Supporting information

Iodine (I) Expulsion at Photoirradiated Mixed Halide Perovskite Interface. *Should I Stay or Should I go?*

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Materials and Methods

Materials

Methylammonium iodide (MAI, Greatcell Solar), methylammonium bromide (MABr, Greatcell Solar), lead(II) iodide (PbI₂, ultra dry, 10 mesh beads, 99.999% metals basis, Alfa Aesar), lead(II) bromide (PbBr₂, Alfa Aesar, 99.999%), dimethyl sulfoxide (DMSO, anhydrous, ≥99.9%, Sigma-Aldrich), n,n-dimethylformamide (DMF, Sigma-Aldrich, anhydrous, 99.8%), diethyl ether (inhibitor-free, ≥99.9%, Sigma-Aldrich), 1-octadecene (ODE, 95%, SigmaAldrich), oleic acid (OAc, technical grade, 90%, Sigma-Aldrich), oleylamine (OAm, technical grade, 70%, Sigma-Aldrich) were used without further purification.

Perovskite film preparation

Perovskite films were fabricated using previously reported procedures^{1–3}. Briefly, 2.5 cm x 2.5 cm FTO coated glass substrates were washed with soap, rinsed with DI water and placed directly into an absolute ethanol bath. The FTO slides were sonicated for 20 minutes before being rinsed with isopropanol and dried with an airstream. To remove any remaining organics, the substrates were plasma cleaned for 10 minutes. The substrates were then transferred to a N₂ filled glovebox for spin coating of perovskite films.

For all perovskite films except CsPbBr_{1.5}I_{1.5}, the precursors were dissolved in DMF and DMSO. For all perovskite compositions, 0.056 g of PbI₂ and 0.045 g of PbBr₂ were used. The amount of other precursors used for each perovskite film composition are given in Table S1. Note that the Br:I ratio in each film is maintained at 1:1.

MA-Cs in	MAI	MABr	Csl	CsBr	Antisolvent	DMF	DMSO
Perovskite	(g)	(g)	(g)	(g)		(μL)	(µL)
MA _{1.0}	0.02	0.014	0	0	Diethyl ether	630	17
MA _{0.75} Cs _{0.25}	0.01	0.014	0.016	0	Diethyl ether	630	17
MA _{0.5} Cs _{0.5}	0	0.014	0.032	0	Chlorobenzene	580	65
MA _{0.25} Cs _{0.75}	0.01	0	0.016	0.026	Chlorobenzene	580	65

Table S1: The amount of precursor materials used for the preparation of the mixed-halide perovskite films.

The solutions were left to stir for 1 hour at room temperature and subsequently filtered through an inorganic membrane filter (0.2 µm pore size, G8549141, Whatman) before use. The MAPbBr_{1.5}I_{1.5} and MA_{0.75}Cs_{0.25}PbBr_{1.5}I_{1.5} films were obtained by static drop casting of 50 µL of precursors and subsequently spin coating at 4000 rpm for 25 s with an acceleration of 1200 rpm. An antisolvent treatment step with diethyl ether was used, with 0.5 mL being rapidly injected after 10 seconds. The films were immediately transferred to a preheated hotplate for 1 min at 65 °C, and then transferred to a 100 °C hotplate for 2 minutes. After annealing, the films were removed from the hotplate and left to cool down before use. The MA_{0.5}Cs_{0.5}PbBr_{1.5}I_{1.5} and MA_{0.25}Cs_{0.75}PbBr_{1.5}I_{1.5} films were obtained using static drop casting of 50 µL of precursors and subsequently spin coating at 1000 rpm for 10 s with an acceleration of 1200 rpm, then at 4000 rpm for 35 s with an acceleration of 1200 rpm. Here 0.1 mL chlorobenzene was used as the antisolvent and was rapidly injected after 20 seconds. The films were immediately transferred to a minutes at 200 °C. After annealing the films were removed from the hotplate and left to cool.

CsPbBr_{1.5} perovskite films were synthesized using a procedure reported from our group³. Briefly, CsPbBr₃ nanocrystals (NCs) were synthesized by modifying the method from Protesescu et al.⁴ Then bulk CsPbBr₃ films were created by using a sequential deposition method described by Hoffman et al.⁵ Aliquots of CsPbBr₃ NCs were spun cast onto FTO slides, which were cleaned as mentioned above. The NC films were annealed for 3 min at 250 °C to become bulk CsPbBr₃ films. The films were briefly washed with hexane in between deposition cycles. This process was repeated until 7 layers were deposited. Gradient halide perovskite films were prepared by soaking the as made CsPbBr₃ films in a lead iodide solution. The lead iodide solution was prepared by combining 68 mg of Pbl₂, 0.6 ml of OAm, 0.4 ml of OAc, and 20 ml of ODE at 170 °C while stirring until dissolved. The solution was cooled to 85 °C. Once at this temperature, a CsPbBr₃ slide was placed in the solution and allowed to react for 10 min. This reaction time was for the film thickness we used. The film (now a gradient perovskite) was rinsed thoroughly with hexane and dried with an air stream to remove any excess exchange solution. The gradient films thus obtained, were homogenized at 90 °C for 60 min, which gave a Br:l ratio of 1:1.

Characterization methods

Steady state UV-vis absorption spectra were recorded with a Cary 50 Bio spectrophotometer (Varian). Except for quantum efficiency measurements, a white light source (AMScope 150-A, 150 Watt halogen variable intensity fiber optic cold light source) was used. For quantum efficiency measurements, a 405 nm CW diode laser with an intensity of 100 mW cm⁻² was used. A neutral density filter was used to control the power of the incident light.

Top-down scanning electron microscopic (SEM) images were captured using a FEI SEM Magellan 400 digital field emission scanning electron microscope operated with a beam voltage of 2 kV.

Surface halide composition analysis was performed using X-ray Photoelectron Spectroscopy, XPS on a PHI VersaProbe II. The compositional analysis was performed using 15kV high power point.

Quantum efficiency calculations

To quantify the iodide expulsion effect, the amount of triiodide generated with photoirradiation was calculated. Since the absorbance of the triiodide species in solution was known, the concentration was calculated from Beer's law. Using the absorption coefficient at 364 nm (2.32 x 10^4 L/mol) and the absorbance of the DCM after 30 min of irradiation the concentration of I_3^- was calculated for each perovskite film. The amount of triiodide can be further used to calculate the quantum efficiency of triiodide expulsion from the perovskite. For calculating the quantum efficiency, a blue laser diode (λ_{max} =405 nm) was used to irradiate the sample. The number of photons, $n_{photons}$, of energy corresponding to the energy of photons emitted by the lamp is given by Equation S1:

$n_{photons}$ = (Power/E)/ N_A (S1)

where E is the energy of the lamp and N_A is the Avogadro's constant. Thus, it was found that 0.76 µmol of photons were generated per second. Since this experiment was over 30 minutes, the total number of photons absorbed by the perovskite was found to be 0.0007 mol. The quantum efficiency of this process for iodide expulsion was determined from the ratio of the number of 3/2 (moles triiodide species (n_{I_3})) and the moles of photons absorbed $(n_{photons})$.

$$QE(\%) = 100 \times \frac{3 \times n_{l_3^-}}{2 \times n_{photons}}$$

Since one mole of I_3^- corresponds to 3 iodide species following the absorption of two photons (reactions 3 and 4 of main text) we employed a multiplication factor of 3/2.





Figure S2. UV-Vis absorbance spectra of $FTO/MA_{0.5}Cs_{0.5}PbBr_{1.5}I_{1.5}$ film under visible light irradiation.









Figure S6: Top-down SEM images of (A) $MAPbBr_{1.5}I_{1.5}$ (B) $MA_{0.5}Cs_{0.5}PbBr_{1.5}I_{1.5}$ (C) $CsPbBr_{1.5}I_{1.5}$ immersed in DCM for 16 hours (without irradiation). No changes in the morphology are apparent upon exposure to DCM.





Figure S8: XPS spectra of MA_{0.5}Cs_{0.5}PbBr_{1.5}I_{1.5}. The probed regions were (A)I3d and (B)Br3d. From the XPS analysis using pseudo-Voigt fitting parameters, the concentration of bromide and iodide ions on the surface of the films was determined (Table S2).

		I (%)	Br (%)
MAPbBr _{1.5} I _{1.5}	Before irradiation	47.4 ±0.38	52.6 ±0.38
	After irradiation	1.8±1.31	98.2±1.31
$MA_{0.5}Cs_{0.5}PbBr_{1.5}I_{1.5}$	Before irradiation	50.6 ±0.25	49.5 ±0.25
	After irradiation	37.1 ±2.1	62.9 ±2.1

Table S2: Compositional analysis of surface of perovskite films before and after irradiation determined from XPS measurements.

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