RSC Advances

Supporting Information

Low-Temperature Processed High-Performance Flexible Perovskite Solar Cells via Optimized Solvent Washing Treatment

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Experimental

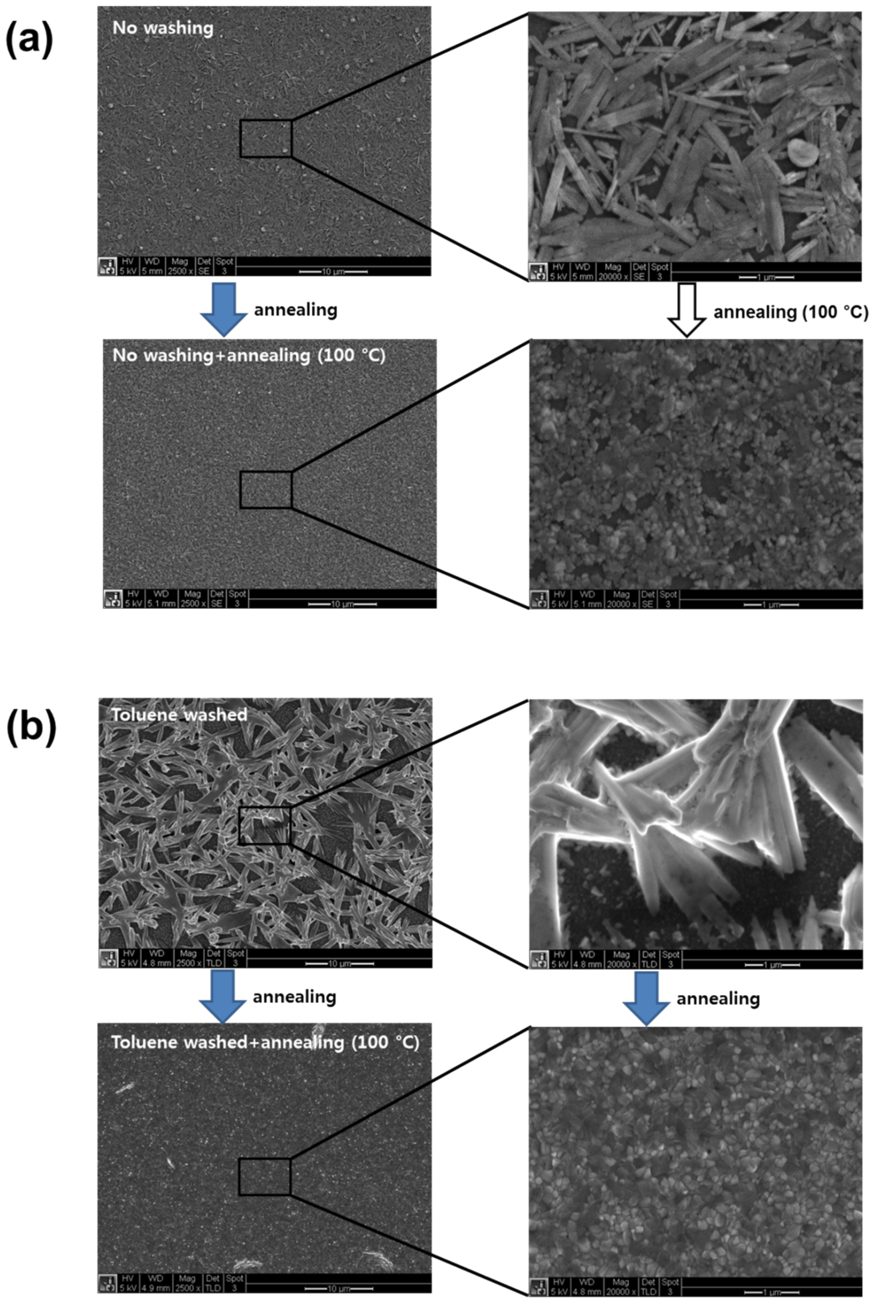
Materials and Sample Preparation. Methylammonium iodide was synthesized by reacting 24 mL of 0.20 mole methylamine (33 wt% in absolute ethanol, Aldrich), 10 mL of 0.04 mole hydroiodic acid (57 wt% in water with 1.5% hypophosphorous acid, Alfa Aesar), and 100 mL ethanol in a 250 mL round bottom flask under nitrogen at 0 °C for 1 h with stirring. After reaction, the white solid of MAI was recovered by rotary evaporation and then recrystallized in mixture of ethanol and diethyl ether. The CH_3NH_3I powder was collected and dried at 50 °C in a vacuum oven for 24 h. To prepare the perovskite precursor solution, CH_3NH_3I and PbI_2 (Aldrich) were dissolved in mixed solvent of dimethylsulfoxide and γ-butyrolactone (3:7 in volume) in 1 M concentration. The solution was stirred overnight at room temperature and filtered with 0.45 μm PVDF filters before spin-coating.

Fabrication of thin-film perovskite solar cells. The devices were fabricated as reported elsewhere.[S1] Briefly, ITO on glass (15 Ω/sq) or PET (50 Ω/sq) substrates were cleaned sequentially with detergent and deionized water, acetone, and isopropanol under sonication for 10 min. After drying under a N_2 stream, substrates were further cleaned by a plasma treatment for 30 s. PEDOT:PSS (Baytron P VP Al 4083, filtered through a 0.45 μm nylon filter) was first spin-coated onto the substrates at 5k rpm for 30 s and annealed at 95 °C for 10 min in ambient atmosphere. After the substrates were into N_2-filled glovebox, the precursor solution was spin-coated at 5k rpm for 45 s. After 25 s, 80 μl of non-polar solvent (toluene, CB or DCB) was poured on top of the substrates during spinnng. After thermal anneailng was finihed, PCBM (15 mg/mL in chloroform) and C_{60}-bis surfactant (2 mg/mL in isopropyl alcohol) were then sequentially deposited by spin coating at 1k rpm for 60 s and 3k rpm for 60 s, respectively. Silver electrodes with a thickness of 120 nm were finally evaporated under high vacuum ($< 2 \times 10^{-6}$ Torr). The device area was defined by the mask area as 3.14 mm^2. All the *J-V* curves in this study were recorded using a Keithley 2400 source meter unit and the scan rate was 1 V/s. For precise measurments of the solar cell performance, both forward and backward scans were recorded for each device. No hysterisises were observed (almosnt the same photovoltaic parameters such as V_{OC}, J_{SC} or FF) in our perovskite solar cell devices as shown in Fig. S4. The device photocurrent was measured under AM1.5 illumination condition at an intensity of 100 mW cm^{-2}. The illumination intensity of the light source was accurately calibrated with a standard Si photodiode detector equipped with a KG-5 filter, which can be traced back to the standard cell of the National Renewable Energy Laboratory (NREL). The EQE spectra performed here were obtained from an IPCE setup consisting of a Xenon lamp (Oriel, 450 W) as the light source, a monochromator, a chopper with a frequency of 100Hz, a lock-in amplifier (SR830, Stanford Research Corp), and a Si-based diode (J115711-1-Si detector) for calibration.

Characterizations. UV-Vis spectra were measured using a Perkin-Elmer Lambda-9 spectrophotometer. Surface of the perovskite thin films were observed using FEI Sirion SEM. X-ray diffraction was investigated by using X-ray diffractometer (Bruker D8 Discover). For time-resolved photoluminescene, the precursor solution was coated on top of the neat glass substrates or PEDOT:PSS coated ITO glass in the same manner to preparation of the solar cell device. To quench the electrons, PCBM layer was also deposited by spin-coating as same manner to the solar cell devices. PMMA was then deposited on top of the film spin-coating chloroform solutions (10 mg/ml) at 1000 rpm. The carrier life time was measured by a time-correlated single photon counting (TCSPC) system (FluoTime 100, PicoQuant GmbH).

Samples were photoexcited using a 467 nm laser beam (LDH-P-C-470, PicoQuant GmbH) pulsed at frequencies between 0.5-10MHz with a pulse duration of 60 ps and fluence of ~10 nJ/cm^2 to avoid nonlinear effects such as exciton-charge annihilation, and the emission light was collected after passing a 665 nm long-pass filter to block reflected excitation laser. The lifetime was obtained by fitting the PL measured from perovskite films with a bi-exponential decay function of the form:

$$I(t) = A_1 \exp(-\frac{t}{\tau_1}) + A_2 \exp(-\frac{t}{\tau_2})$$


(a)
No washing
annealing
annealing (100 °C)
No washing+annealing (100 °C)
(b)
Toluene washed
annealing
annealing
Toluene washed+annealing (100 °C)
10 μm
1 μm

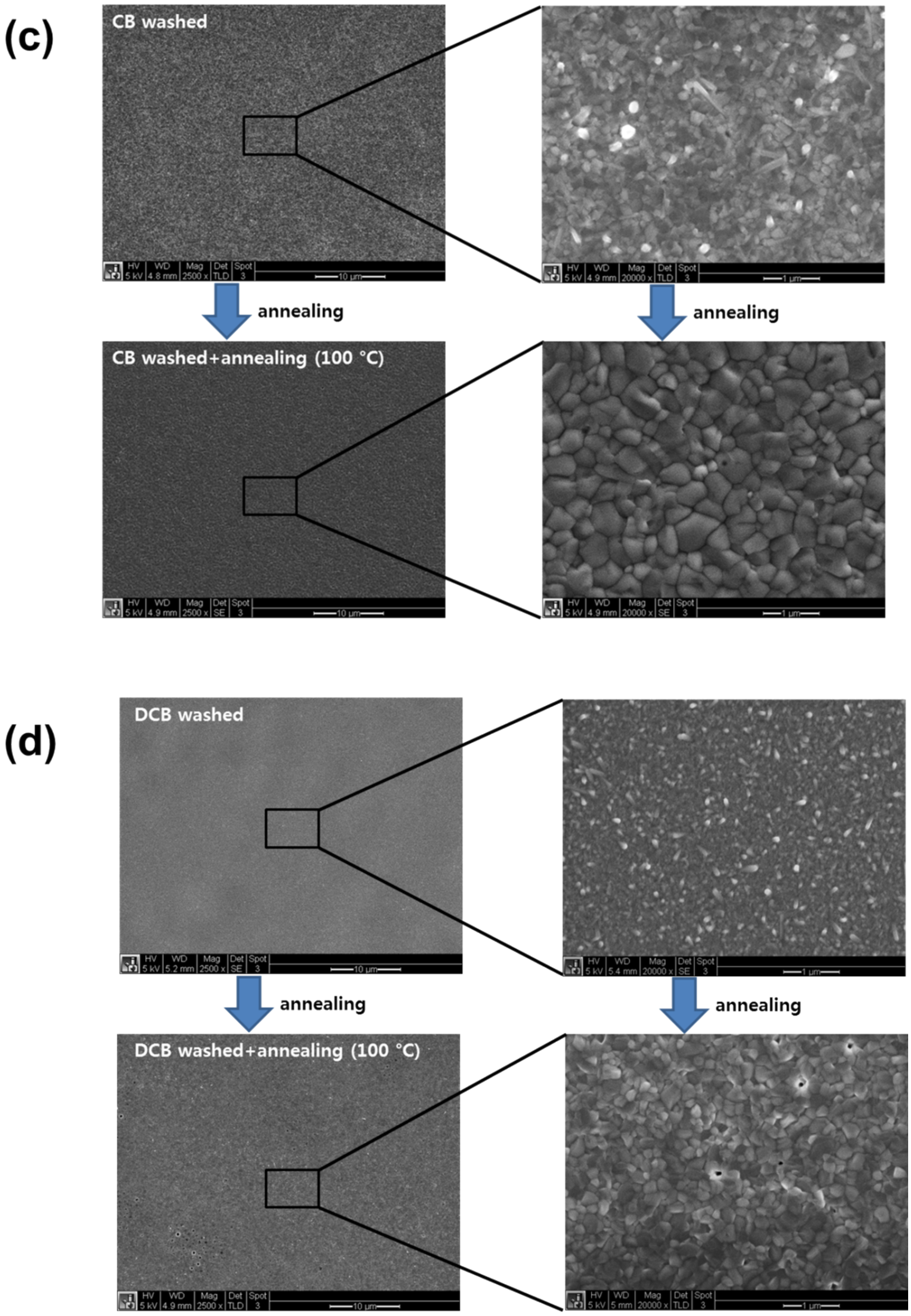


Fig. S1 SEM images of surface morphology of $CH_3NH_3PbI_3$ thin films fabricated through solvent washing (top) and subsequent thermal annealing at 100 °C (bottom). (a) no solvent washing, (b) toluene washing, (c) CB washing, (d) DCB washing

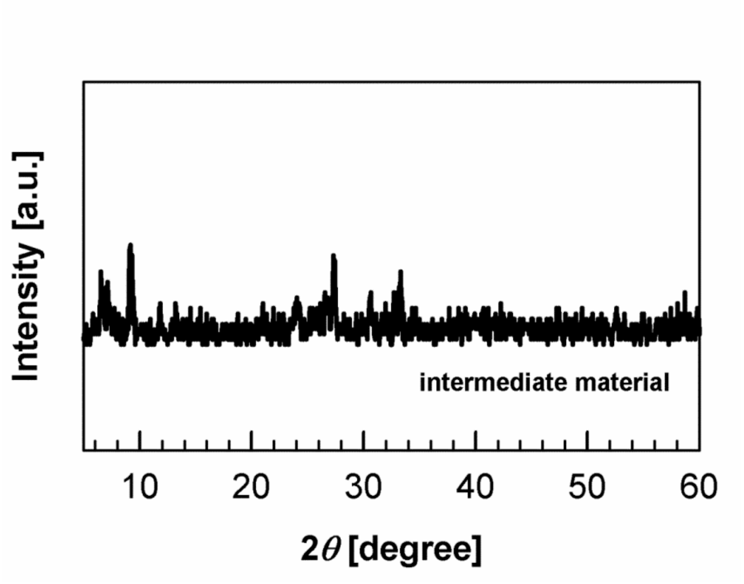


Fig. S2 X-ray diffractogram of intermediate phase materials.

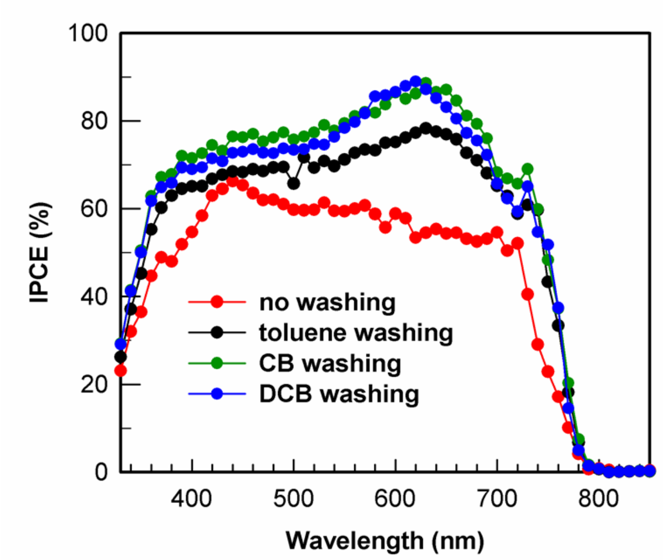


Fig. S3 IPCE spectra of the PSCs processed by different washing solvent.

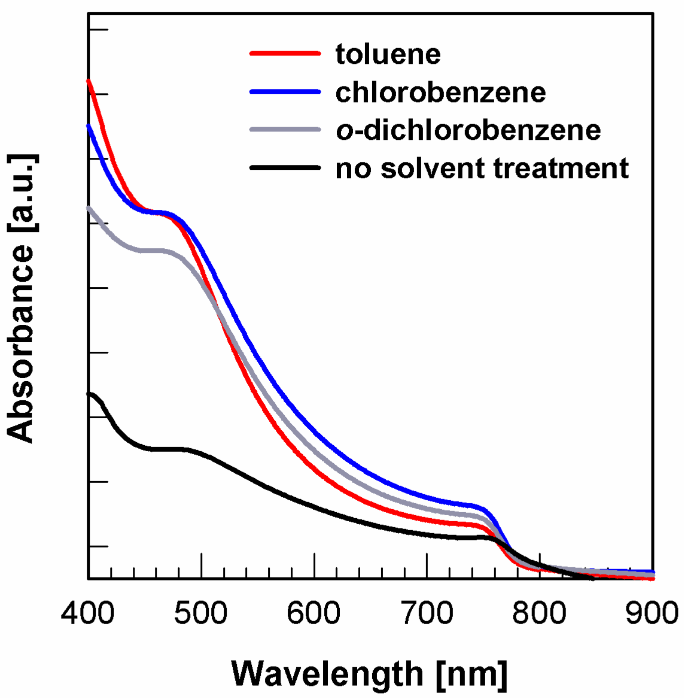


Fig. S4 UV-Vis absorption spectra of the perovskite films fabricated through solvent-washing and thermal annealing at 100 °C for 15 min.

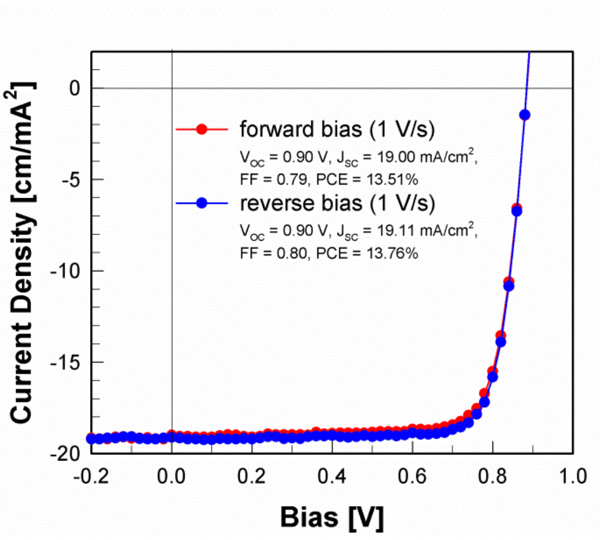


Fig. S5 J-V curves of forward and reverse scan from CB-washed PSCs.

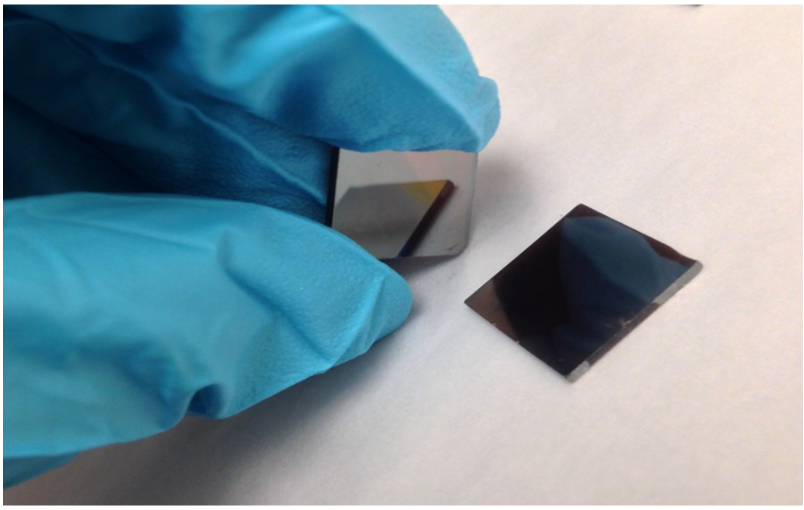


Fig. S6 Photograph of CB-washed perovskite film. Two films are annealed at 60 °C for 10 min and showing mirror-like smooth surface with dark film color.

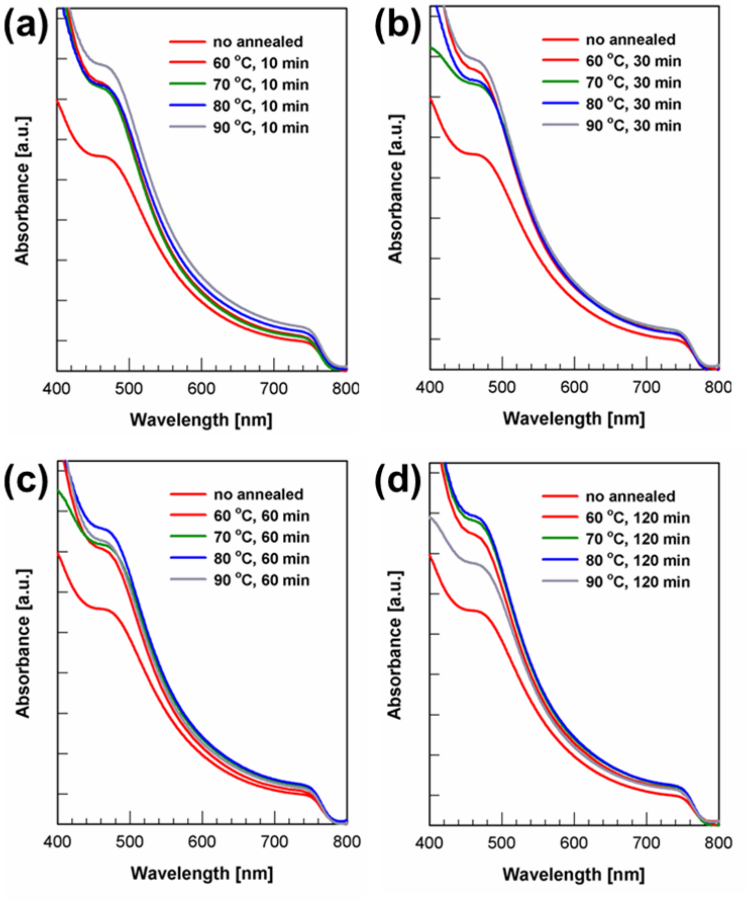


Fig. S7 UV-Vis absorption spectra of the perovskite films fabricated through solvent-washing and low-temperature annealing for (a) 10 min, (b) 30 min, (c) 60 min, and (d) 120 min.

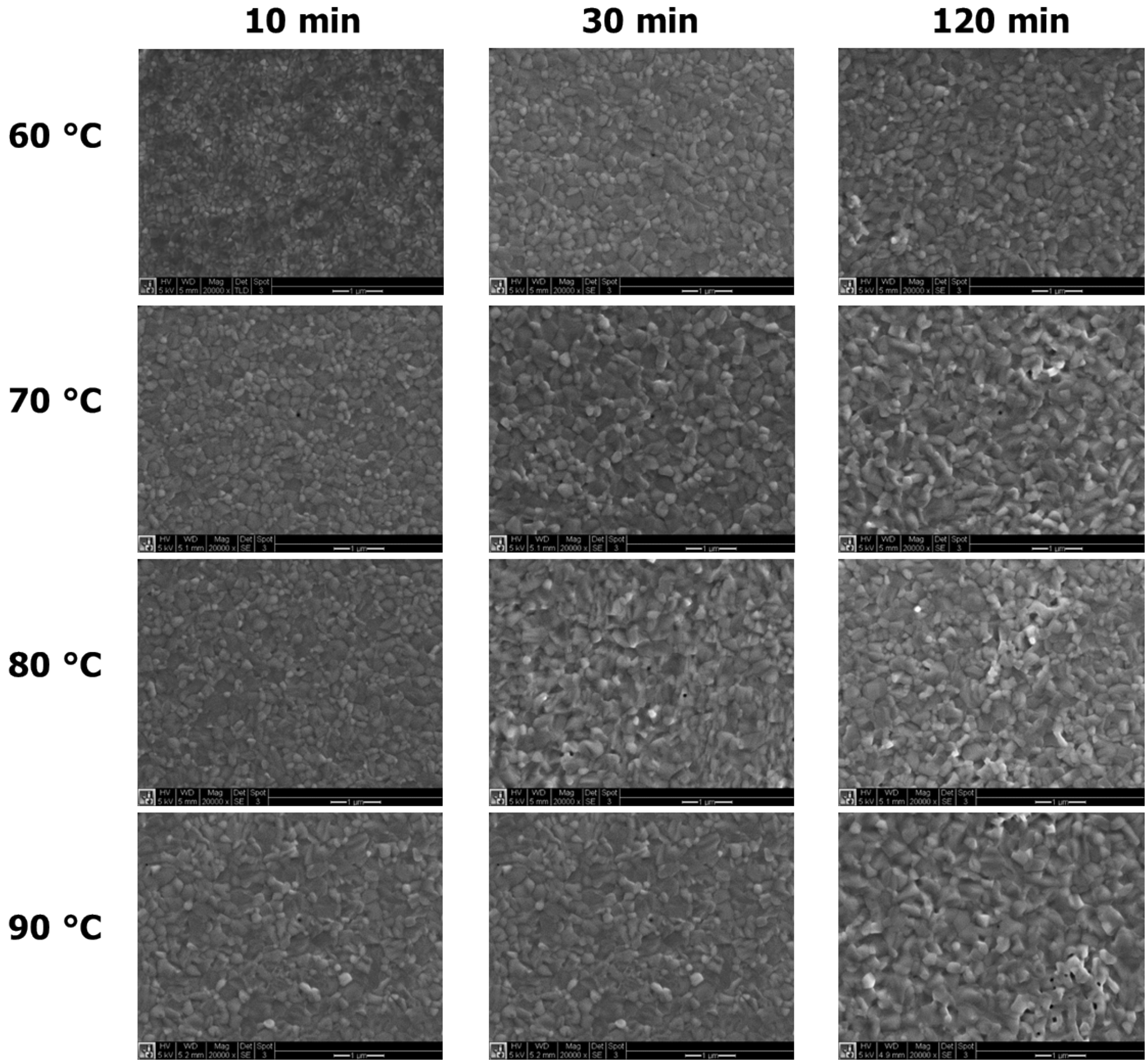


Fig. S8 SEM images of surface morphology of perovskite thin films fabricated through CB washing and subsequent low-temperature annealing for different time.

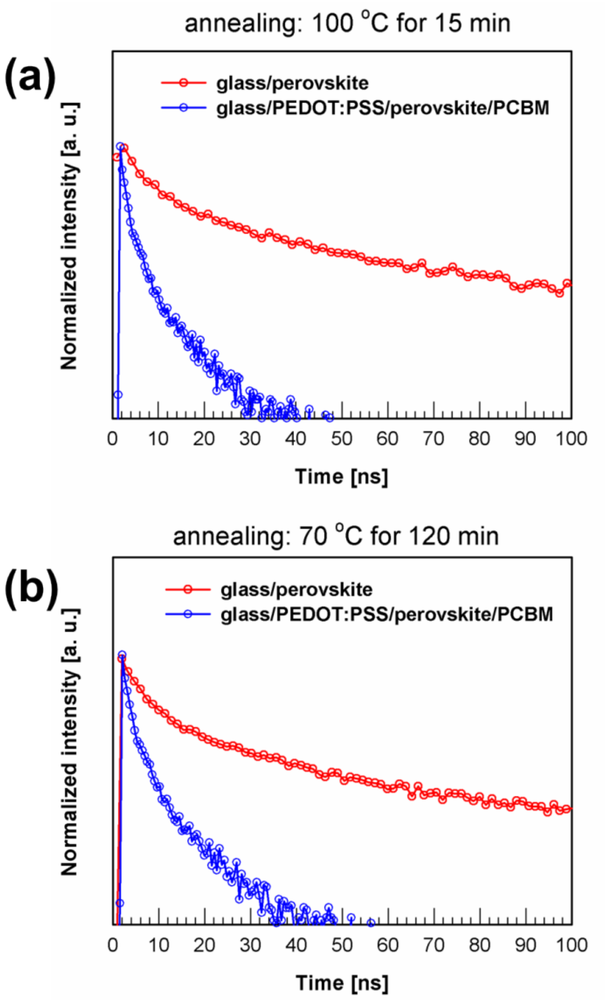


Fig. S9 Time resolved photoluminescence characterization of the CB-washed perovskite films annealed at (a) 100 °C and (b) 70 °C.

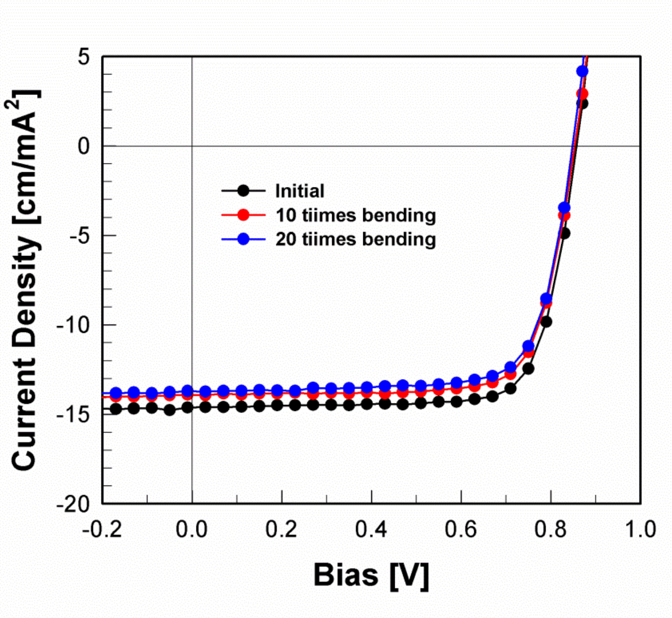


Fig. S10 J−V curvse of the perovskite solar cells on flexible substrated after different bending time. (Initial: V_{OC} = 0.86 V, J_{SC} = 14.62 mA/cm^2, FF = 0.75, PCE = 9.43%; 10 times bending: V_{OC} = 0.86 V, J_{SC} = 13.91 mA/cm^2, FF = 0.74, PCE = 8.85%; 20 times bending: V_{OC} = 0.85 V, J_{SC} = 13.57 mA/cm^2, FF = 0.73, PCE = 8.42%)

Table S1. Comparison of performance of the solution-processed flexible perovskite solar cells with other devices reported in the literature.

Reference	annealing temperature (°c)	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	PCE (%)
this work	70	0.86	14.62	0.75	9.43
S2	70	0.80	7.52	0.43	2.59
S3	90	0.86	16.5	0.64	9.08
S4	100	0.88	14.4	0.51	6.46
S5	-[a]	1.04	14.3	0.47	6.99

[a] vacuum deposition

Reference

S1. Liang *et al.*, *Advanced Materials*, **2014**, *26*, 3748.
S2. Kumar *et al.*, *Chemical Communications*, **2013**, *49*, 11089.
S3. You *et al.*, *ACS Nano*, **2014**, *8*, 1674
S4. Docampo *et al.*, *Nature Communications*, **2014**, *4*, 2761.
S5. Roldán-Carmona et al., *Energy &Environmetal Science*, **2014**, *7*, 994.