

Manipulating Crystallization of Organolead Mixed-Halide Thin Films in Antisolvent Baths for Wide-Bandgap Perovskite Solar Cells

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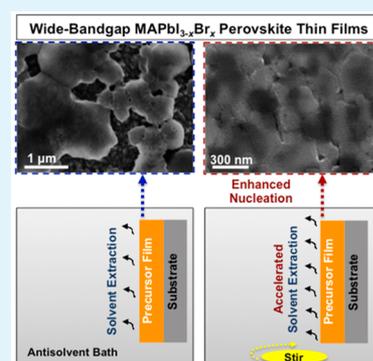
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Supporting Information

ABSTRACT: Wide-bandgap perovskite solar cells (PSCs) based on organolead (I, Br)-mixed halide perovskites (e.g., MAPbI₂Br and MAPbIBr₂ perovskite with bandgaps of 1.77 and 2.05 eV, respectively) are considered as promising low-cost alternatives for application in tandem or multijunction photovoltaics (PVs). Here, we demonstrate that manipulating the crystallization behavior of (I, Br)-mixed halide perovskites in antisolvent bath is critical for the formation of smooth, dense thin films of these perovskites. Since the growth of perovskite grains from a precursor solution tends to be more rapid with increasing Br content, further enhancement in the nucleation rate becomes necessary for the effective decoupling of the nucleation and the crystal-growth stages in Br-rich perovskites. This is enabled by introducing simple stirring during antisolvent-bathing, which induces enhanced advection transport of the extracted precursor-solvent into the bath environment. Consequently, wide-bandgap planar PSCs fabricated using these high quality mixed-halide perovskite thin films, Br-rich MAPbIBr₂, in particular, show enhanced PV performance.

KEYWORDS: antisolvent–solvent extraction, nucleation, grain growth, solar cells, wide-bandgap perovskite



1. INTRODUCTION

Perovskite solar cells (PSCs) have attracted a great deal of interest due to their low-temperature solution-processability and high power conversion efficiencies (PCEs).^{1–8} While the lower-bandgap (~1.5 eV) organolead triiodide perovskite, CH₃NH₃PbI₃ (MAPbI₃), absorber has been studied extensively for the purpose of realizing the highest PCEs in single-junction solar cells,^{1–8} (I, Br)-mixed halide perovskites with wider bandgaps show promise for application in tandem or multijunction solar cells.^{9–13} Among these mixed halide perovskites, CH₃NH₃PbI₂Br (MAPbI₂Br) and CH₃NH₃PbIBr₂ (MAPbIBr₂) perovskites, with bandgaps of 1.77 and 2.05 eV, respectively,¹⁴ are particularly interesting compositions that are near-ideal for application as the top-cell absorber materials in tandem and triple-junction solar cells.^{9–13,15,16}

Since the morphology of the perovskite absorber thin film is one of the most critical factors that influence the overall PCE of PSCs,^{17–19} unprecedented amount of effort has been devoted toward controlling perovskite crystallization for improved film uniformity, and gaining better understanding of these processes.^{1–4} In the case of the MAPbI₃, it has been shown that inducing rapid nucleation of perovskite crystals at room temperature through antisolvent treatments, which enables

better decoupling of the nucleation and the growth stages, is an effective way to achieve large-area, pinhole-free MAPbI₃ films, and it is proving to be a promising processing protocol.^{20–26} In a recent report, we studied the room-temperature crystallization behavior of MAPbI₃ perovskite in antisolvent baths,²² and showed that uniform precipitation of MAPbI₃ in the antisolvent environment, coupled with the ‘antisolvent–solvent extraction’ process, results in the formation of ultrasoft, dense perovskite thin films.²² The enhanced nucleation of the solid perovskite over the entire substrate area upon contact of the precursor film with the antisolvent in the bath is crucial for achieving large-area uniformity in these MAPbI₃ perovskite thin films.^{25,26} This is, to some extent, similar to what occurs in the “solvent-dripping” process reported by Jeon et al.²³ and Xiao et al.²¹ While the solution crystallization behavior has been studied extensively, it is almost exclusively limited to MAPbI₃ perovskite thin films, with only a handful of reports dealing with (I, Br)-mixed halide perovskite thin films.^{10,12,13} It has been observed by others^{27,28} and by us (Figure S1 in

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Supporting Information (SI)) that with the increase in the Br content, the perovskite grains tend to grow in an exaggerated fashion from the precursor solution, which results in the formation of incomplete coverage and pinholes. While a number of factors (ions, bond energies, solvation, etc.) may be responsible for this, the most basic explanation is that the growth of perovskite crystals is mainly driven by the diffusion of the ions to the as-formed nuclei.²⁹ Since Br^- ($r = 1.96 \text{ \AA}$)²⁸ has a smaller ionic radius than I^- ($r = 2.20 \text{ \AA}$),³⁰ the diffusivity of Br^- (D_{Br^-}) in the solvent is expected to be higher than I^- (D_{I^-}) according to the Stokes–Einstein equation, $D = \frac{k_{\text{B}}T}{6\pi\eta r}$, where k_{B} is the Boltzmann's constant, T is the absolute temperature, η is the dynamic viscosity of the solution, and r is ionic radius.³¹ Thus, faster overall growth kinetics of perovskite grains in the Br-rich precursor solution, as compared with the I-rich precursor solution, are expected. In order to enhance the uniformity of the (I, Br)-mixed halide perovskite thin films, it is necessary to accelerate further the nucleation rate for better decoupling of the nucleation and the grain growth stages. Since antisolvent–solvent extraction is one of the important factors that induces supersaturation and nucleation in this method,²² the nucleation rate is expected to be enhanced by stirring the antisolvent bath. Such continuous mechanical perturbation enables rapid advection transport of extracted precursor–solvent, which maximizes the concentration gradient across the precursor–film/antisolvent interface and promotes rapid mixing of the precursor–solvent into antisolvent in the bath. Here we show that stirring is particularly important in the case of Br-rich perovskites, as compared to I-rich perovskites, in obtaining dense, pinhole-free, thin films. Planar PSCs incorporating mixed-halide perovskite thin films of Br-rich composition ($\text{MAPbI}_{3-x}\text{Br}_x$), in particular, synthesized using this accelerated “antisolvent–solvent extraction” method, show enhanced PV performance.

2. EXPERIMENTAL SECTION

2.1. Crystallization of Mixed-Halide Perovskite Thin Films. A solution (30 wt %) of PbI_2 (Alfa-Aesar, Ward Hill, MA) and MABr (molar ratio 1:1) in *n*-methyl-2-pyrrolidone (NMP) was spin-coated onto compact- TiO_2 -coated FTO glass substrates (Hartford Glass Co., Hartford City, IN), which was immediately followed by immersing the film in a bath (1000 mL) of anhydrous diethyl ether (DEE; Fisher Scientific, Fair Lawn, NJ) antisolvent at room temperature. In order to introduce advection in the antisolvent bath, magnetic stirring (400 rpm) was used. Within 30 s, MAPbI_2Br perovskite thin film was formed. The substrate was then taken out of the bath and dried rapidly under blowing nitrogen gas. For the preparation of MAPbIBr_2 thin films, a precursor solution (30 wt %) of PbBr_2 (Alfa-Aesar, Ward Hill, MA) and MAI (molar ratio 1:1) was used and dipped in stirred DEE antisolvent bath for 15 s.

2.2. Materials Characterization. X-ray diffraction (XRD) was performed on a X-ray diffractometer (D8-Advance, Bruker, Germany) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at step size/time $0.02^\circ/1 \text{ s}$ conditions. Surface morphology of the films and cross sections (fractured) of the whole solar cells were observed in a scanning electron microscope (SEM; LEO 1530VP, Carl Zeiss, Germany). The local roughness of the perovskite thin films were characterized using an atomic force microscope (AFM; 5500, Agilent, Santa Clara, CA) operated in noncontact mode. Optical spectroscopy (transmission, reflection, absorption) was conducted on a UV-vis-NIR spectrophotometer equipped with diffuse reflectance accessories (Cary 6000i, Agilent Technologies, Englewood, CO) with 10 nm step size. Transmission electron microscopy (TEM) was used to characterize cross sections of the whole PSCs. Note that this particular PSC has a thinner HTM layer compared to most of the other PSCs fabricated in

this study. TEM specimens from specific locations on the cross sections were prepared by focused ion beam (FIB; Helios 600, FEI, Hillsboro, OR) and extracted by in situ lift-out. These specimens were examined using a TEM (2100F, JEOL, Japan) operated at 200 kV accelerating voltage. Fourier-transform infrared (FTIR) spectra are recorded on a spectrometer (4100, Jasco Instruments, Easton, MD). The powder sample used for FTIR was scratched from a relatively thick spin-coated films (30 wt % precursor solution, 2000 rpm, 10 s).

2.3. Device Fabrication and Characterization. For the fabrication of the PSCs, a compact- TiO_2 electron selective layer (ESL) was first deposited on prepatterned FTO-coated glass by spray pyrolysis at 450°C . The perovskite layer was then optimally deposited based on the procedure described above, followed by spin-coating a hole-transporting material (HTM) solution, which consisted of 80 mg 2,2',7,7'-tetrakis(*N,N*-dip-methoxyphenylamine)-9,9'-spirobifluorene (Spiro-MeOTAD), 30 μL bis(trifluoromethane) sulfonimide lithium salt stock solution (500 mg Li-TFSI in 1 mL acetonitrile), 30 μL of 4-*tert*-butylpyridine (TBP), and 1 mL of chlorobenzene solvent. The HTM spin-coating process was performed in a dry-air atmosphere with humidity < 10%. Finally, a $\sim 150 \text{ nm}$ Ag layer was deposited using thermal evaporator and a shadow mask. The incident photon-to-current efficiency (IPCE) or external quantum efficiency (EQE) spectra were recorded at a chopping frequency of 5 Hz in AC mode on a solar cell quantum efficiency measurement system (QEX10, PV Measurements, Boulder, CO). The current density (J)–voltage (V) characteristics of the cells were obtained using a 2400 SourceMeter (Keithley, Cleveland, OH) under simulated one-sun AM 1.5G illumination (100 mW cm^{-2}) (Oriol Sol3A Class AAA Solar Simulator, Newport Corporation, Irvine, CA). Typical J – V scan started from short-circuit to forward-bias and then back to short-circuit at the rate of 20 mV s^{-1} . The maximum-power output stability of the solar cells was measured by monitoring J output at the maximum-power V bias using a VersaSTAT MC potentiostat (Princeton Applied Research, Acton, MA). A shutter was used to control the one-sun illumination on the PSC. A typical active area of 0.12 cm^2 was defined using a nonreflective mask for the J – V measurements.

3. RESULTS AND DISCUSSION

Figure 1A and B show schematic illustrations of the standard and accelerated “antisolvent–solvent extraction” processes, respectively. In the standard procedure (Figure 1A), the spin-coated NMP solution film of $\text{MAPbI}_{3-x}\text{Br}_x$ mixed halide perovskite is dipped vertically in a large bath of DEE

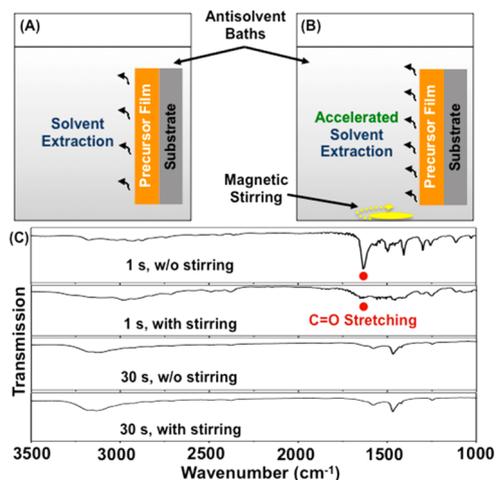


Figure 1. Schematic illustration of the crystallization of perovskite in antisolvent bath: (A) standard process without stirring; (B) accelerated process with magnetic stirring; (C) FTIR spectra of the as-formed film after 1 and 30 s dipping in antisolvent baths with and without stirring.

antisolvent. This is identical to what we have reported in the case of MAPbI₃.²² The supersaturation of MAPbI_{3-x}Br_x in the NMP solution is induced immediately upon contact with the DEE antisolvent, which is highly miscible with the precursor solvent NMP. The relatively small amount of NMP solvent diffuses into the large-volume DEE bath; this is referred to as the “antisolvent–solvent extraction” process. This ambient process contributes to the enhancement of the rate of nucleation of solid perovskite, compared with the conventional solution crystallization processes at higher temperatures that promote crystal growth over nucleation.²² In Figure 1B, continuous mechanical perturbation is introduced in the DEE antisolvent bath by using simple magnetic-stirring. With stirring, the DEE solvent continuously swipes across precursor-film surface for advection transport of the extracted NMP, which is more rapid than the unforced diffusion process. This advection transport of NMP is also expected to induce abrupt mass gradient across the NMP–DEE interface, which facilitates the extraction of NMP out of the precursor films. The accelerated extraction of NMP is confirmed by FTIR measurements (MAPbI₂Br is demonstrated here as an example). Figure 1C shows an FTIR spectrum from the MAPbI₂Br perovskite precursor film after 1 s dipping without stirring. A strong band, corresponding to C=O stretching, is observed in that FTIR spectrum, which indicates that a relatively large amount of NMP is still present in the film.²² However, when dipped in the stirring bath for 1 s, the intensity of this band is significantly reduced, and better-resolved characteristics of the perovskite appear in the spectrum. This indicates that the perturbation of antisolvent by stirring has accelerated the rate of precursor-solvent extraction in promoting the nucleation of solid perovskite. FTIR spectra for the film dipped for 30 s in the antisolvent bath with and without stirring are shown in Figure 1C. Both exhibit typical perovskite features with no obvious presence of NMP, indicating that the antisolvent–solvent extraction is complete in 30 s. Note that this time period is much shorter compared with the MAPbI₃ case (2 min),²² which is consistent with the accelerated growth kinetics with increasing Br content.

Figure 2 shows XRD patterns of the as-crystallized perovskites thin films. Phase-pure MAPbI₂Br or MAPbIBr₂

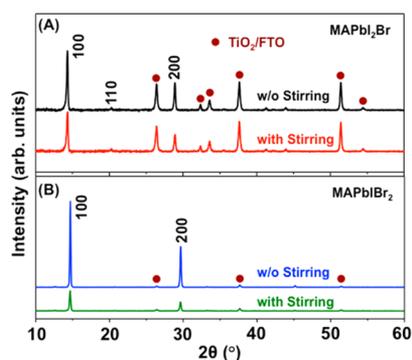


Figure 2. XRD patterns of as-crystallized (A) MAPbI₂Br and (B) MAPbIBr₂ thin films with and without stirring of the antisolvent bath.

perovskite is observed in all the films, indicating that crystallization of the perovskites is complete under these experimental conditions. The bandgap of crystallized MAPbI₂Br and MAPbIBr₂ is confirmed to be 1.77 and 2.05 eV, respectively, from the Tauc plots shown in Figure S2 in SI.

Note that 15 s dipping time appears to be adequate in the case of MAPbIBr₂ films under the same condition, while 30 s dipping time is necessary for the MAPbI₂Br films. The characteristic (200) peak in the XRD patterns from the MAPbIBr₂ film appears sharper (fwhm: 0.17° without stirring, 0.20° with stirring) than that from MAPbI₂Br films (fwhm: 0.23° without stirring, 0.26° with stirring), as shown in Figure S3 in SI, indicating better crystallinity in the MAPbIBr₂ films overall. The characteristic XRD peaks in both films are indexed according to cubic perovskite symmetry (*Pm* $\bar{3}$ *m*). The characteristic MAPbI₂Br (100) peak in Figure 2A has shifted to higher 2θ in MAPbIBr₂ in Figure 2B, corresponding to a reduction in the lattice parameter from $a = 0.616$ nm to $a = 0.604$ nm with the increase in the Br content, which is consistent with what is reported in the literature.¹¹ The effect of stirring on the crystallinity of the as-formed mixed-halide perovskites is also revealed in the XRD patterns. In the case of the MAPbI₂Br films (Figure 2A), the diffraction peaks without stirring appears to be slightly sharper and more intense compared to those with stirring. With its higher Br content (in the MAPbIBr₂ case), the difference is much more evident (Figure 2B). The broader XRD peak (0.20° fwhm for (200) peak) in the stirred MAPbIBr₂ case compared with the nonstirred case (0.17° fwhm) suggests finer microstructure, although the grain size appears to be beyond the validity of quantitative analysis using the Scherer equation.³²

The surface morphology of the perovskite film is examined using scanning electron microscopy (SEM) and atomic force microscopy (AFM), and the results are presented in Figure 3. In Figure 3A,C, the film produced without stirring is composed of ~100 nm grains with occasional large grains (~250 nm), while for the stirred case, the grains are more uniform in size (~100 nm). The overall roughness of both MAPbI₂Br films produced without (Figure 3A,B) and with (Figure 3C,D) stirring is similar (~9 nm). Note that, similar to the MAPbI₃ case,²² the overall coverage and uniformity of the mixed-halide films from the antisolvent-bathing route are much better than those obtained from simple thermally driven solution crystallization (Figure S4 in SI). In the case of MAPbIBr₂, the as-crystallized film without stirring exhibits poor coverage, with large gaps between micron-sized large grains (Figure 3E). However, when stirring is introduced in the formation process of the MAPbIBr₂ thin films, the coverage is improved significantly, resulting in a more compact film (Figure 3G). Also, the roughness of the MAPbIBr₂ thin films decreases from ~160 nm (Figure 3F) to ~15 nm (Figure 3H). The apparent grain size of MAPbIBr₂ film in the stirred case is much smaller (~300 nm). These AFM and SEM results suggest fine grain structures exist in those perovskite thin films produced from stirred baths, which is consistent with the relatively less intense XRD peaks in those films as discussed above.

The above results (FTIR, XRD, SEM, AFM) suggest the obvious effect of acceleration in the antisolvent–solvent extraction on the final thin film morphology of MAPbI_{3-x}Br_x perovskites, which becomes even more pronounced for the Br-richer perovskites. To clarify this effect, the proposed processes for nucleation and grain growth of Br-rich perovskite thin films in antisolvent baths are shown schematically in Figure 4. In a stationary antisolvent bath (Figure 4A), the number of the nuclei on the substrate is few, which rapidly grow into large MAPbI_{3-x}Br_x grains due to the fast diffusion of ions toward the nuclei. Assuming Volmer–Weber growth, those grains eventually result in the formation of “islands” with gaps in

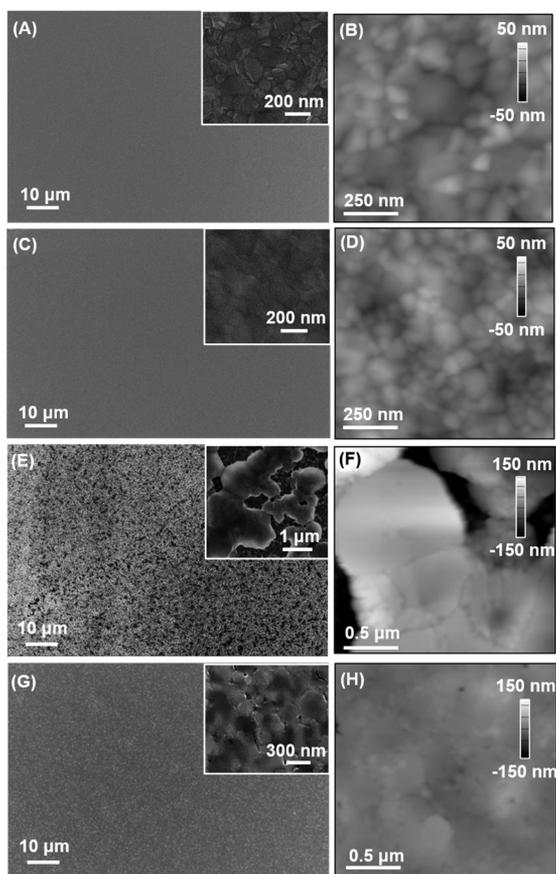


Figure 3. SEM images of the top surface of as-crystallized MAPbI₂Br thin films: (A) without and (C) with stirring of the antisolvent bath; SEM images of the top surface of as-crystallized MAPbIBr₂ thin films: (E) without and (G) with stirring. AFM images in (B), (D), (F), and (H) correspond to SEM images in (A), (C), (E), and (G), respectively.

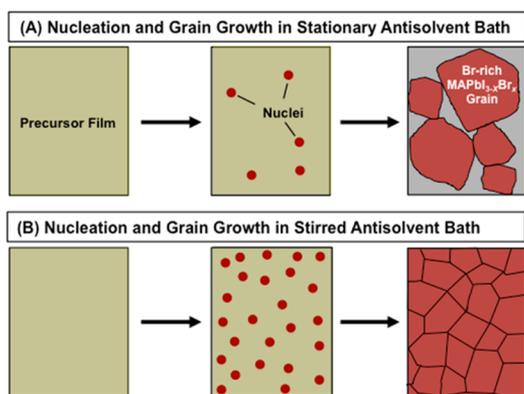


Figure 4. Proposed processes for nucleation and grain growth of Br-rich perovskite thin films in antisolvent baths: (A) stationary and (B) stirred.

between (see Figure 3E). However, when stirring is introduced in the bath, the nucleation rate is expected to increase due to accelerated antisolvent–solvent extraction (see Figure 1C), in which case a higher concentration of nuclei are expected to be uniformly distributed all over the substrate. Consequently, these nuclei grow into grains and ultimately coalesce into a dense polycrystalline grain structure in the thin film (see Figure 3G). Note that in this discussion it has been assumed that

classical nucleation and growth are at play, considering the paucity of data on nucleation and growth in the solution processing of hybrid perovskites proving otherwise.²⁵ There are several nonclassical mechanisms³³ that could also be involved, but the identification of those mechanisms in the context of hybrid perovskites await detailed in situ characterization studies and quantitative nucleation/growth experiments.²⁵

In order to assess the quality of the above mixed-halide perovskite thin films, planar PSCs were fabricated and tested. Here, perovskite thin film is sandwiched between compact-TiO₂ ESL and spiro-OMeTAD HTM layer to form a typical planar PSC, with FTO-coated glass and Ag electrodes on either side. The morphology of a PSC based on MAPbI₂Br thin film produced from a stirred antisolvent bath is studied here as an example. Figure 5A is a cross-sectional TEM image of the PSC

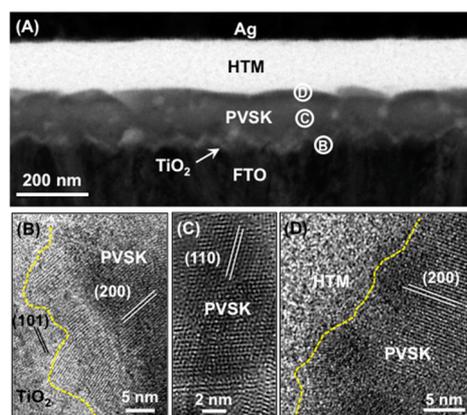


Figure 5. (A) Cross-sectional TEM image of a typical planar PSC based on MAPbI₂Br perovskite thin film (stirred antisolvent bath). The FTO, TiO₂-ESL, perovskite (PVSK), HTM, and Ag layers are marked. (B–D) HRTEM images of the regions marked in (A).

showing the FTO, ESL, perovskite, HTMs, and Ag layers. The compactness of the perovskite absorber layer is apparent from this micrograph. The perovskite–HTM interface, the perovskite layer, and the perovskite–TiO₂ interface are examined using high-resolution TEM (HRTEM), and the images from that study are shown in Figure 5B, C, and D, respectively. In Figure 5C, (200) and (110) planes are indexed based on the interplanar spacings of 0.31 and 0.44 nm for the perovskite, respectively. The indexed (101) planes within the TiO₂ ESL (Figure 5B) and the amorphous nature of the organic HTM layer (Figure 5D) are visible. The compact perovskite layer extends from the ESL to the HTM layer, with abrupt interfaces between the layers indicating intimate contact. These represent high-quality charge-transport paths and junctions in the PSC, which are the important characteristics of an efficient photovoltaic device.

Figure 6 shows the *J*–*V* characteristics of the PSCs based on MAPbI₂Br and MAPbIBr₂ thin films without and with stirring and their corresponding EQE spectra. Overall, PSCs based on mixed-halide perovskite films produced from stirred baths show improved PCEs (see Table S1 in SI for the statistics of the PV performance parameters). Since there is no striking difference between the MAPbI₂Br films produced without or with stirring, there is only a small increase in the typical PSC PCE (from 9.3% to 10.5%), which may be associated with the more uniform and dense microstructure formed under accelerated solvent extraction. In contrast, the effect of stirring is dramatic

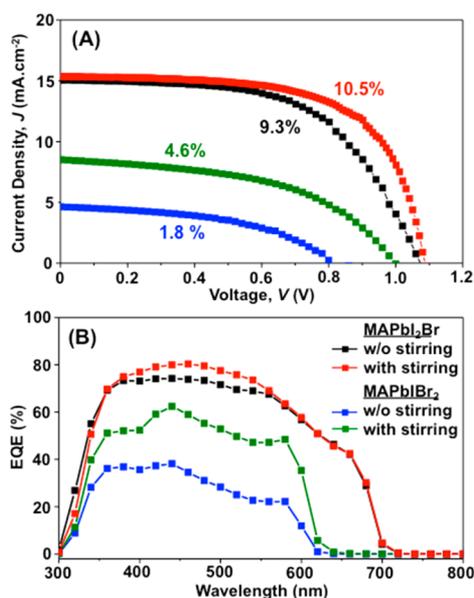


Figure 6. (A) J - V characteristics of PSCs based on MAPbI₂Br and MAPbIBr₂ thin films at reverse scan made without and with antisolvent bath stirring and (B) the corresponding EQE spectra.

in MAPbIBr₂-based PSCs, as evinced by over 2-fold increase in the PCE, from 1.8 to 4.6%. This is attributed to the reduced porosity and pinholes, and better coverage in the films as discussed earlier, although other factors (e.g., grain size, thickness variation) may have some effects. Typical hysteresis is observed in these planar cells as shown in Figure 7A, and thus, the maximum-power-point power output is monitored under continuous illumination. The typical MAPbI₂Br-based

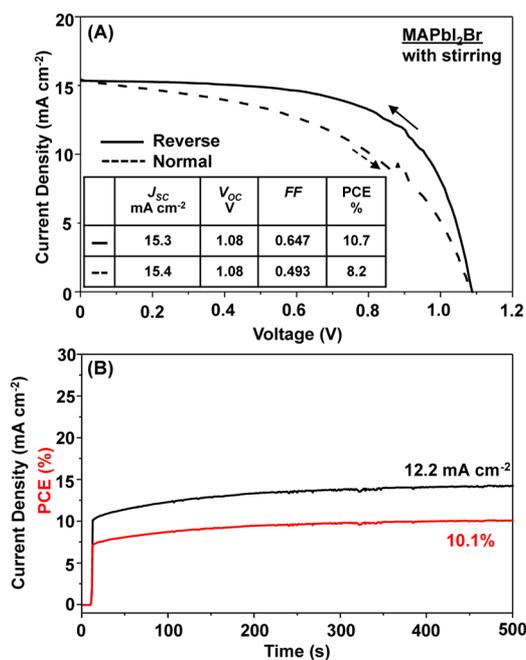


Figure 7. (A) J - V hysteresis of the typical PSC made using MAPbI₂Br perovskite thin films from a stirred antisolvent bath. The inset table shows the extracted PV parameters from both normal and reverse scans; (B) The stabilized maximum-power-point current/power outputs of the typical PSC made using MAPbI₂Br perovskite thin films from a stirred antisolvent bath.

PSC produced from a stirred antisolvent bath shows a stabilized PCE of 10.1% (Figure 7B). It is interesting that the wider-bandgap PSCs do not necessarily show higher open-circuit voltage (V_{OC}), which could be due to the following: (i) the Br-rich MAPbI_{3-x}Br_x perovskite film appears to be less perfect in morphology as discussed above, and (ii) fine-grain (I, Br)-mixed halide perovskites under illumination may exist as segregated phases, within which those lower-bandgap, I-rich domains pin the V_{OC} .^{34–36} Thus, optimization of the processing conditions (e.g., solvent selection, bath volume, stirring speed, etc.) and solutions for retarding perovskite phase segregation (e.g., grain coarsening,³⁴ etc.) for each specific composition may result into higher-performance wide-bandgap PSCs, which are subjects for future research.

CONCLUSIONS

We have demonstrated a facile antisolvent-bathing approach for the fabrication of high quality organolead (I, Br)-mixed halide perovskite thin films. MAPbI₂Br and MAPbIBr₂ perovskites with bandgaps of 1.77 and 2.05 eV, respectively, are studied as example compositions. Since the antisolvent–solvent extraction plays an important role in the room-temperature nucleation of solid perovskite during antisolvent bathing, the nucleation rate is further enhanced through advection transport of the extracted precursor–solvent in the antisolvent by simple magnetic-stirring. This is particularly important in the case of Br-rich compositions for the formation of full-coverage, dense perovskite thin films. This approach is highly versatile and it can be applied to a broad range of wide-bandgap perovskite thin films with tailored compositions, and its rapid, low-temperature nature holds promise for the future development of high-performance tandem or multijunction PVs based on PSCs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b10987.

Additional results from SEM, XRD and optical spectroscopy characterization studies, and PV-performance statistics of PSCs (PDF).

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Notes

The authors declare no competing financial interest.

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