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Low-Temperature, Simple and Efficient Preparation of Perovskite Solar Cells Using Lewis Bases Urea and Thiourea as Additives: Stimulating Large Grain Growth and Providing a PCE up to 18.8%

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Materials Analysis, Device Fabrication, and Characterization

Device Fabrication and Characterization PSCs were prepared using the following device fabrication procedure. Glass/ITO substrates [Sanyo, Japan (8 Ω/□)] were sequentially patterned lithographically, cleaned with detergent, ultra-sonicated in acetone and isopropyl alcohol, dried on a hot plate at 140 °C for 10 min, and treated with oxygen plasma for 5 min. PEDOT: PSS (Baytron P VP AI4083) was passed through a 0.45-μm filter and deposited onto ITO (thickness: ca. 40 nm) through spin-coating (3000 rpm) in air; the sample was then dried at 140 °C for 20 min inside a glove box. The perovskite precursor solution was prepared by dissolving MAI and lead(II) chloride at 25 wt% urea and thiourea were first dissolved in DMF at a concentration of 25 wt%, and then stirring continuously overnight. Then add the solution of the additive to the perovskite precursor solution at different concentrations. Shake with a shaking mixer for 10 minutes to mix the additive well with the precursor. PVSK devices were made with layered configuration of glass/ITO/PEDOT:PSS/$MAPbI_{3-x}Cl_x$ /$PC_{61}BM$/Al. To study the effects of the additive on the morphology, absorption, and crystallization of the perovskite films, we fabricated such films under the same conditions as those described above, but with different concentrations (0.5,1, and 3 vol%) of urea and thiourea in the precursor solutions and variations of the annealing time, respectively. Then the precursor solution was deposited on top of the PEDOT:PSS. We used the annealing temperature of 75 °C,65 ^{o}C with the time necessary to fully crystallize $MAPbI_{3-x}Cl_x$ being between 2.5 and 4.5 h. The fully generation of perovskite films can be observed clearly with the naked eye, with a color change from yellow to dark brown. An optimized annealing times for our normal (no urea or thiourea) and urea and thiourea derived perovskite films were 2.5 and 4.5 h, respectively. PCBM was spin-coated (2000 rpm) from a chlorobenzene solution (10 mg mL^{-1}). The layers of Al (100 nm) were deposited thermally under vacuum. Device Fabrication of $MAPbI_3$ PSC : The ITO-coated glass substrates (sheet resistance of 15 Ω sq^{-1}) were ultrasonically cleaned with abstergent aqueous solution, deionized water, acetone, and isopropyl alcohol for 20 min and then, dried with a nitrogen (N_2) stream before use. Then, the substrates were cleaned with air plasma for 10 min. A NiO_x film (≈20 nm) was prepared by spin-coating a solution containing NiO_x precursor (nickel (II) acetylacetonate (129mg) dissolved in ethanol (5ml EtOH) with the 50μL HCl (38wt%)). The NiO_x-coated substrates were then baked at 320 °C for 45 min in air.[1] The $MAPbI_3$ precursor solution was prepared by dissolving the 1.2 M PbI_2 and MAI (molar ratio of 1:1) in anhydrous DMF:DMSO(4:1). The solution was stirred at 60 °C for 2 h in an argon glovebox. The perovskite precursor solutions were then spin coated on the NiO_x-coated substrates with 2-step spin rate (step1 2000 rpm for 10 s and step2 4000rpm for 20s), and 300 μL of toluene was rapidly dropped on the substrates to induce a fast crystallization after ≈6 s of spin coating. The sample was annealed at 100 °C for 10 min to complete the transformation of perovskite.[2] The $PC_{61}BM$ (20 mg mL^{-1} in anhydrous chlorobenzene) was then sequentially deposited and following deposited the BCP (2 mg mL^{-1} in IPA) via spin coating at 6000 rpm for 30 s. Finally, the device was completed upon the evaporation of Ag or Au contact electrodes (100 nm) at a vacuum level of 10^{-7} Pa through a shadow mask. The active area of this electrode was fixed at 0.01 cm^2. All device measurements were performed in the ambient environment (below 40% humidity) at room temperature. The active area of the device was 10 mm^2. The cell performance was measured inside a glove box. The current–voltage (I–V) properties of the devices were measured using a computer-controlled Keithley 2400 source measurement unit (SMU) and a Newport solar simulator (Oriel® Sol2A Class ABA Solar Simulators) under AM 1.5 illumination (100 mW cm^{-2}). The illumination intensity was calibrated using a standard Si reference cell and a KG-5 filter. EQEs were measured using an Enlitech QE-R spectral response measurement system to calibrate the current densities of the devices. UV–vis absorption spectra were recorded using a Hitachi U-3300 spectrophotometer. Image was used to calculate the surface coverages of the films. GIWAXS patterns were collected using a Philips Panalyticalx'PertPROMRD instrument; the incident beam angle was above the critical angle (ca. 0.5°). SEM images were measured using a HITCHI S-3400N scanning electron microscope. The electrochemical impedance spectra (EIS) of all devices were measured with an electrochemical workstation (IM 6, Zahner, Germany). The frequency ranges of EIS measurement went from 4 MHz to 0.1 Hz with ac amplitude 10 mV under illumination, which calibrated to same light intensity as AM1.5G. The EIS curves were fitted with Z-view software (version 3.4e) based on the electronic circuit model.

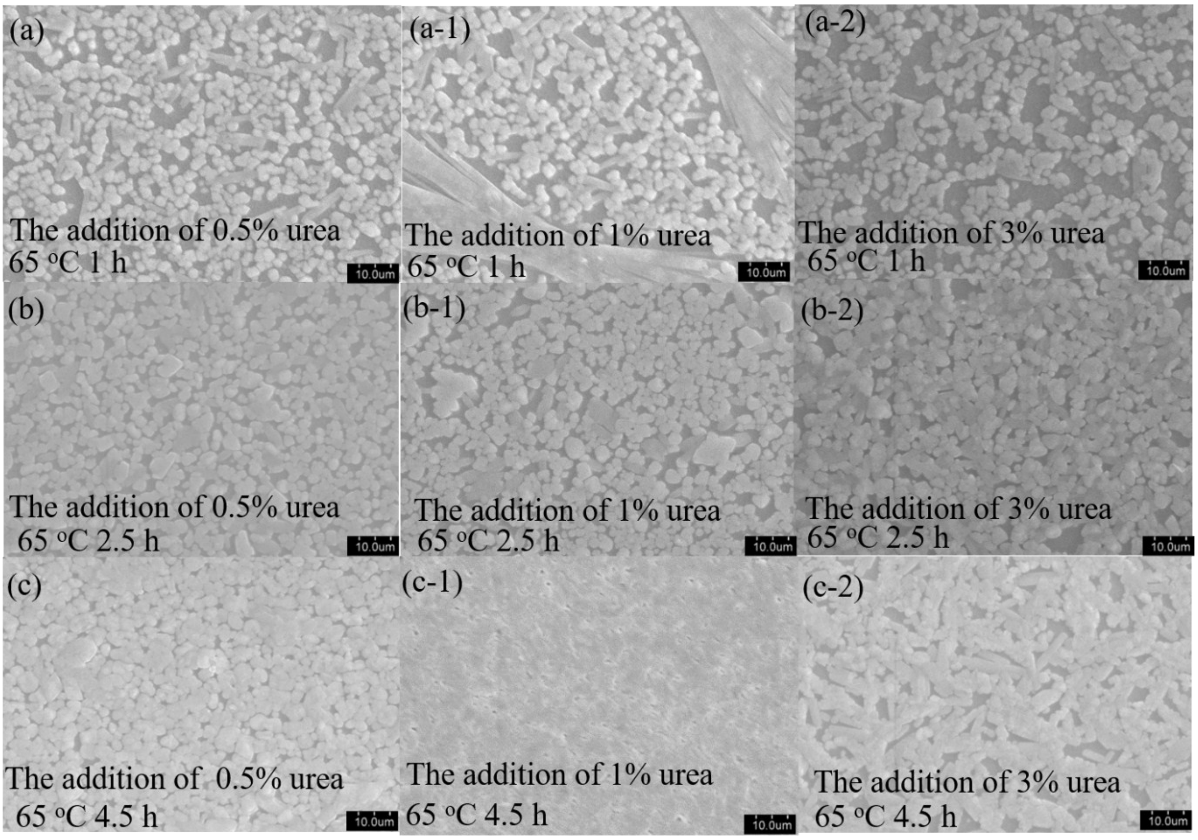

Fig. S1 FE-SEM images of $MAPbI_{3-x}Cl_x$ perovskite thin films with the addition of urea at different annealing times and concentrations at 65 °C of (a) to (a-2) were annealing for 1 hour at concentrations of 0.5%, 1%, 3% respectively. (b) to (b-2) were annealing for 2.5 hours at concentrations of 0.5%, 1%, 3% respectively. (c) to (c-2) were annealing for 4.5 hours at concentrations of 0.5%, 1%, 3% respectively. ; magnification by 5000 times.

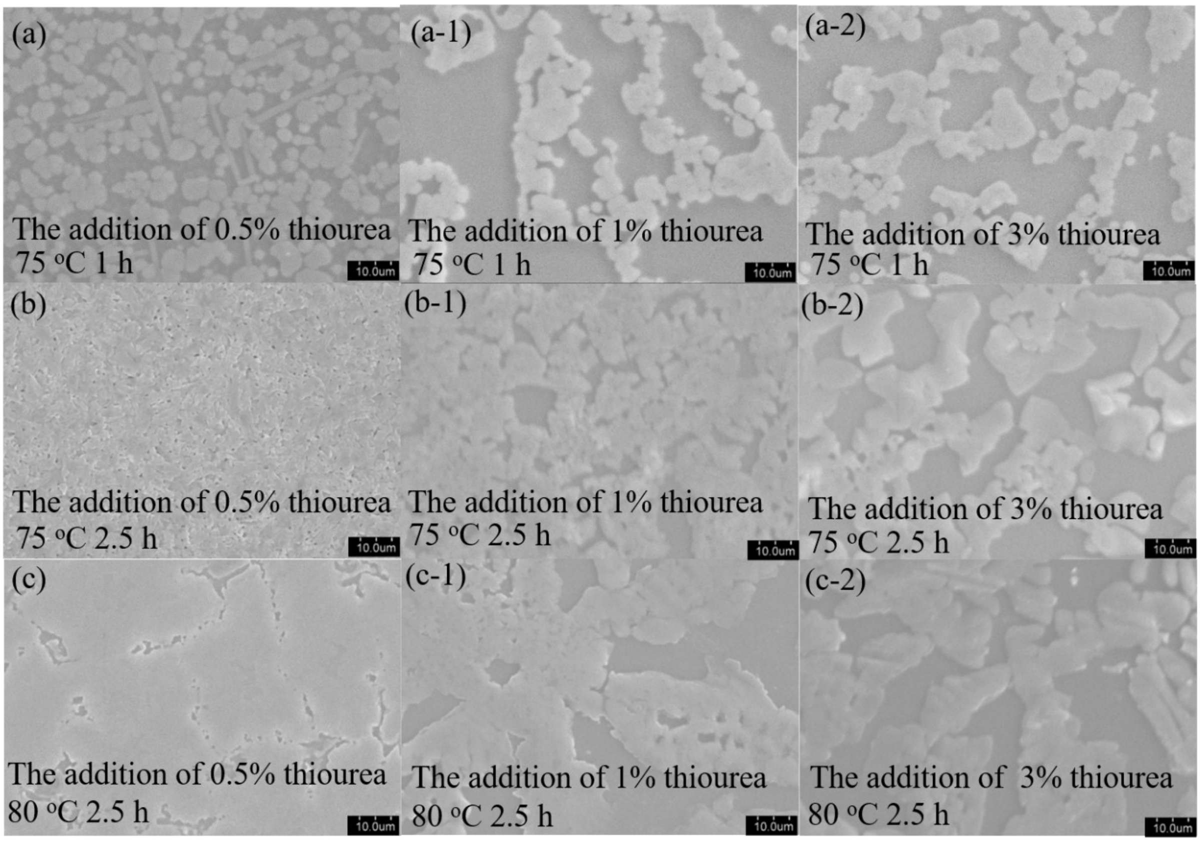

Fig. S2 FE-SEM images of $MAPbI_{3-x}Cl_x$ perovskite thin films with the addition of thiourea at different annealing times and concentrations at 75 °C of (a) to (a-2) were annealing for 1 hour at concentrations of 0.5%, 1%, 3% respectively. (b) to (b-2) were annealing at 75 °C for 2.5 hours at concentrations of 0.5%, 1%, 3% respectively；(c) to (c-2) were annealing at 80 °C for 2.5 hours at concentrations of 0.5%, 1%, 3% respectively. ; magnification by 5000 times.

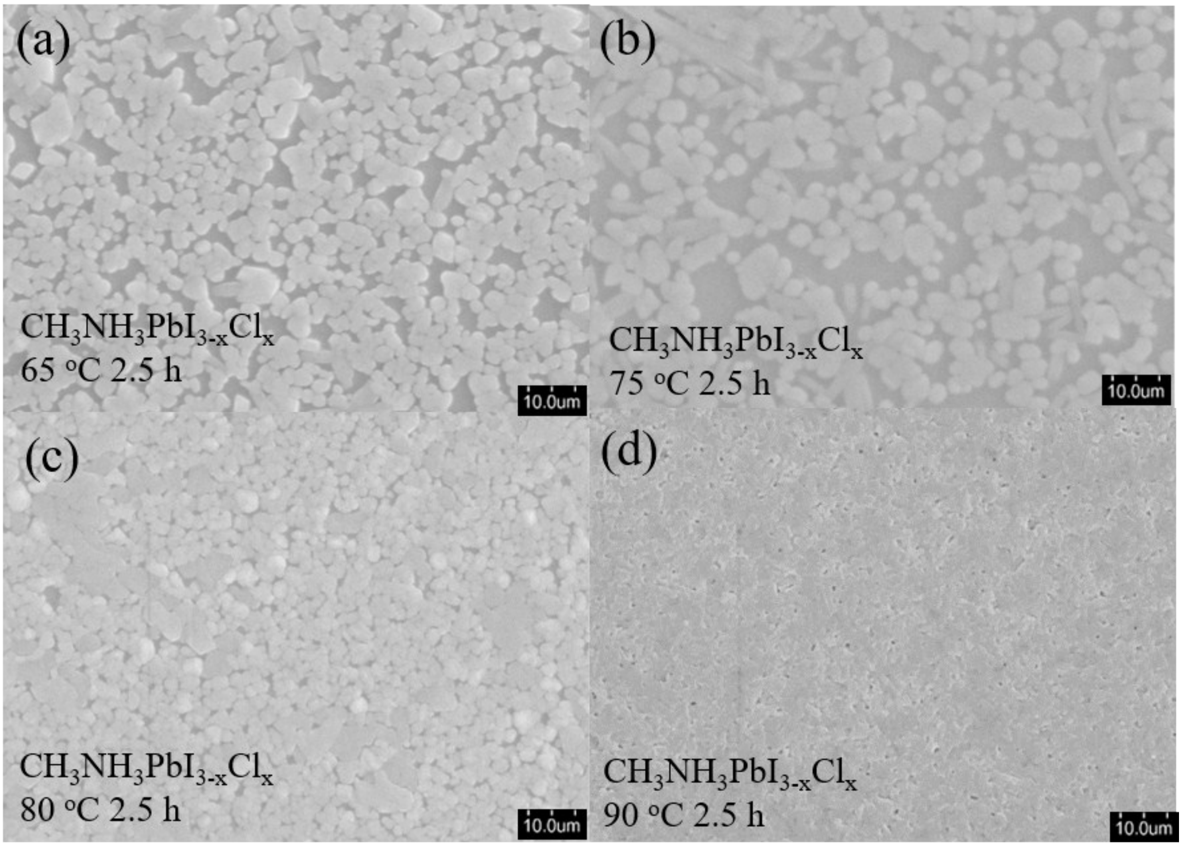

Fig. S3 FE-SEM images of $MAPbI_{3-x}Cl_x$ perovskite thin films at different annealing times and temperature of (a) to (d) were annealing for 2.5 hours at temperature of 65 ^{o}C, 75 ^{o}C, 80 ^{o}C, 90 ^{o}C respectively. ; magnification by 5000 times.

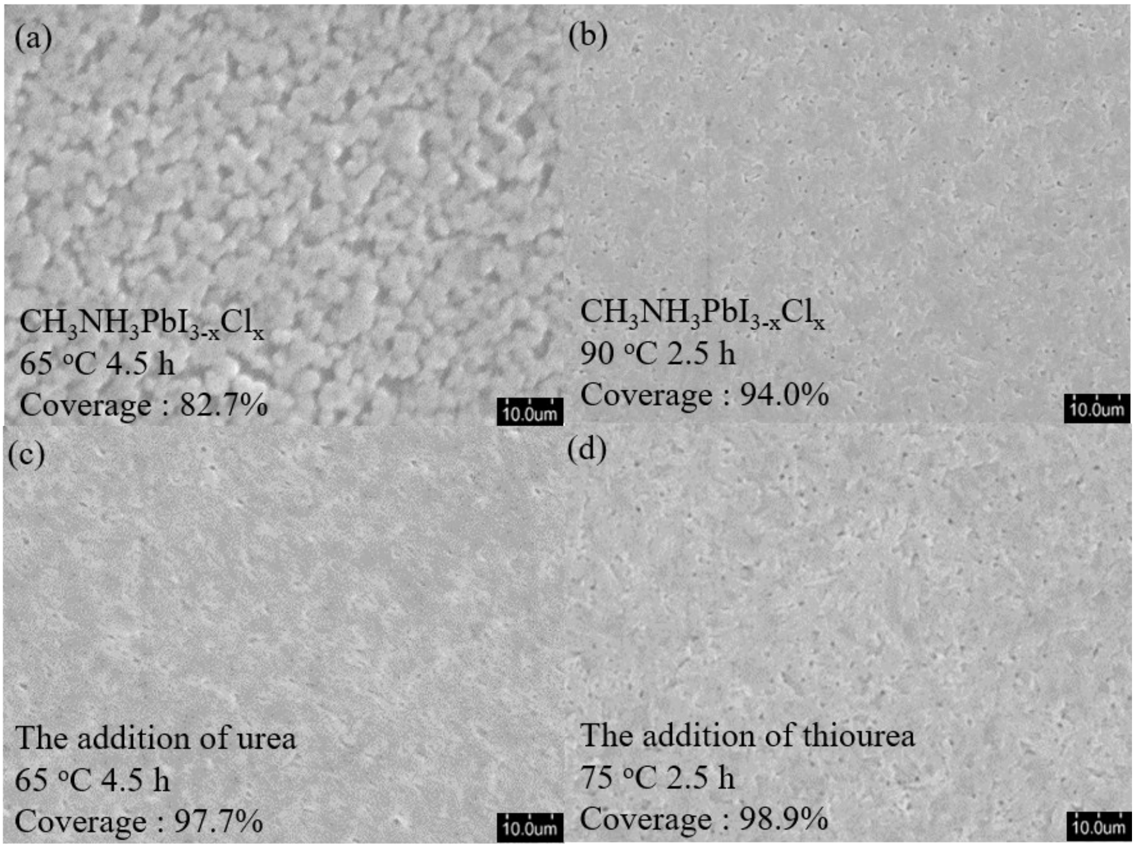

Fig S4. FE-SEM images and coverage of $CH_3NH_3PbI_{3-x}Cl_x$ perovskite thin films with different annealing temperatures (a) at 65 °C for 4.5 hours (b) at 90 °C for 2.5 hours (c) addition of 1% urea at 65 °C for 4.5 hours and (d) addition of 0.5% thiourea at 75 °C for 2.5 hours, respectively; magnification by 5000 times.

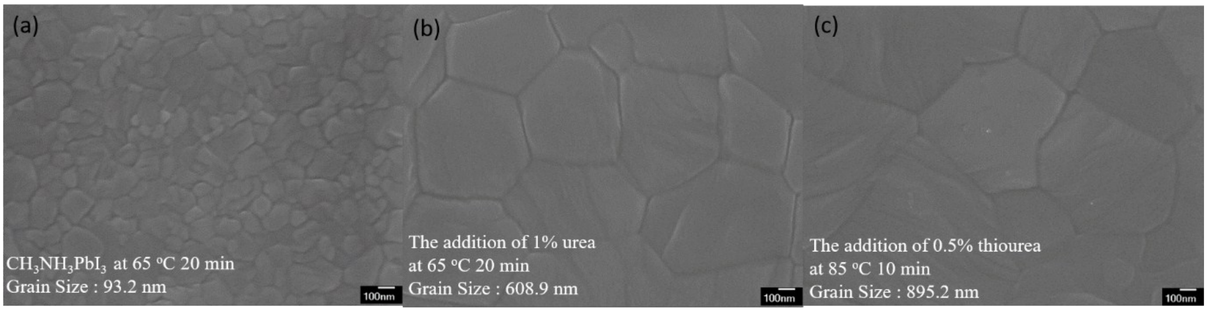

Fig. S5 FE-SEM images of $MAPbI_3$ perovskite thin films under different conditions (a) $MAPbI_3$, (b) addition of 1% urea, (c) addition of 0.5% thiourea at 65 °C for 20 min, respectively, magnification by 50000 times.

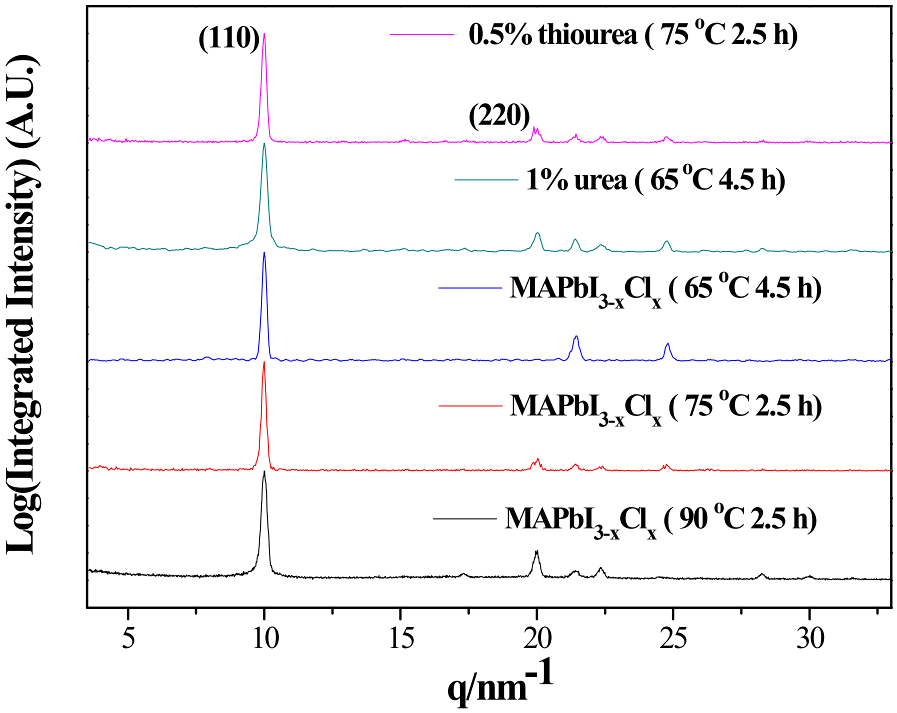

Fig. S6 GIWAXS patterns for $MAPbI_{3-x}Cl_x$ thin films with different annealing temperature after using urea and thiourea as additives.

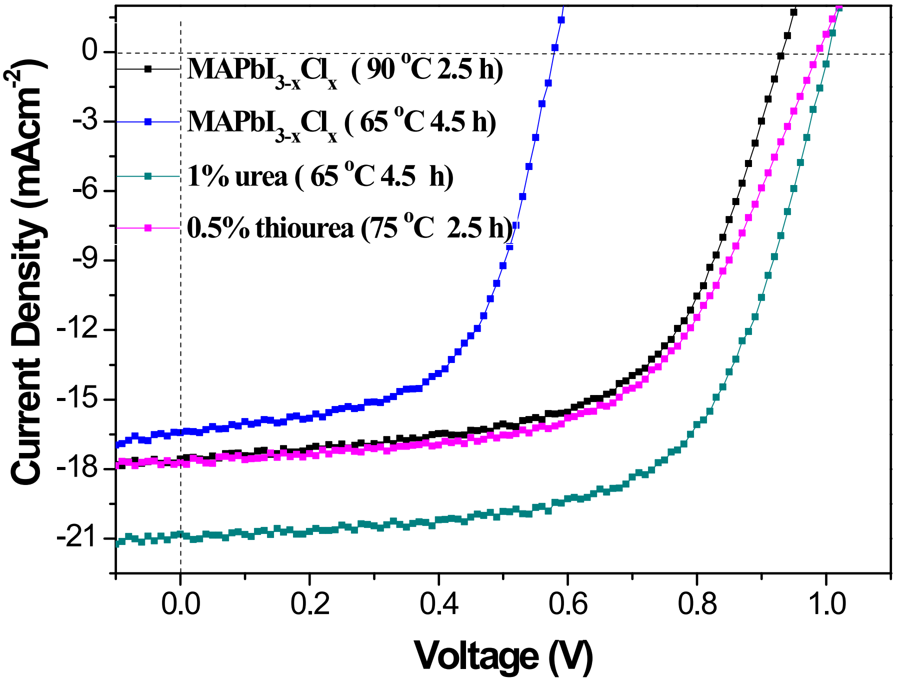

Fig. S7 J-V curves of the $MAPbI_{3-x}Cl_x$ devices with thin films prepared under different annealing temperature after doping urea and thiourea.

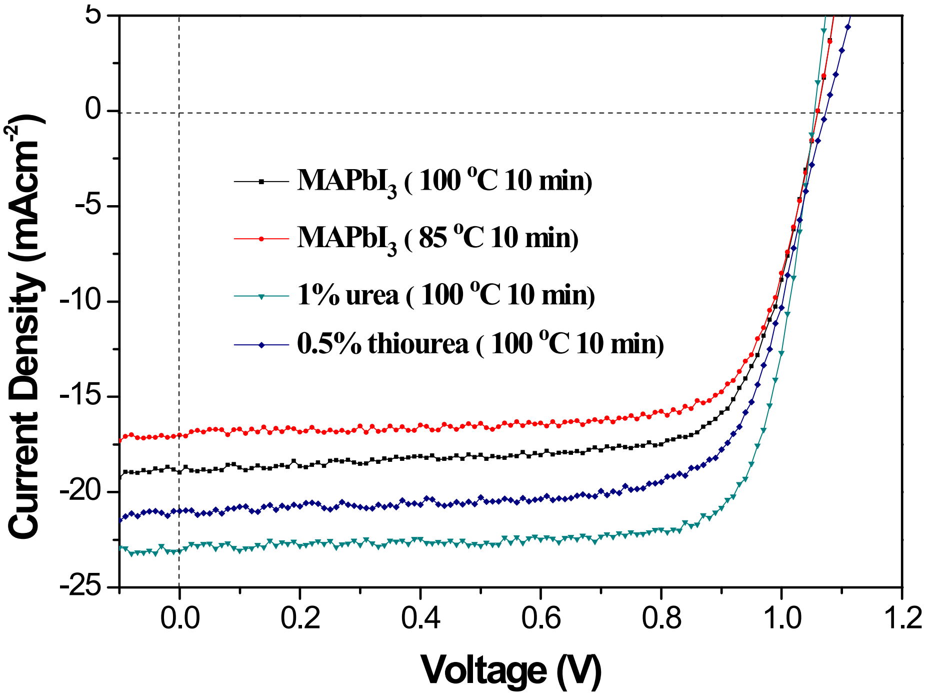

Fig. S8 J-V curves of the MAPbI$_3$ devices with thin films prepared under different annealing temperature after doping urea and thiourea.

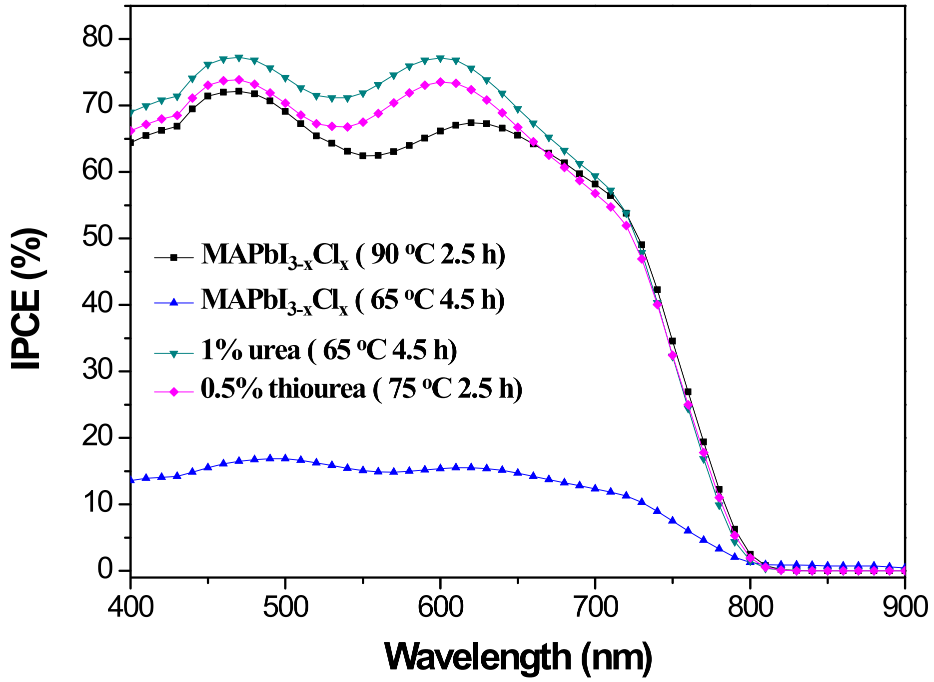

Fig. S9 Incident photon-to-current efficiency (IPCE) for $MAPbI_{3-x}Cl_x$ devices.

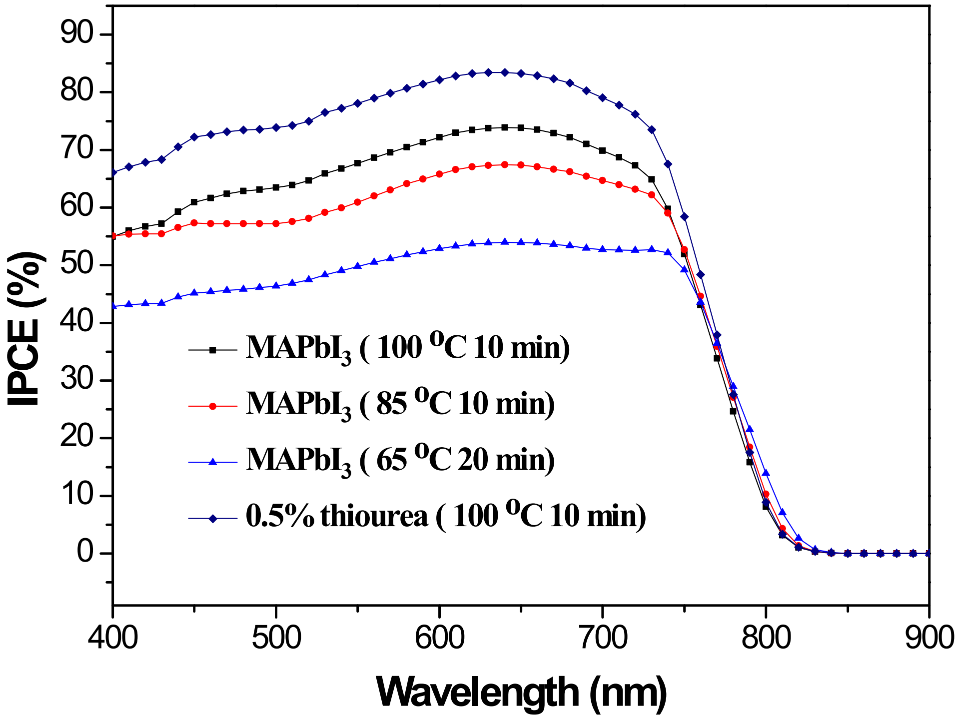

Fig. S10 Incident photon-to-current efficiency (IPCE) for $MAPbI_3$ devices.

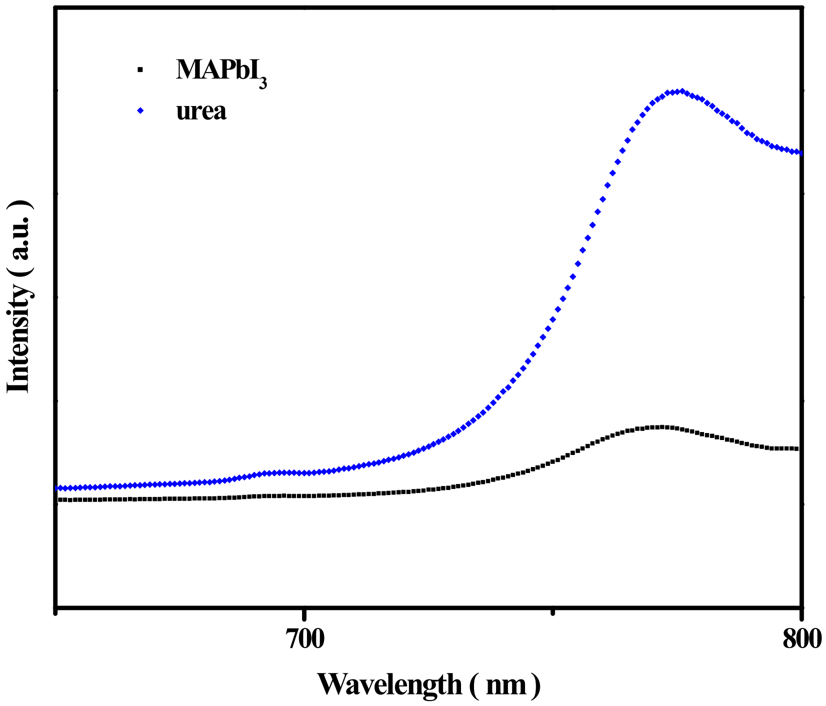

Fig. S11 PL spectra of the perovskites with or without urea.

Table S1. Photovoltaic parameters of MAPbI$_{3-x}$Cl$_x$ devices prepared using various fabrication conditions and different annealing temperature.

Devices	**Annealing condition**	J_{sc} **(mA cm^{-2})**	**V$_{oc}$ (V)**	**FF (%)**	**PCE (%)**	**Best PCE(%)**	**R$_{sh}$ (Ω cm^2)**	**R$_s$ (Ω cm^2)**
Normal	90 °C (2.5 h)	17.0±0.86	0.86±0.06	59.9±3.70	8.8±0.9	9.8	451.5	12.9
Control	65 °C (4.5 h)	16.1±0.88	0.52±0.06	49.1±8.42	4.1±1.0	5.6	231.6	3.7
thiourea	75 °C (2.5h)	17.9±0.62	0.93±0.03	60.3±0.51	10.1±0.2	10.2	453.5	25.4
urea	65 °C (4.5 h)	20.9±0.21	1.02±0.01	61.0±2.62	13.0±0.4	13.2	576.7	18.2

Table S2. Photovoltaic parameters of $MAPbI_3$ based PSC devices prepared under various fabrication conditions and different annealing temperature.

Devices	**Annealing condition**	J_{sc} **(mA cm^{-2})**	V_{oc} **(V)**	**FF (%)**	**PCE (%)**	**Best PCE (%)**	R_{sh} **(Ω cm^2)**	R_s **(Ω cm^2)**
Control	85 ^oC (10min)	16.7±0.4	1.07±0.01	73.7±0.7	13.1±0.3	13.4	1260.3	56.6
Control	65 ^oC (20min)	14.1±0.5	0.98±0.01	51.0±4.2	7.0±0.2	7.2	157.4	30.2
urea	100 ^oC (10min)	21.9±0.5	1.06±0.01	74.4±2.3	17.3±0.7	18.4	1982.8	33.8
urea	65 ^oC (20min)	20.5±0.1	1.06±0.01	73.5±0.7	15.9±0.3	16.2	1462.9	34.5
thiourea	100 ^oC (10min)	21.0±0.01	1.07±0.01	72.2±0.1	16.2±0.05	16.2	1030.2	30.2
thiourea	65 ^oC (20min)	17.8±1.2	0.99±0.0	50.0±0.3	8.8±0.6	9.2	172.7	22.6

Table S3. The parameters of J–V characterization of 1% urea (85 ^oC) dervied $MAPbI_3$ based perovskite devices under different scan directions.

Scans (delay times)	J_{sc} **(mA cm^{-2})**	V_{oc} **(V)**	**FF (%)**	**PCE (%)**
Forward(0.2s)	22.09	1.06	78.7	18.4
Reverse(0.2s)	22.25	1.07	77.4	18.4
Forward(0.1s)	22.74	1.06	77.6	18.7
Reverse(0.1s)	22.58	1.06	78.5	18.8

Table S4. The lifetime of perovskite thin films of $MAPbI_3$ based perovskite devices and addition of urea perovskite devices .

	τ_1 (ns)	**τ_2 (ns)**	**τ_3 (ns)**
$MAPbI_3$	10.3	2.3	41.1
urea	16.1	4.3	43.6

Table S5. Electrochemical impedance spectral (EIS) results of the PSC devices with and without urea.

Sample	**Rs/ Ω**	**R1/ Ω**	**C1-T/ F**	**C1-P**	**R2/ Ω**	**C2-T/ F**	**C2-P**
$MAPbI_3$	17.3	768.2	1.11E-8	0.97	3004	4.30E-5	0.55
urea	14.07	461.3	5.64E-9	1.0	3014	3.33E-5	0.57

1. G. E. Eperon, D. Moerman and D. S. Ginger, *ACS Nano*, 2016, **10**, 10258-10266.
2. H. Tan, A. Jain, O. Voznyy, X. Lan, F. P. Garcia de Arquer, J. Z. Fan, R. Quintero-Bermudez, M. Yuan, B. Zhang, Y. Zhao, F. Fan, P. Li, L. N. Quan, Y. Zhao, Z. H. Lu, Z. Yang, S. Hoogland and E. H. Sargent, *Science*, 2017, **355**, 722-726.