Supporting Information

Mechanosynthesis of pure phase mixed-cation MA$_x$FA$_{1-x}$PbI$_3$ hybrid perovskite: photovoltaic performance and electrochemical properties

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Experimental

Materials and Methods

All the perovskite powders were synthesized by grinding an organic salts (MAI and FAI) and PbI₂ in an electric ball mill (Retsch Ball Mill MM-200, agat grinding jar with a volume of 10 ml and 1 agat ball, diameter size 10 mm) for 30 min at 30 Hz. 0.039 g of MAI (0.25 mmol), 0.129 g (0.75 mmol) of FAI and 0.461 g (1.00 mmol) of PbI₂ were mixed to prepare the (MA)₀.₂₅(FA)₀.₇₅PbI₃ black powder. The synthesis was conducted in glove box under an argon atmosphere. Other materials were obtained by the same procedure.

Solar cell device fabrication

Devices were prepared on plasma-cleaned conductive fluorine-doped tin oxide (FTO) coated glass substrates. A compact thick titanium dioxide layer was deposited by spray pyrolysis of 9 ml ethanol solution containing 0.6 mL titanium diisopropoxide bis(acetylacetonate) solution (75% in 2-propanol, Sigma-Aldrich) and 0.4 mL acetylacetone at 450° C in air. On top of this compact layer, a 150 nm-thick mesoporous titanium dioxide layer was prepared by spin-coating 30 nm sized nanoparticles (Dyesol 30NRD, Dyesol) diluted in ethanol (1:6 wt/wt) at 5000 rpm for 10 s. The films were then gradually heated to 500 °C and sintered at that temperature for 1.5 h under oxygen atmosphere. The stock 1.3 M solution of (MA)₀.₂₅(FA)₀.₇₅PbI₃ mechanoperovskite particles was prepared by dissolving them in anhydrous DMSO by vigorous stirring at 60 °C. Perovskite stock reference solution in anhydrous DMSO was prepared from PbI₂ (0.598 g) by mixing it with MAI (0.05 g) and FAI (0.166 g) by vigorous stirring at 60°C. The perovskite solution was spin coated in a two steps program at 1000 and 6000 rpm for 10 and 20 s respectively. During the second step, 100 µL of chlorobenzene was poured on the spinning substrate 10 s prior to the end of the program. The substrates were then annealed (at 100 °C unless stated otherwise) for 30 min in a nitrogen filled glove box. Hole transporting material (HTM) solution was prepared by dissolving 74 mg spiro-MeOTAD in 1 ml chlorobenzene and additionally mixing it with 17.5 µL of lithium bis(trifluoromethylsulphonyl)imide (stock solution Li-TFSI 520 mg·mL⁻¹ in acetonitrile), 28.8 µL tert-butylpyridine and 29 µl of tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)cobalt(III) bis(trifluoromethylsulphonyl) imide (stock solution FK 209, 300 mg·ml⁻¹ in acetonitrile). Subsequently, HTM was deposited on top of the perovskite layer by spin coating at 4000 rpm for 20 s. Finally, 80 nm of gold top electrode was thermally evaporated under high vacuum. The active area of the devices is approximately 0.16 cm².
Device characterization

Current voltage characterization
The J-V characteristics of the devices were measured under 100 mW/cm² conditions using a 450 W Xenon lamp (Oriel), as a light source, equipped with a Schott K113 Tempax sunlight filter (Prazisions Glas & Optik GmbH) to match the emission spectra to the AM1.5G standard in the region of 350-750 nm. The current–voltage characteristics of the devices were obtained by applying external potential bias to the cell while recording the generated photocurrent using a Keithley (Model 2400) digital source meter. The J–V curves of all devices were measured by masking the active area with a metal mask of area 0.16 cm². AC measurements were performed using a potentiostat Biologic SP300 equipped with a frequency response analyser. IS measurements were performed in the DC bias range of 0 to open circuit voltage with an AC perturbation signal of 10 mV in the frequency range of 1 Hz to 100 kHz.

Techniques

Powder X-Ray diffraction
Powder XRD data were collected on Empyrean diffractometer (PANalytical). Measurements employed Ni-filtered Cu Kα radiation of a copper sealed tube charged with 40 kV voltage and 40 mA current and Bragg-Brentano geometry with beam divergence of 1 deg. in the scattering plane. Diffraction patterns were measured in the range of 4-50 degrees of scattering angle by step scanning with step of 0.02 degree.

Structure characterization
The surface morphology of the perovskite film was explored by a ZEISS Merlin HR-SEM.

Optical properties
UV–vis measurements were performed on a Varian Cary 5.

![Fig 1S. UV-Vis absorption spectra of the investigated (MA)₀.₂₅(FA)₀.₇₅PbI₃ thin film.](image-url)
**Fig. S2.** IPCE spectrum of the investigated (MA)$_{0.25}$(FA)$_{0.75}$PbI$_3$ device.

**Fig. S3.** Photovoltaic characteristics of (MA)$_{0.25}$(FA)$_{0.75}$PbI$_3$ device containing perovskite material synthesized from the direct solvothermal reaction between precursors.
Fig. S4. Comparison of experimental and simulated PXRD patterns for a) (MA)$_{0.25}$(FA)$_{0.75}$PbI$_3$ thin film, b) α-FAPbI$_3$, c) δ-FAPbI$_3$ and d) PbI$_2$. Reflection of FTO are labelled with (#).