Supplementary Information

An efficient planar-heterojunction solar cell based on wide-bandgap $CH_3NH_3PbI_{2.1}Br_{0.9}$ perovskite film for tandem cell application

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Experimental details:

Materials

Lead iodide (PbI_2, 99.999%), Li-bis-(trifluoromethanesulfonyl) imide (Li-TFSI, 98%), dimethylformamide (DMF, anhydrous 99.5%), and 4-tert-butylpyridine (TBP, 98%) were purchased from Aladdin Reagents. Hydroiodic acid (47 wt % in water), hydrobromic acid (48 wt % in water) and methylamine (33 wt% in absolute ethanol) were purchased from Sigma-Aldrich. Diethanolamine, isopropanol (IPA), chlorobenzene, acetonitrile, tetrabutyl titanate and were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). 2,2',7,7'-tetrakis (N,N-di-p-methoxy-phenylamine)-9,9'-spirobifluorene (Spiro-MeOTAD, ≥99%) was purchased from Shenzhen Feiming Science and Technology Co., Ltd. (China). CH_3NH_3Br (MABr) and CH_3NH_3I (MAI) were synthesized by the recipe reported previously.

Solar cell fabrication

Preparation of the TiO_2 films: Fluorine-doped tin oxide (FTO) glass substrates with sheet resistance of about 14 Ω sq^{-1} were cleaned by ultrasonic washing in detergent solution, acetone, absolute alcohol, and deionized water for 30 min in succession, and then cleaned by UV-ozone treatment for 15 min. 30 μL TiO_2 sol was spin-coated on the pre-cleaned substrates to form compact TiO_2 layer with the thickness of about 60 nm by annealing at 480 °C for 40 min in air.

Preparation of $CH_3NH_3PbI_3$ ($MAPbI_3$) films and halide exchange with Br: 461 mg PbI_2 was dissolved in 1 mL DMF under vigorous stirring at 70 °C. The solution was spin-coated on the TiO_2 films at 3000 rpm for 30 s. After spinning, the films were dried at 70 °C for 5 min and then 95 °C for 15 min. To convert the PbI_2 layer to $MAPbI_3$, the MAI solution in IPA with the concentration of 45 mg mL^{-1} was spun on the top of PbI_2 layer at 3000 rpm for 20 s. The samples were then put on the top of a hot plate with the temperature of 100 °C and covered by a glass petri dish. During this process, 10 µL of DMF solvent was added at the edge of the petri dish the film. After about 90 min, the samples were cooled down to room temperature. Thus the sample $MAPbI_3$ films were obtained. In the halide exchange process, the obtained $MAPbI_3$ films were dipped in the solution of MABr in in IPA (5 mg/mL) for various durations at room temperature. After that, they were then annealed at 100 °C for 5 min to obtain the $MAPbI_{3-x}Br_x$ films. When the dipping time was 120 s, the $MAPbI_{3-x}Br_x$ film with the bandgap of 1.75 eV can be obtained.

Preparation of $MAPbI_{2.1}Br_{0.9}$ film by solvent annealing-induced interdiffusion process: 461 mg PbI_2 was dissolved in 1 mL DMF under vigorous stirring at 70 °C. The solution was spin-coated on the TiO_2 film at 3000 rpm for 30 s. After spinning, the film was dried at 70 °C for 5 min and then 95 °C for 15 min. To convert the PbI_2 layer to $MAPbI_{2.1}Br_{0.9}$ film, 45 mg mL^{-1} MAI: MABr blended solution in IPA with 50 wt% MABr was spun on the top of PbI_2 layer at 3000 rpm for 20 s. The sample was then put on top of a hot plate with the temperature of 100 °C and covered by a glass petri dish. During this process, 10 µL of DMF solvent was added at the edge of the petri dish the film. After about 90 min, the sample was cooled down to room temperature. Thus the $MAPbI_{2.1}Br_{0.9}$ film with the bandgap of 1.75 eV was attained.

Fabrication of Devices: 72.3 mg spiro-MeOTAD, 28.8 mL TBP and 17.5 µL lithium Li-TFSI in acetonitrile (520 mg/ml) were mixed in 1mL chlorobenzene to form the hole transport material (HTM) solution. Then, the solution was coated on the $MAPbI_{2.1}Br_{0.9}$ film to form HTM layer by spin-coating at 3000 rpm for 30 s. After being preserved in dark in dry box for 24 h, the Ag counter electrode with the thickness of about 100 nm and the area of 0.28 cm^2 was deposited on the top HTM layer by thermal evaporation technique.

Characterizations

A FEI NOVA NanoSEM230 scanning electron microscopy (SEM) was employed to characterize the morphological properties of the samples. X-Ray diffraction (XRD) patterns were collected on a Rigaku Ultima Ш X-ray diffractometer (Cu Kα) in the range of 10^o-60^o. A Shimadzu UV-2550 UV-vis spectrometer fitted with an integrating sphere was used to investigate the absorption properties of the samples. Time-resolved photoluminescence (PL) decay property was obtained using the time-correlated single-photon counting technique (Picoharp 300). The samples were photoexcited using a laser beam pulsed at 5 MHz. The incident photon conversion efficiency (IPCE) was measured using a 150 W xenon lamp (Oriel) fitted with a monochromator (Cornerstone 74004) as a monochromatic light source. The J-V curves of the fabricated solar cells were carried on a Keithley 2400 source measurement unit under AM1.5 illumination (standard 100 mW cm^{-2}) cast by an Oriel 92251A-1000 sunlight simulator calibrated by the standard reference of a Newport silicon solar cell. A black mask with a circular aperture (0.09 cm^2) was applied on top of the solar cell.

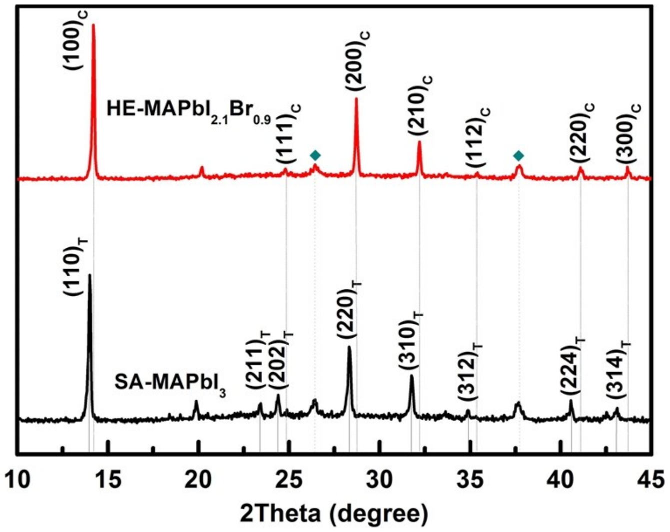

Fig. S1 The comparison of XRD patterns of the parent $MAPbI_3$ film (SA-$MAPbI_3$) with the $MAPbI_{2.1}Br_{0.9}$ films prepared by halide exchange (HE-$MAPbI_{2.1}Br_{0.9}$). The subscript "C" and "T" of the indices of lattice planes represent the cubic and tetragonal perovskite phase, respectively.

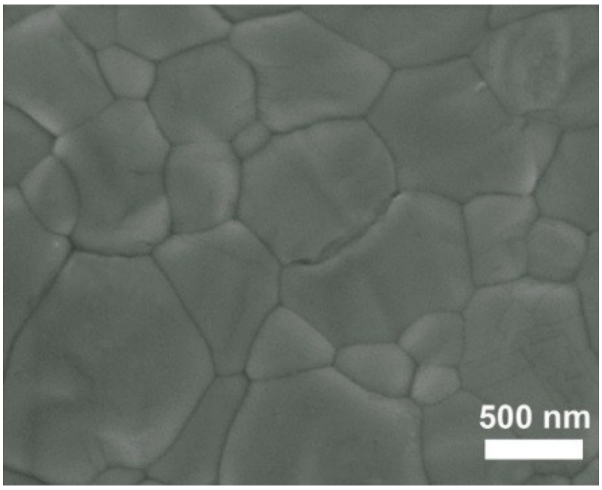

Fig. S2 The surface SEM images of the parent $MAPbI_3$ film prepared by solvent annealing-induced interdiffusion process.