Article

A Bifunctional Lewis Base Additive for Microscopic Homogeneity in Perovskite Solar Cells

Here, Yang and colleagues introduce an approach to simultaneously controlling grain growth and passivating grain boundaries in perovskite films. The addition of a Lewis base additive to a perovskite precursor solution results in significant enhancement of grain size and reduction in defect density. The additive increases the activation energy to slow down crystal growth and subsequently precipitate at the grain boundary to passivate defects.

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HIGHLIGHTS

- A bifunctional urea additive for PVSK grain growth and passivation was developed
- The urea additive induces crystallization of large grains by increasing activation energy
- The urea additive subsequently precipitates at grain boundary to passivate defects
- Charge-carrier lifetime and microscopic homogeneity in conductivity are greatly enhanced

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A Bifunctional Lewis Base Additive for Microscopic Homogeneity in Perovskite Solar Cells

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SUMMARY
Certified power conversion efficiencies (PCEs) of perovskite solar cells have increased to reach an impressive 22.1%. However, there exists microscopic inhomogeneity that limits high PCE, primarily as a result of defects at grain interiors and boundaries of perovskite films. Here, we report a strategy for reducing heterogeneity by using a bifunctional non-volatile Lewis base additive urea. The addition of 4 mol % urea results in significant enhancement of the macroscopic photoluminescence lifetime from 200.5 to 752.4 ns and elimination of trap-mediated non-radiative recombination, resulting in an improved PCE. The Lewis base urea is found to interact with solution precursors to retard crystal growth and enhance crystallinity, which subsequently precipitates at grain boundaries to passivate defects after completion of crystal growth. The resulting perovskite films show superior homogeneity in conductivity at both grain interior and boundaries in comparison with the bare perovskite films.

INTRODUCTION
Research efforts have focused on organo-lead halide perovskite (PVSK) photovoltaics for the last few years since the important 2012 milestone reporting higher-efficiency solid-state PVSK solar cells,1,2 which originated from the pioneering work on liquid-junction PVSK-sensitized solar cells.3,4 Superior optoelectronic properties of PVSK, such as high absorption coefficient,5 long-range balanced electron and hole diffusion lengths,6,7 and high defect tolerance8 have provided insight into the evolution of device architecture, and advanced processes and compositions have enabled fabrication of uniform perovskite films with high optoelectronic quality.9–14 As a result, the certified power conversion efficiency (PCE) has reached 22.1%, making perovskite solar cells a new class of photovoltaics to replace the prevailing silicon solar cell.15 Rapid enhancement of PCE accompanied understanding of the fundamental physics of PVSK materials.16–21 On the basis of photo-physical studies, the superior optoelectronic properties of perovskite materials were found to be comparable with those of GaAs. In particular, the absorption coefficient and related Urbach tail slope of PVSK are similar to GaAs,21 resulting in an effective photon recycling process to assist in energy transport.18–20 Thermalization of hot carriers was more than three orders of magnitude slower than with GaAs, implying fewer interactions between charge carriers and phonons, which can be correlated to the long carrier lifetimes.18–20 Such unprecedented optoelectronic properties have resulted in a calculated maximum achievable PCE of 31%, which is close to the Shockley-Queisser limit.22

The Bigger Picture
Perovskite (PVSK) solar cells have shown great potential as a next-generation solar-energy harvester in the past 5 years. Superior optoelectronic properties and processability of the PVSK materials provide positive prospects for commercialization in the near future. Achievable power conversion efficiency (PCE) is expected to exceed 30%; increasing microscopic homogeneity has been suggested as the key to further improving the current certified PCE of 22.1%. Here, we introduce a method for increasing the homogeneity by a Lewis base urea additive, which facilitates control of crystallization kinetics and passivation of defects in the PVSK layer. The improved crystallinity and decreased defects result in greatly enhanced charge-carrier lifetime and microscopic homogeneity in conductivity, which enhances the PCE of PVSK solar cells. We believe that this work presents an effective strategy for further enhancing the photovoltaic performance of PVSK solar cells toward their great potential.
Recent studies utilizing microscale spatially resolved spectroscopy have uncovered clues for further enhancement. Although the macroscopic properties of the perovskite film have been found to be superior to other types of materials, heterogeneity at the microscale still exists, where some areas of the film on a nano- to microscale show good optoelectronic properties and others show poor optoelectronic properties. Such areas with poor optoelectronic properties degrade the overall photovoltaic performance. The origin of the heterogeneity in perovskite film was suggested to be a structural disorder at (1) grain boundaries and (2) grain interiors. Structural disorders (defects) at grain boundaries induce shallow trap states, localizing charge carriers that are ultimately lost through non-radiative recombination, and the defect density across the grain interior is found to be dependent on the crystal facet, resulting in facet-dependent photovoltaic performance within a single grain. As a result, several methods to control crystal growth or passivation of defects have been developed previously although their effect on microscopic optoelectronic properties has not been fully understood.

In this study, we developed a strategy for decreasing the heterogeneity in optoelectronic properties of perovskite films by using a bifunctional Lewis base additive, urea, for grain growth and boundary passivation, enabling high-efficiency CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$) perovskite solar cells. The MAPbI$_3$ perovskite layer was formed by the Lewis acid-base adduct approach, in which non-volatile Lewis base urea was added to assist grain growth and boundary passivation. Crystal growth and molecular interactions were monitored by X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy. Charge-carrier lifetime and trap densities were investigated by time-resolved photoluminescence (PL) measurements. Conducting atomic force microscopy (c-AFM) was used to correlate macroscopic enhancement with local properties. The non-volatile Lewis base additive was found to be advantageous for both crystal growth and defect passivation to reduce heterogeneity in the optoelectronic properties, resulting in an improved steady-state PCE from 16.80% to 18.25% for MAPbI$_3$ perovskite solar cells.

RESULTS AND DISCUSSION
Perovskite Film Formation via the Adduct Approach
As seen in Figure 1A, the MAPbI$_3$ perovskite layer was prepared by the adduct approach, in which urea was added to the perovskite precursor solution. Whereas DMSO was found to be volatile at around 70°C, urea was confirmed to be non-volatile at temperatures <130°C from thermogravimetric analysis (TGA) (Figure S1). The adduct film formed without urea (MAI$\cdot$PbI$_2$$\cdot$DMSO) was immediately converted to MAPbI$_3$ upon heating at 65°C, whereas a much slower conversion with an increased temperature of 100°C was observed with addition of urea (Figure 1B). This effect is most likely a result of the change in intermolecular interactions upon addition of urea. We confirmed the interaction of urea with MAI, PbI$_2$, and DMSO by measuring the FTIR spectra of the synthesized adducts (Figure S2) in Figures 1C and 1D. The characteristic S=O stretch peak of DMSO in the MAI$\cdot$PbI$_2$$\cdot$DMSO adduct was shifted from 1,018 to 1,010 cm$^{-1}$ upon addition of urea. Also, the C=O stretch peak in urea was shifted from 1,676 to 1,651 cm$^{-1}$, which is most likely caused by the interaction between urea and the MAI$\cdot$PbI$_2$$\cdot$DMSO adduct to form a MAI$\cdot$PbI$_2$$\cdot$DMSO$\cdot$urea adduct. Considering the negligible shift of the C=O stretch peak of urea in MAI$\cdot$PbI$_2$-urea, the interaction of urea with MAI$\cdot$PbI$_2$ seems to be weak in the absence of DMSO, which probably allows the formation of MAPbI$_3$ at a lower temperature than the sublimation temperature of urea. According to the Arrhenius equation, crystallization kinetics is inversely exponentially proportional to
the activation energy ($E_a$) at constant temperature. Slower crystallization with the addition of urea is thus thought to originate from the strengthened interaction between perovskite precursors and Lewis bases (DMSO and urea), which increases the $E_a$. The stronger interaction is probably due to higher dipole moment of urea (4.56 D) than of DMSO (3.96 D) and the resulting enhanced Lewis acid-base interaction. The slower crystallization implies a higher critical Gibbs free energy ($\Delta G_c$), which decreases the number of nuclei formed and growth proceeds from a fewer number of nuclei. Therefore, the growth of larger grains is expected from the addition of urea. Furthermore, it has been reported that Lewis bases can interact with grain boundaries of perovskite films to passivate the defect sites. We presume that urea likely precipitates at grain boundaries and can interact with these defects after completion of crystal growth. However, too much residual photo-inactive urea can degrade photovoltaic performance. Thus, our motivation was to investigate the effects of the amount of urea added on photovoltaic performance.

**Effect of the Addition of Urea on Photovoltaic Performance**

The photovoltaic performance of MAPbI$_3$ perovskite solar cells was evaluated with different amounts of added urea, as detailed in Figure 2. The amount of urea varied from 0 mol % (without urea) to 6 mol % (0.06 mmol) with respect to MAI and PbI$_2$ (1 mmol). As the urea amount increased from 0 (reference) to 4 mol %, the open-circuit voltage ($V_{OC}$) and fill factor (FF) were systematically enhanced. With the addition of 4 mol % urea, the average $V_{OC}$ and FF were enhanced from 1.049 ± 0.016 to 1.089 ± 0.028 V (3.81% enhancement) and 0.72 ± 0.03 to 0.75 ± 0.03 (4.1%
enhancement), respectively. This resulted in an improvement in the average PCE from 16.10% ± 0.70% to 17.75% ± 0.71% (10% enhancement). The current density and voltage (J-V) curves of the best-performing devices are shown in Figure 1B. A PCE of 18.55% was achieved with the addition of 4 mol % urea and 17.34% was achievable without urea. The steady-state PCEs of the best-performing devices were 16.80% and 18.25% without and with urea, respectively (Figure S3). Also, J-V hysteresis with different scan directions was decreased after addition of urea. The hysteresis index decreased from 0.29 to 0.10 upon addition of 4 mol % urea (Figure S4 and Table S1). The enhanced PCE was partially ascribed to a slight enhancement in \( J_{SC} \), which was confirmed from the external quantum efficiency (EQE) spectra in Figure 2F. The integrated \( J_{SC} \) was calculated to be 20.91 mA/cm\(^2\) for the reference and 21.26 mA/cm\(^2\) with 4 mol % urea, which is well matched with the \( J_{SC} \) measured from the J-V curve.

Crystal Growth and Morphology

The FTIR spectra were measured (Figure 3A) to investigate whether urea remained in the film after film formation. A magnified region containing the fingerprint region for the C=O stretch, N–H bend, and C–N stretch is shown in Figure 3B. Asymmetric peaks around 1,647 and 1,577 cm\(^{-1}\) (red arrows in Figure 3B) in the bare MAPbI\(_3\) film are reported to originate from N–H bending.\(^{35,42}\) With the addition of 4 mol % urea to the perovskite precursor solution, the peak at 1,647 cm\(^{-1}\) shifted to 1,665 cm\(^{-1}\) (black arrow), which can be attributed to overlap with the C=O stretching peak of urea at 1,676 cm\(^{-1}\), confirming the presence of urea.\(^{36}\) Furthermore, the XRD patterns in Figure 3C show no additional peaks or peak shifts upon addition of 4 mol % urea in comparison with the bare MAPbI\(_3\) film (even with a much larger amount of urea as seen in Figure S5), implying that the added urea does not react with precursors to produce byproducts and exists in an amorphous form. The (110) orientation peaks of MAPbI\(_3\) were enhanced with addition of urea, whereas the intensity of the other peaks was essentially unchanged (intensity\(_{(110)}\)/intensity\(_{(222)}\) increased from 1.25 to 1.34). The occurrence of the preferred orientation
by urea was further confirmed by XRD patterns with a higher amount of urea, in which the (110) orientation peaks were further enhanced (Figure S5). Furthermore, the full-width half-maximum (FWHM) values of the peaks originating from perovskite were reduced (e.g., from 0.133 to 0.109 for the (110) peak), confirming that added urea interacted with perovskite precursors during crystal growth to enhance crystallinity and induce the preferred orientation.

The effect of added urea on the surface and cross-sectional morphology of the MAPbI$_3$ layer is investigated in Figure 4. As seen in the AFM images in Figures 4A and 4B, the constitutive grains were significantly enlarged from about 200 nm to larger than 1 µm, which correlates with enhanced FWHM in the XRD measurements in Figure 3C. The cross-sectional scanning electron microscopic (SEM) images of the perovskite solar cell based on MAPbI$_3$ with and without 4 mol % urea are shown in Figures 4C and 4D, respectively. The thickness of the MAPbI$_3$ layer was around 580 nm regardless of the addition of urea; the perovskite film with added urea displayed single interfaces of large grains along the direction perpendicular to the substrate, whereas the bare MAPbI$_3$ film showed multiple interfaces between several smaller grains. The enlarged grains are also confirmed in the top-view SEM images in Figure 56, in which nano-sized bumps can be observed on the surface of MAPbI$_3$ grains with the addition of 4 mol % urea. We speculate that the nano-sized bumps are related to the added urea. Because urea does not integrate as part of the perovskite lattice, it is possible that it can precipitate at the grain boundary of MAPbI$_3$ and the surface of the film after completion of crystal growth, as has been
previously observed for excess CH$_3$NH$_3$I and CH$_3$NH$_3$Br.\textsuperscript{40,43} It is expected that the precipitated urea interacts with the grain boundaries of perovskite to change the optoelectronic properties of perovskite film.

**Macroscopic PL and the Role of Remnant Urea**

In Figure 5, UV-visible and PL of the MAPbI$_3$ perovskite films were measured to evaluate the effect of added urea on the absorption and charge-carrier properties of the film. The absorption of the MAPbI$_3$ film in the wavelength region from 600 to 780 nm was slightly enhanced with the addition of urea, which can be correlated with the enhanced EQE in the same wavelength region. The enhancement of the absorption might result from the larger crystal size, which was found to enhance light-harvesting efficiency caused by enhanced light scattering, as reported previously.\textsuperscript{44,45} From closer inspection of the (1 – transmittance) spectra in Figure S7, steeper onset of absorption was observed with 4 mol % urea (slope of linear fit = 6.83) than with that of bare MAPbI$_3$ film (slope of linear fit = 6.64). Thus, smaller Urbach ($E_u$) energy is expected with 4 mol % urea, which indicates a higher level of electronic order with 4 mol % urea.\textsuperscript{21} The steady-state PL is shown in Figure 5B. Notably, the PL peak
intensity was increased more than three times from $0.9114 \times 10^5$ to $3.1839 \times 10^5$ upon addition of urea. The time-resolved PL decay profiles of the MAPbI$_3$ films were monitored at the peak emission (770 nm) in Figure 5C to find the origin of the enhanced PL intensity. The fitted parameters are shown in Table S2. The bare MAPbI$_3$ film shows biexponential decay with fast ($t_1 = 5.8$ ns) and slow ($t_2 = 200.5$ ns) components, whereas single exponential decay was observed ($t_2 = 738.3$ ns) with 4 mol % urea without the fast component. The fast component ($t_1$) might be related to trap-mediated monomolecular non-radiative recombination derived by defects at the grain boundaries.\textsuperscript{23,40,46,47} It has been reported that trap-mediated non-radiative recombination becomes dominant with a low intensity of excitation as a result of slow depopulation of charge carriers from the trap states.\textsuperscript{23,48} Figure S8A shows the time-resolved PL spectra of bare MAPbI$_3$ films under different intensities of excitation. As the excitation intensity decreased, $t_1$ was highly increased from 17.15\% to 92.51\% (Table S3), indicating that monomolecular trap-mediated recombination becomes dominant, which supports the correlation between the fast-decaying component and trap-mediated non-radiative recombination. In contrast, the PL decay profile of MAPbI$_3$ film with 4 mol % urea shows a single exponential decay with $t_2 \sim 700$ ns regardless of the excitation intensity, which suggests a significantly decreased defect density after the addition of urea. Furthermore, $t_2$, which is associated with bimolecular radiative recombination of the perovskite film in bulk, was greatly increased from 200.5 to 752.4 ns with the addition of urea. This indicates that the charge-carrier lifetime is highly prolonged, which likely contributes to the enhanced $V_{OC}$ and FF observed.\textsuperscript{49} The measured PL lifetime of

Figure 5. Absorption and Fluorescence Data with and without Urea

(A–C) UV-visible absorption (A), steady-state photoluminescence (PL) (B), and time-resolved PL decay profiles (C) of MAPbI$_3$ film without and with 4 mol \% urea. The films were deposited on a glass substrate. Inset in (C): magnified spectra showing the initial decay profile. Empty circles and solid lines indicate measured data and fitted curves, respectively.

(D) Schematics showing film crystallization and corresponding charge transporting characteristics.
MAPbI₃ film with 4 mol % urea is superior to that of MAPbI₃ film prepared with a variety of techniques to enlarge the grain size (Table S4). The decrease in defect density with the addition of urea can be attributed to increased grain size as a result of slower crystallization with higher activation energy during the crystallization (Figure 5D), resulting in decreased grain boundaries and their associated defects. Moreover, the Lewis base urea is most likely precipitated at grain boundaries in the final film, which serves to passivate the grain boundary defect sites and remove trap states,³⁹,⁴⁰ which will facilitate charge transport and enhance the quasi-Fermi level and thereby \( V_{OC} \) (Figure 5D).

To further confirm the nature of the decreased defects, we first tried to check the presence of coordination species defects by using absorption spectra (Figure S9).⁵⁰ To avoid saturation of absorption, we diluted the precursor solutions five times to decrease the thickness of MAPbI₃ films. As seen in Figure S9, an increase in absorption from 420 to 500 nm was reproducibly observed after the addition of urea. The absorption at these wavelength regions was reported to originate from coordination species such as \( \text{PbI}_2S_2^{2-} \) (S is undesired coordinating species such as solvent molecules),⁵⁰ thus the increase in the absorption indicates an increase in the coordination species, which seems to be reasonable because remnant urea with higher dipole moment than DMSO is expected to form more coordinating species in the resulting MAPbI₃ film. Therefore, in this study, the reduced defect density does not originate from coordination species defects. We carried out admittance spectroscopy to measure the density of the trap (Figures 6A and 6B). The structural disorders at the grain boundaries were reported to form a shallow trap state close to the valance band maximum (VBM),⁴⁶ which can be monitored by admittance spectroscopy.¹³,⁵¹,⁵² The density of the trap (\( N_T \)) was estimated from the angular-frequency-dependent capacitance according to the following equation:⁵¹

\[
N_T(E_u) = \frac{V_{bi}}{qW} \frac{dC}{d\omega} \frac{\omega}{kT},
\]

where \( V_{bi} \) represents the built-in potential, \( W \) denotes the depletion width, \( C \) is the capacitance, \( \omega \) is the angular frequency, \( k \) is the Boltzmann constant, and \( T \) is the temperature. \( E_u = E_T - E_V \), where \( E_T \) and \( E_V \) are the trap energy and valance band maximum, respectively. \( V_{bi} \) and \( W \) were measured with a Mott-Schottky plot (inset in Figure 6A), in which the measured \( V_{bi} \) values were 1.05 and 1.17 V for the devices without and with urea, respectively, correlating with enhanced \( V_{OC} \) with urea. The calculated \( N_T \) from frequency-dependent capacitance spectra (Figure 6A) is demonstrated in Figure 6B. With the addition of 4 mol % urea, the trap density is more than one order of magnitude decreased at around \( E_u = 0.25 \text{ eV} \), corresponding to a shallow trap state, which possibly originates from structural disorder at the grain boundaries.⁴⁶ Thus, we concluded that the addition of urea effectively reduces the trap state originating from grain boundaries.

Although the effect of urea on crystal growth is obvious, it was difficult to confirm the presence of urea at the grain boundaries and its passivation effect. We carried out supplemental experiments to investigate the passivation effect of urea. Urea was dissolved in 2-propanol at different concentrations (13.5, 27, and 54 mM) and was spin-coated on MAPbI₃ film followed by drying at 100 °C for 5 min. As can be seen in Figure S10A, with 27 mM of urea, the average PCE of the devices was enhanced from 16.19% ± 0.65% to 16.86% ± 0.98%, and the steady-state PCE (Figure S10B) of the best-performing devices was enhanced from 17.11% to 17.94%. The enhanced PCE mainly resulted from enhanced \( V_{OC} \) (1.089 ± 0.017 to 1.103 ± 0.027 V) and FF (0.693 ± 0.018 to 0.707 ± 0.024); no significant change in \( J_{SC} \)
was found as confirmed from the EQE spectrum (Figure S10C). Steady-state and time-resolved PL decay profiles of the film with and without urea post-treatment (Figures S11A and S11B) were measured to investigate the origin of the improved photovoltaic performance. As seen in Figure S11C, steady-state PL intensity was increased more than 2 times after treatment with urea solution. In the time-resolved PL decay profiles (Figure S11D), the fast-decay component ($t_1 = 5.4$ ns) associated with trap-mediated non-radiative recombination observed from the reference film was significantly retarded to 30.7 ns (Table S5 and inset of Figure S11D), which is probably related to a radiative component resulting from passivation of the traps by urea considering the enhanced steady-state PL intensity. $t_2$, which can be related to the bulk carrier lifetime, was hardly changed probably because the morphology (grain size) of the MAPbI$_3$ film was preserved. Finally, the photovoltaic performance of perovskite solar cells based on bare MAPbI$_3$ with post-treatment urea and with 4 mol % urea is compared in Figure S12; the devices with 4 mol % urea show the highest performance.

With a small amount of urea (4 mol %), however, it was difficult to identify the remnant urea at the grain boundaries of MAPbI$_3$ film. We increased the amount of urea by 50 mol % to see whether the excessive urea crystallized at the grain boundaries. In SEM images of the MAPbI$_3$ perovskite film with 50 mol % urea (Figure S13), we identified the formation of the secondary phase at the grain boundaries (yellow
arrows in Figure S13). To investigate the chemical composition, elemental distribution mapping was carried out (Figures 6C–6H). The mapping images clearly indicate the absence of Pb and I and the presence of C and N in the secondary phase as indicated in the dashed rectangular boxes, probably detected from urea (oxygen possibly comes from indium tin oxide [ITO] substrate). Therefore, we concluded that the added urea is precipitated at the grain boundaries of perovskite films. The urea was reported to behave like a semiconductor as a result of electron delocalization via $\pi$-bond formation ($C=NH, C=NH^+$) and generation of a highly polar resonance hybrid structure. However, its conductivity is still low ($3 \times 10^{-8}$ S/cm). As a result, the thick layer of urea impedes extraction of the photo-generated hole from the perovskite layer. We also found from c-AFM that the conductivity of the ITO glass decreased after spin coating with 108 mM urea solution (Figure S14). Therefore, we expected the thickness of precipitated urea at the grain boundaries and the surface of MAPbI$_3$ film to be <3 nm, which allows tunneling of charge carriers.

Microscopic c-AFM and Stability

C-AFM measurements were carried out (Figure 7) to investigate the spatially resolved electrical properties of the MAPbI$_3$ films. Figures 7A and 7B show the distribution of the current signal measured between the tip and the perovskite film, which is overlaid on the topological images (grayscale). The current was measured under a DC bias voltage of 1.0 V in an ambient atmosphere and room-light conditions. For the bare MAPbI$_3$ film (Figure 7A), the measured current was highly heterogeneous over the whole film. The heterogeneity existed between grains and different regions of the grain interior, which is in accordance with previous studies. Some of the grains showed a very low current signal (red region), indicating poor mobility and/or depleted charge carriers in this region, which degrades the overall photovoltaic performance of the perovskite solar cell. Figure 7C shows the trajectory of the scan of the height and current signal, in which the measured current varied significantly along the trajectory. The current signal was measured to be relatively higher at grain boundaries than in the grain interior, which was found to be caused by downward bend-bending at the grain boundary causing electron trapping. With the addition of urea (Figure 7B), the current signal was enhanced overall with much better homogeneity than bare MAPbI$_3$ film. The homogeneous current can be confirmed from the scan trajectory in Figure 7D. The measured current was relatively constant across the two different grains regardless of the grain boundary present between grains, indicating that urea successfully passivates the grain boundaries to reduce carrier trapping at grain boundaries. Moreover, we attribute the homogeneous current signal across the grain interior to higher crystallinity with preferred orientation, which decreases the bulk defects and their dependency on facet. The probability distribution of the measured current from the MAPbI$_3$ films with and without urea is shown in Figure 7E. Upon addition of urea, the overall current signal was greatly increased with a narrower distribution, implying improved mobility and/or carrier density, which correlates with decreased trap density and improved carrier lifetime in the PL measurements.

Finally, the effect of the addition of urea on ex situ and in situ stability of the device was evaluated in Figure S15. For ex situ measurements (Figure S15A), the devices were stored under dark conditions and measured over time; the devices were kept under light at maximum power for the in situ measurements (Figure S15B). The reference device showed 43% degradation (from 17.1% to 9.8%) over 27 days; the device with urea showed 35% degradation (from 18.27% to 11.82%). During in situ measurement for 1 hr, the reference device showed 5% degradation but almost no degradation was observed with urea. The improved stability is
probably a result of decreased grain boundaries, which can act as a pathway for ingress of moisture. However, accelerated degradation of MAPbI3 film under prolonged light exposure was observed (Figure S16). The initial degradation was slower with urea but was accelerated after 90 min of light exposure. Further study will be required to fully understand the effect of added urea on the stability of the perovskite film and device.

In conclusion, we have successfully demonstrated a bifunctional Lewis base additive for enhanced grain growth and grain boundary passivation. Addition of the Lewis base urea was found to retard crystal growth to enhance crystallinity and induce a preferred orientation. Because of the non-volatile nature of urea, we propose that it precipitates at the grain boundary after completion of film formation to passivate the defects at the grain boundaries. As a result of the enhanced crystallinity and grain boundary passivation, the trap density in both the grain interior and at the boundaries was significantly reduced, resulting in an enhanced carrier lifetime and a more homogeneous conductivity across the film. Finally, the steady-state PCE of the MAPbI3-based solar cell was enhanced from 16.80% to 18.25% upon an optimized addition of urea. We believe this work presents an effective strategy for
decreasing microscopic heterogeneity in optoelectronic properties of perovskite films and will open up new approaches to further enhancing the photovoltaic performance of perovskite solar cells toward their great potential.

EXPERIMENTAL PROCEDURES
The experimental procedures are included in the Supplemental Information.

SUPPLEMENTAL INFORMATION
Supplemental Information includes Supplemental Experimental Procedures, 16 figures, and 5 tables and can be found with this article online at http://dx.doi.org/10.1016/j.chempr.2017.05.020.

AUTHOR CONTRIBUTIONS
J.-W.L. and Y.Y. conceived the experiments and prepared the manuscript. J.-W.L. prepared and characterized the materials and devices. S.-H.B. performed c-AFM and FTIR spectroscopy. Y.-T.H. and N.D. assisted with device fabrication and TGA analysis. M.W. performed admittance spectroscopy. P.S. assisted with PL measurements. All authors discussed the results and commented on the manuscript.

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REFERENCES AND NOTES


