trap densities are in the range of 10¹⁷-10¹⁸ m³·eV⁻¹ for the Sample 3 devices. The trap densities in the same energy region were 2-5 times lower for the Sample 4 devices. The trap densities in this energy region correspond to shallow trap states near the valence band of perovskite. However, at a larger E_{ω} (i.e., deep trap states) the trap densities of Sample 4 were one order of magnitude lower than those of Sample 3. Thus air exposure reduced the trap density of states, with greater suppression of the deep trap states. To evaluate the local electronic properties of the perovskite films, frequency-modulation KPFM (FM-KPFM) was performed. Figure 2(d) shows FM-KPFM images of the surfaces of Samples 3 and 4, and topographic images are shown in Fig. S9 in the ESM. A lower surface potential was observed at certain grain boundaries, similar to the observations of Green et al., which is attributed to the downward band bending at the defective interfaces [37]. Such variations were also observed in the grain interiors of Sample 3 and are attributed to intra-grain defects. The root-mean-square (RMS) variation of the surface potential for Sample 3 was measured as 52.7 meV. Sample 4 exhibited a more uniform surface potential, with an RMS variation of 35.2 meV. The potential variations along the line profiles for Samples 3 and 4 are plotted in Fig. 2(e). The profiles of Sample 3 exhibit several valleys, with potential drops ranging from 100 to 150 meV. These potential variations functioned as energetic barriers for the charge transport and increased the trap-assisted recombination. The surface-potential variations along the line profiles were smaller and fewer for Sample 4 than for Sample 3, indicating the lower amount of defective grains and grain boundaries in Sample 4. The surface-potential distributions for the KPFM images are plotted in Fig. 2(f). The average surface potential of Sample 3 was ~100 meV lower than that of Sample 4. However, the opposite trend of the observed V_{oc} indicates that the higher defect densities and potential barriers were due to the reduction in V_{oc} . The large variation in the surface potential of Sample 3 is attributed to the higher distribution of defects with varied surface potential. Hence, the ambient exposure of the perovskite films before the annealing led to the formation of textured films with a suppressed trap density.

To identify the chemical changes with air exposure, FTIR spectroscopy was performed, as shown in Fig. 3(a). The FTIR spectra for MAI, perovskite (CH₃NH₃PbI₃), and MAAc are plotted for reference. No peaks unique to O-H vibrations in the 3,400–3,500 cm⁻¹ region are observed for any of the films, which indicates the negligible formation of hydrate phases [23]. In the FTIR spectrum for the Sample 1 film, the peak at 1,015 cm⁻¹ (characteristic of CH₃ rocking) and those at 1,410 and 1,338 cm⁻¹ (characteristic of the CH₃ bending vibrations of the acetate functional group) confirm the presence of MAAc in the film. The characteristic vibration modes of MAAc are assigned as shown in Table S2 in the ESM and illustrated in Fig. S2 in the ESM. Additionally, the characteristic peaks of MAI in the spectra for the as-deposited films-at 1,404, 1,248, and 990 cm⁻¹—correspond to the CH₃ bending, NH₃ rocking, and C-N stretching vibrations of MAI, respectively. Hence, the coated films prepared without thermal annealing and air exposure comprised both MAAc and MAI. The FTIR spectrum for Sample 2 shows that the MAI and MAAc peaks diminished in intensity and that new peaks developed at 911, 960, and 1,467 cm⁻¹ which correspond to the CH₃ rocking, C–N stretching, and NH₃ bending vibrations of the CH₃NH₃PbI₃ phase, respectively. The disappearance of the MAI characteristic peaks and the appearance of MAPbI₃ characteristic peaks are attributed to the enhanced ionic diffusion of MAI due to the solvation in moisture under exposure to air [23, 38]. After annealing, the characteristic peaks of MAI and MAAc disappeared, indicating a pure MAPbI₃ phase. Therefore, we conclude that the exposure to air resulted in two important physiochemical changes: the removal of the acetate functional group in the film and the formation of the perovskite phase.

To confirm the chemical composition of the intermediate phase, FTIR and XRD were performed on the



Figure 3 (a) FTIR spectra for the Sample 1 and 2 films and MAAc, MAI, MAPbI₃. (b) UV–vis absorption spectra and (c) XRD of Sample 1 and films coated from the two mixture solutions of PbI₂:MAI:MAAc (1:1:2) and PbI₂:MAAc (1:2).

Sample 1 films. According to the right-hand side of Eq. (1), we also prepared films derived from PbI₂:MAI: MAAc (1:1:2) and PbI₂:MAAc (1:2) mixtures, for comparison. Interestingly, the film derived from the PbI₂:MAI:MAAc (1:1:2) mixture exhibited the same excitonic absorption peak at 460 nm as Sample 1, as shown in Fig. 3(b), as well as the same XRD peaks, as shown in Fig. 3(c). The strong excitonic absorption and weak intermediate-phase peaks suggest that the PbI₂-MAI-MAAc intermediate was amorphous. The formation of this amorphous phase during the spincoating process was critical for the formation of a homogenous and uniform film.

Because the sublimation or dissociation of MAAc is crucial for the intermediate-to-perovskite phase transition, we monitored the weight loss of MAAc in inert and ambient atmospheres. Figure 4(a) shows the thermogravimetric analysis (TGA) of MAAc measured in nitrogen (N_2) and in air. The decomposition temperatures for 5% weight loss in N_2 and air were 88.5

and 66.7 °C, respectively, indicating that the MAAc decomposed significantly faster in the ambient atmosphere. The MAAc was extremely hygroscopic. Within a few minutes of air exposure, it was liquefied. The fact that the MAAc dissociated faster at lower temperatures in air is attributed to the dissociation of the MAAc into methyl amine gas and acetic acid, both of which are volatile and easily evaporated from the film. Figure 4(b) shows the XRD patterns of Sample 1 films with different air-exposure durations. As the duration increased, two critical phase changes were observed. First, the intermediate-phase peak at 9.76° diminished. Second, the preferred orientation changed from (002) to (110). The ratio of the peak intensities of (110) to (002) increased from 0.844 to 1.16 after 60 min of air exposure. Similarly, the intensity ratio of the (110) peak to the intermediate phase at 9.76° changed from 4.83 to 10.12. The changes in the absorption and the diminished XRD peaks indicate that the formation of the perovskite



Figure 4 (a) TGA of MAAc under N_2 and air conditions. (b) XRD spectra evolution of Sample 1 films with different time of air exposure.

phase was enhanced in air, without the need for thermal annealing. This conclusion accords with that of Eperon et al., who observed faster conversion after air annealing for perovskite films coated with PbCl₂based precursors [14].

The XRD, absorption, and FTIR results indicate that the moisture in air served two purposes: (i) It aided in the removal of the MAAc, and (ii) it allowed the formation of perovskite by dissolving the MAI and increasing its ionic diffusion in the film to react with lead iodide in the intermediate phase. The crystallization kinetics of the perovskite phase in films coated with excess MAI depend on the removal of the organic byproduct formed by the reaction between the organic and lead salt. The aforementioned results suggest that in the as-deposited films, the nuclei of the perovskite phase were embedded in an amorphous intermediate precursor-PbI2-MAI-MAAc—as shown in Fig. 5 and indicated by Eq. (2). Upon thermal annealing, the predominant intermediate phase was converted into the perovskite phase:

$$MAI + Pb(Ac)_{2} \rightarrow (PbI_{2}-MAI-MAAc)_{n} + (CH_{3}NH_{3}PbI_{3})_{1-n} \Delta CH_{3}NH_{3}PbI_{3}$$
(2)

Upon ambient exposure, moisture caused the dissociation of the hygroscopic MAAc, leading to the conversion of a larger fraction of the intermediate phase into the final perovskite phase. The thermal



Figure 5 Schematic showing the conversion and grain growth mechanism in films annealed with and without air exposure.

annealing of the air-exposed films led to the complete conversion of the residual intermediate phase and caused grain coarsening. While the thermal annealing of the Sample 1 films can achieve the same conversion, the MAAc removal and grain coarsening for the airexposed films were significantly faster and occurred simultaneously, yielding uneven grain growth and a higher density of defects in the film. The exposure to air was an intermediate step that slowed the MAAc sublimation and decoupled the conversion from the coarsening process. In this scenario, the atoms had more time to relax and form crystalline and oriented perovskite seeds. Upon the thermal annealing of the air-exposed films, grain growth occurred, yielding films with lower defect density, which is critical for efficient photovoltaic devices.

4 Conclusions

We demonstrated the improved photovoltaic performance of air-exposed solar cells, which originated from the longer charge-carrier lifetime and lower spatial distribution of trap states. We investigated the composition of the precursor intermediate phase and showed that the air exposure caused the preferential removal of MAAc and aided the formation of the perovskite phase. This decoupled intermediate-phase conversion led to the formation of high-quality perovskite films upon thermal annealing. Our study reveals the critical benefits of moisture-driven phase transition for growing perovskite films for efficient optoelectronic devices.

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spectra and AFM topography) is available in the online version of this article at http://dx.doi.org/10.1007/s12274-017-1515-5.

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