

Direct Conversion of Pb (& Sn) metal to Halide Perovskite Films

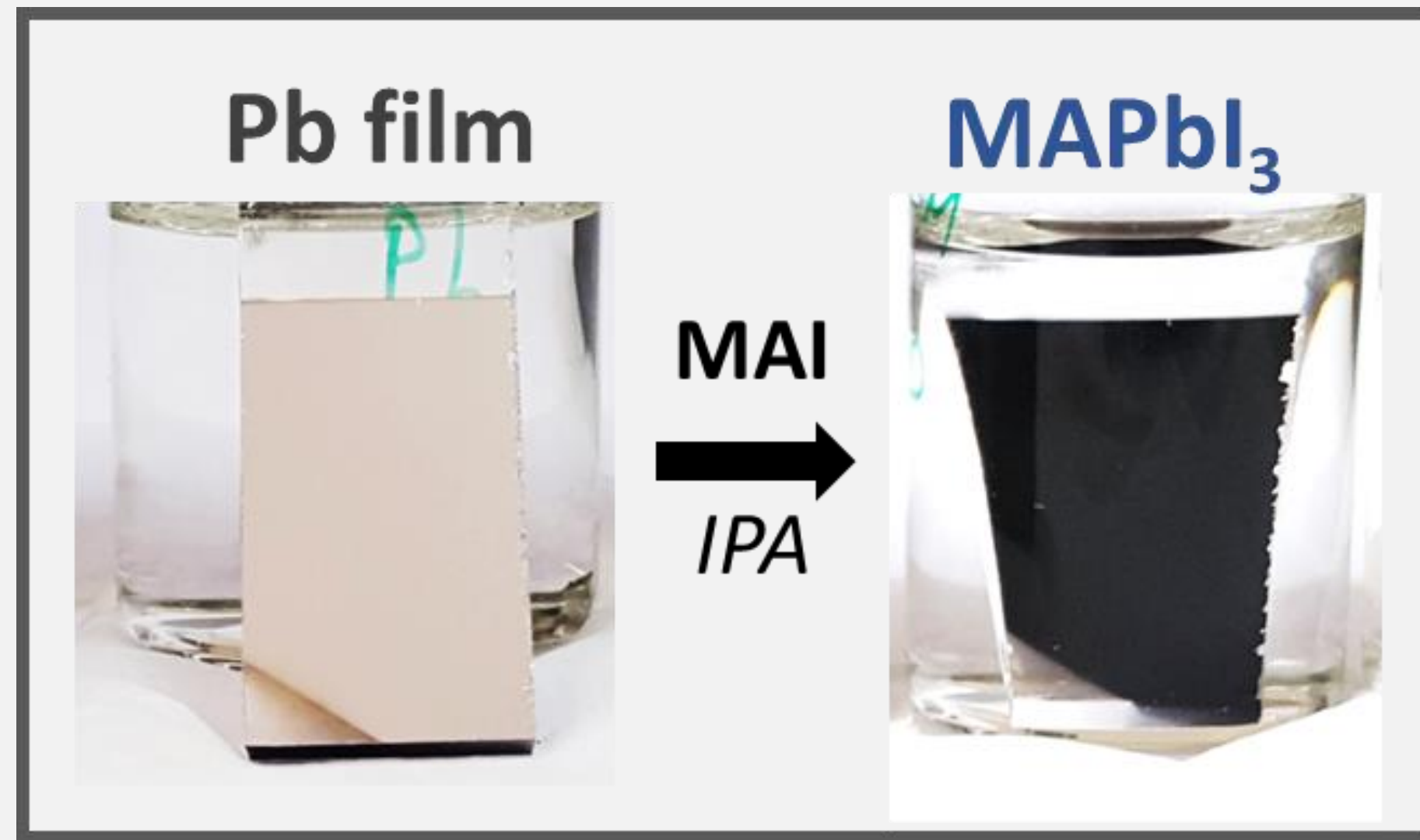
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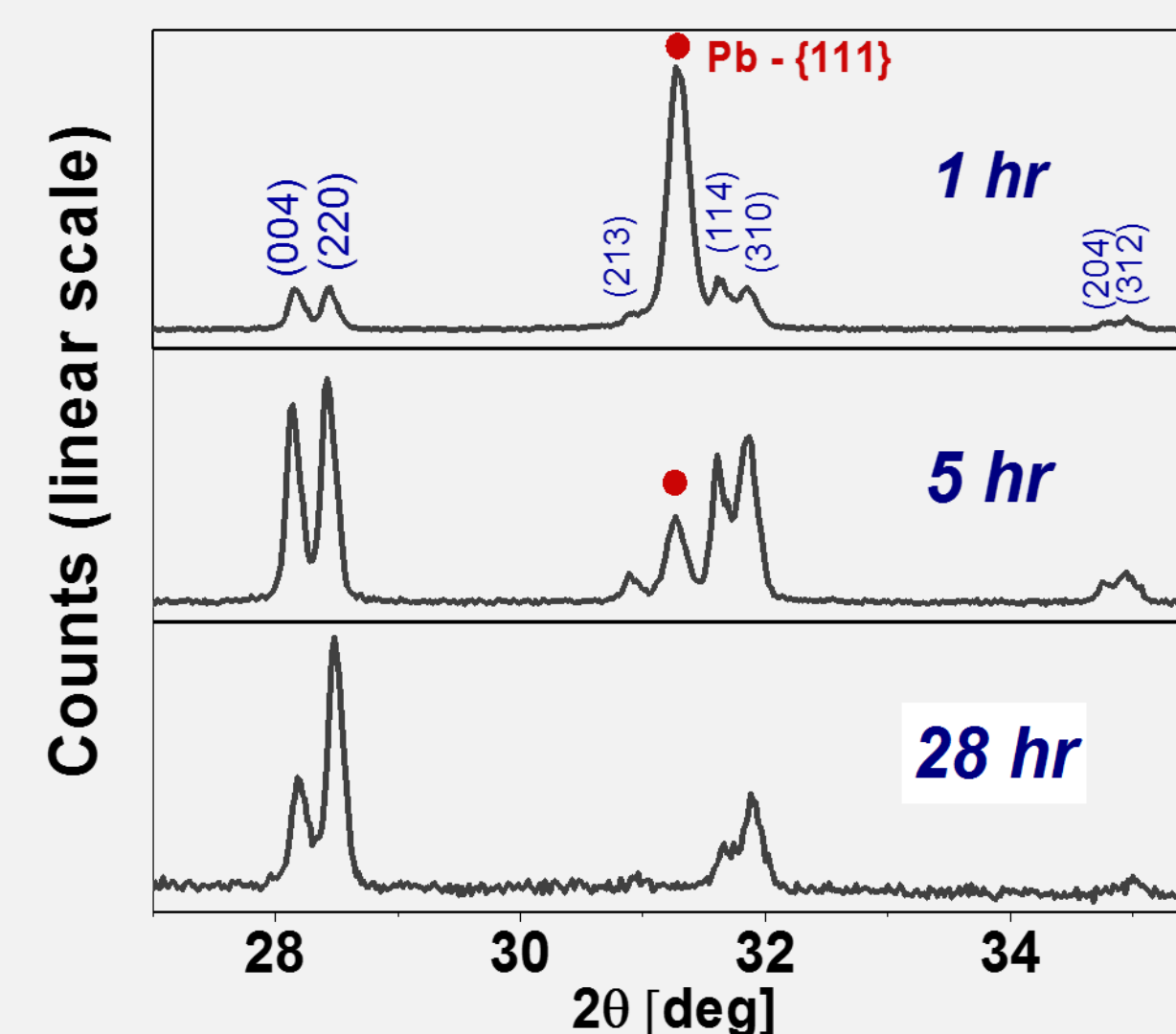
Thin films of halide perovskites (AMX_3 ; A = methylammonium (MA), formamidinium (FA) or Cs; M = Pb or Sn; X = Br, I) are usually synthesized by spin- or spray- coating of a precursor solution (of an aprotic solvent, e.g., dimethylformamide, dimethylsulfoxide) containing MX_2 and/or AX . Such solutions are *highly toxic if they contain MX_2* . Alternatively thermal evaporation of MX_2 and/or AX , is done, a rather complex procedure. Whenever MX_2 is deposited first, sequential dipping of an alcoholic solution (usually iso-propyl alcohol, IPA) of AX onto the film is done. We show a **third approach**, where a metallic coating of thermally evaporated Pb (or Sn) is transformed into a halide perovskite layer, by dipping it in an alcoholic (e.g., methanol, ethanol, IPA) solution of the relevant AX salt.

Overview

Following the transformation reaction

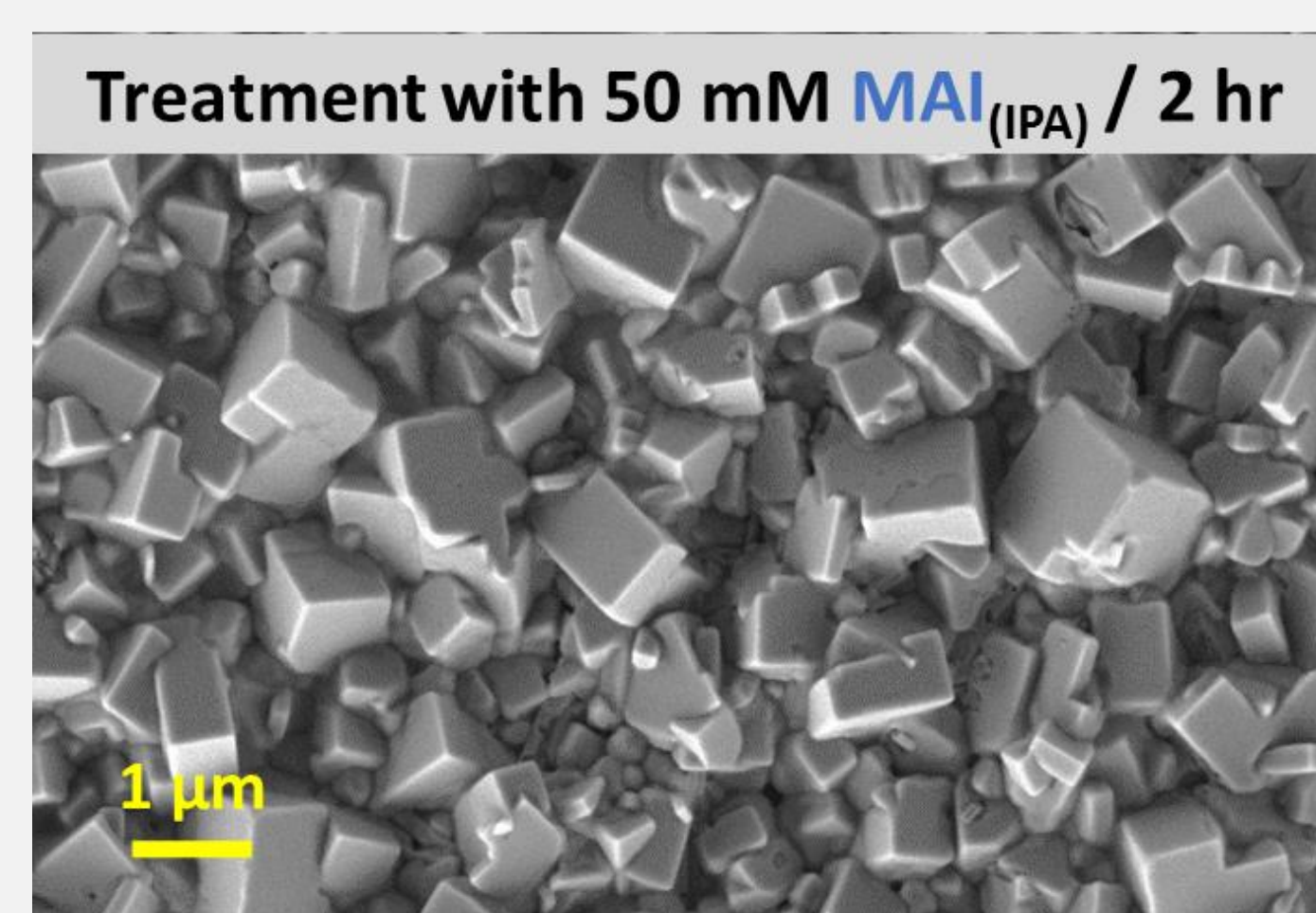
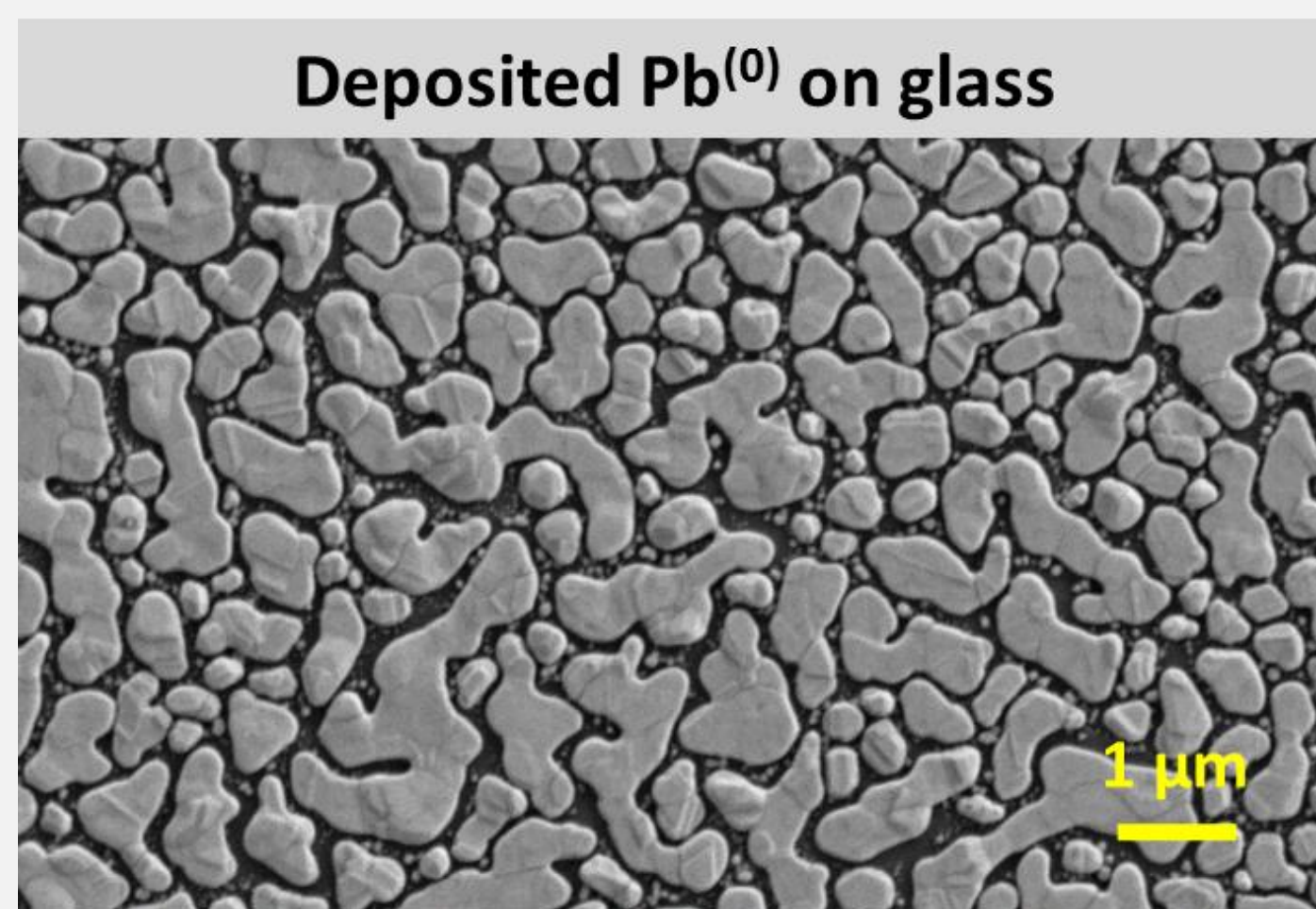


Pb film (~ 100 nm) evaporated on d-TiO₂ /FTO/glass substrate glass before and after treatment with MAI (50 mM for ~ 2 hr) dissolved in IPA



XRD patterns of reacted Pb film, deposited on glass substrate, with 50 mM MAI solution in IPA

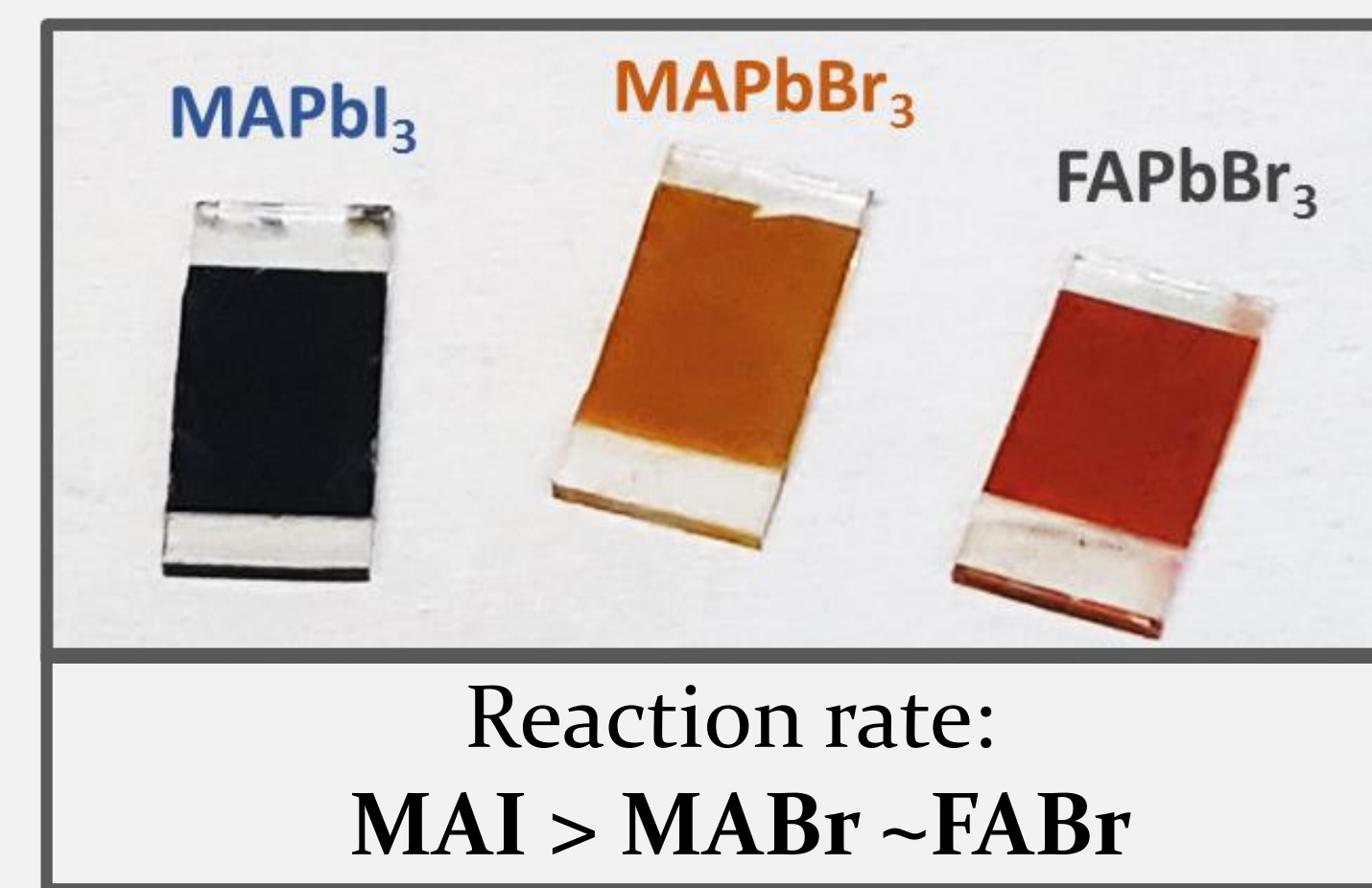
volume expansion of the Pb conversion to perovskite is ~ x3
→ dense perovskite layer can form from porous Pb layer



Plane-view SEM images of before (left) and after (right) dipping a Pb film deposited on glass in 50 mM MAI, dissolved in IPA.

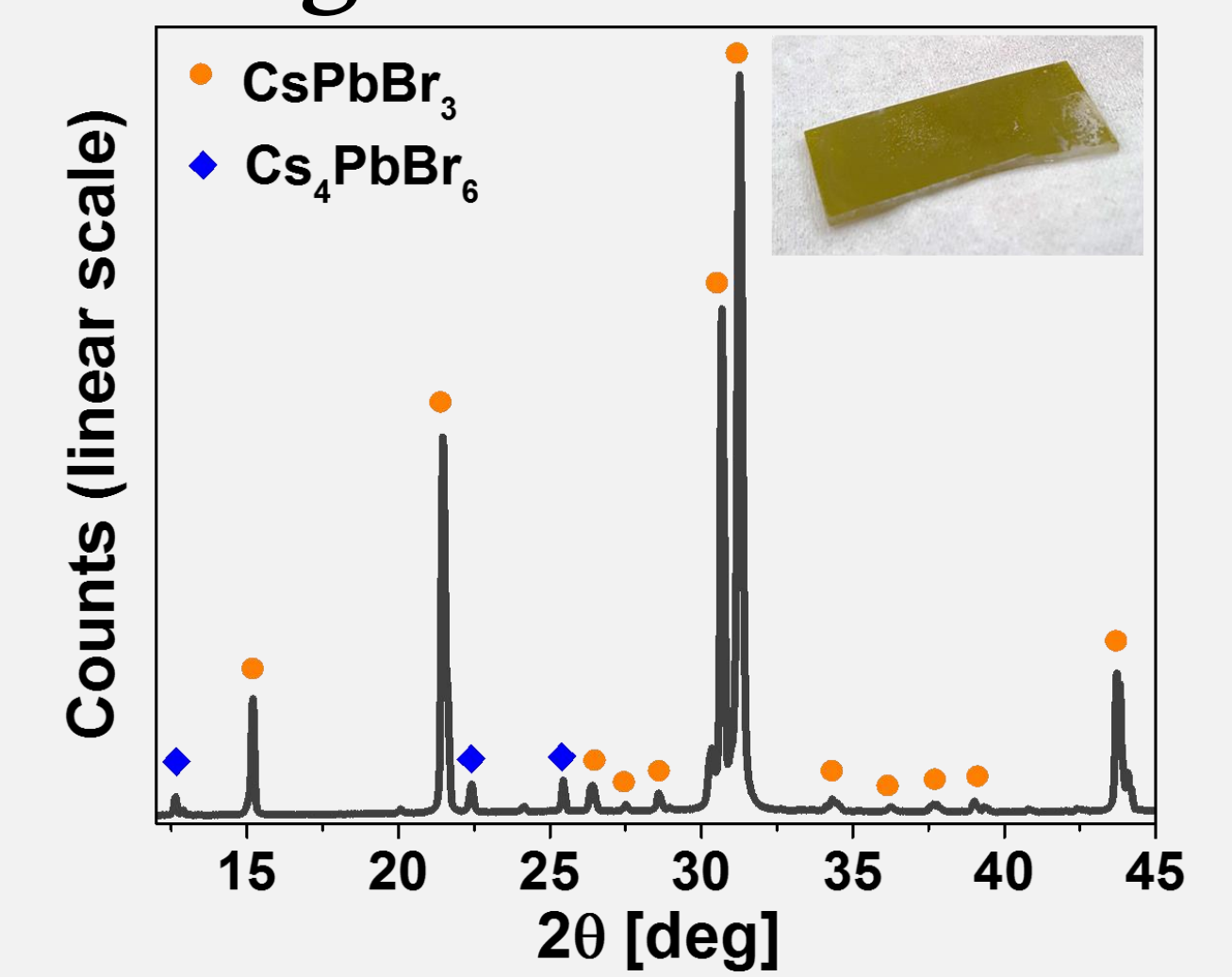
Variability

Various A cations and X anions



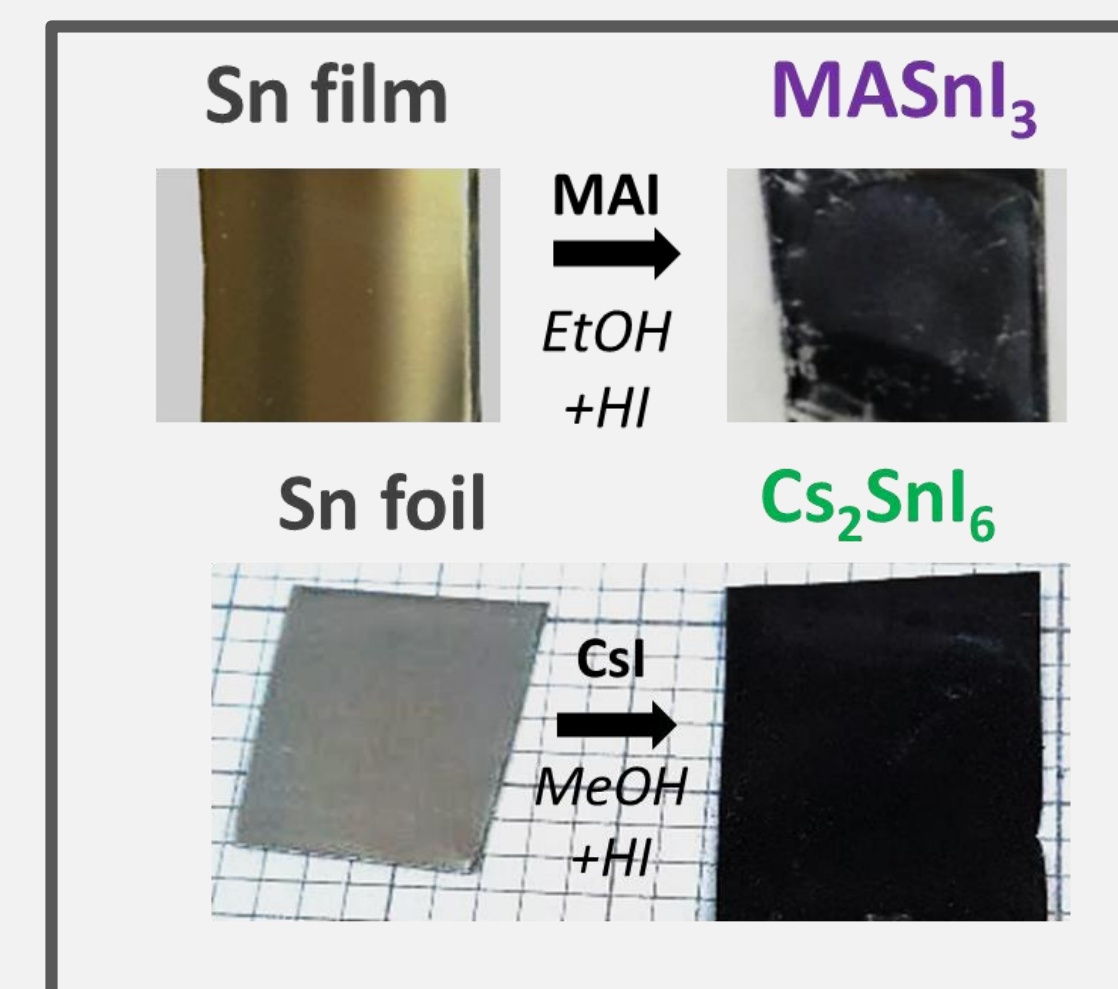
Perovskite films after treatment of similar Pb films in solutions of (from left to right) 50mM MAI, 70mM MABr and 70 mM FABr

Not limited to organic A cations

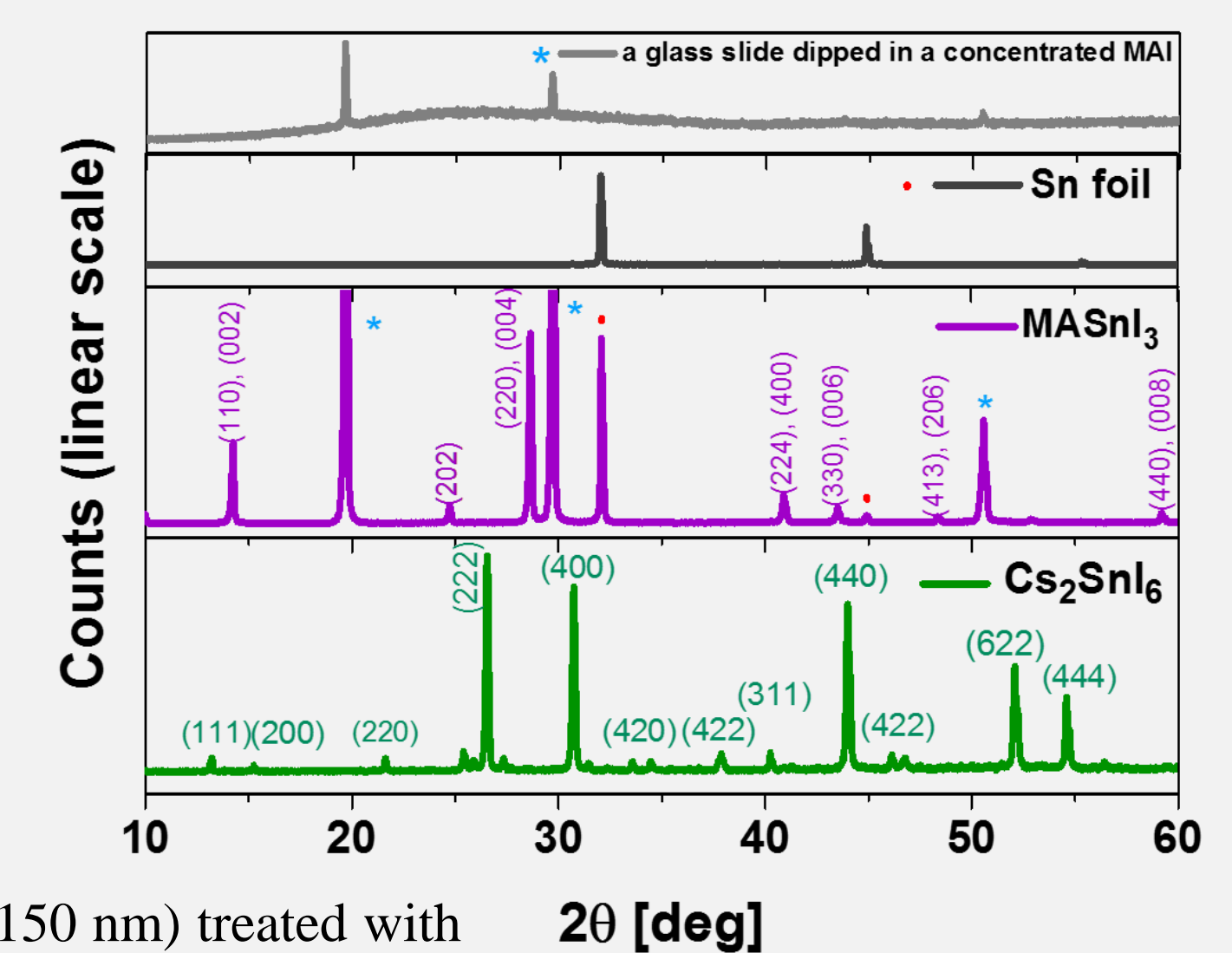


XRD pattern after treating Pb film in solution of 80 mM CsBr + 60% (molar) HBr in MeOH.

Not limited to Pb²⁺ halide perovskites: MASnI₃ (Sn²⁺) ; Cs₂SnI₆ (Sn⁴⁺)

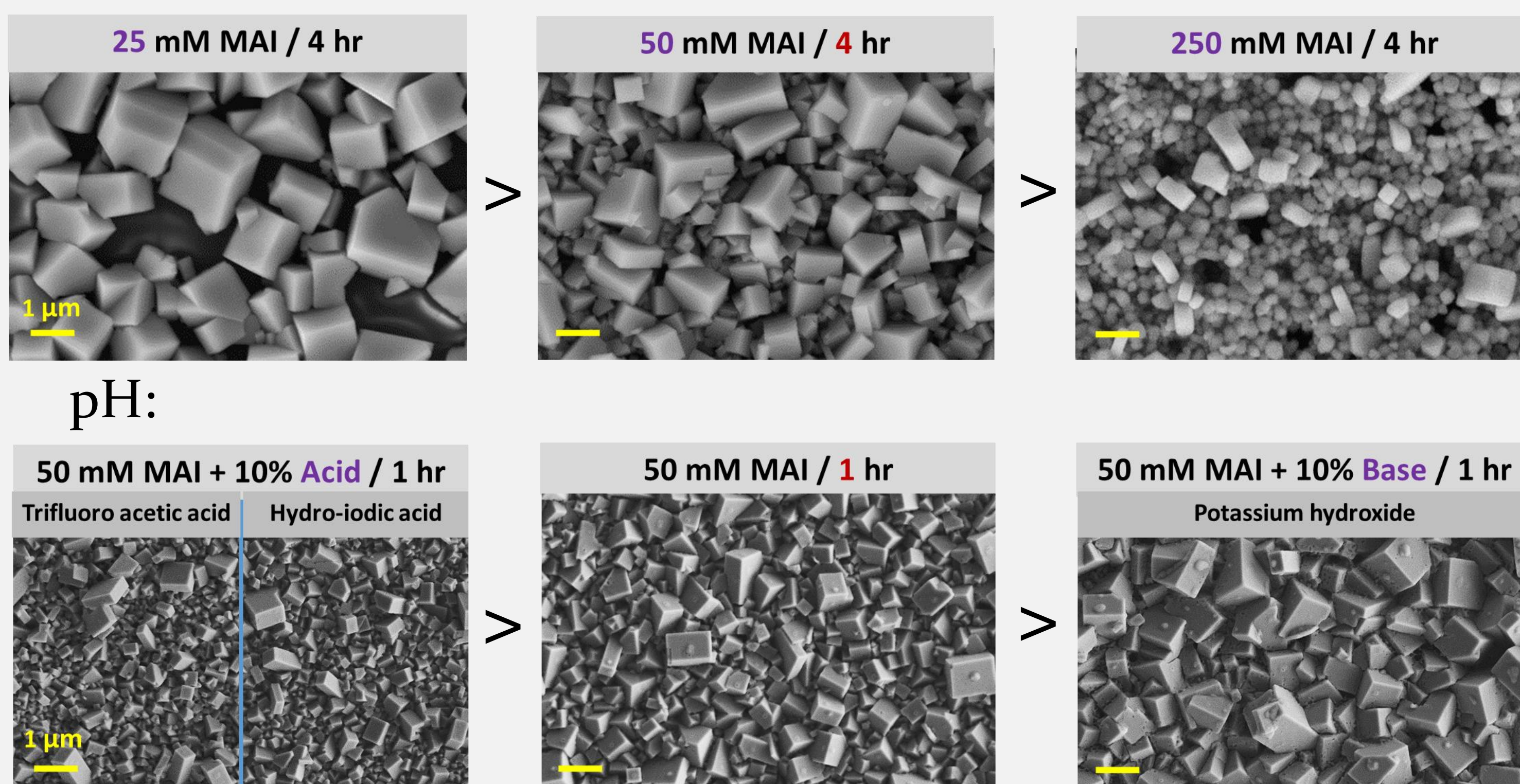


Left - (Top) thermally-evaporated Sn film on glass (~150 nm) treated with 0.5 M MAI in EtOH containing 0.5 M of HI for few seconds. (Bottom) Sn foil treated in a saturated CsI solution dissolved in MeOH containing 0.5 M of HI. Right - XRD patterns of the treated Sn films.



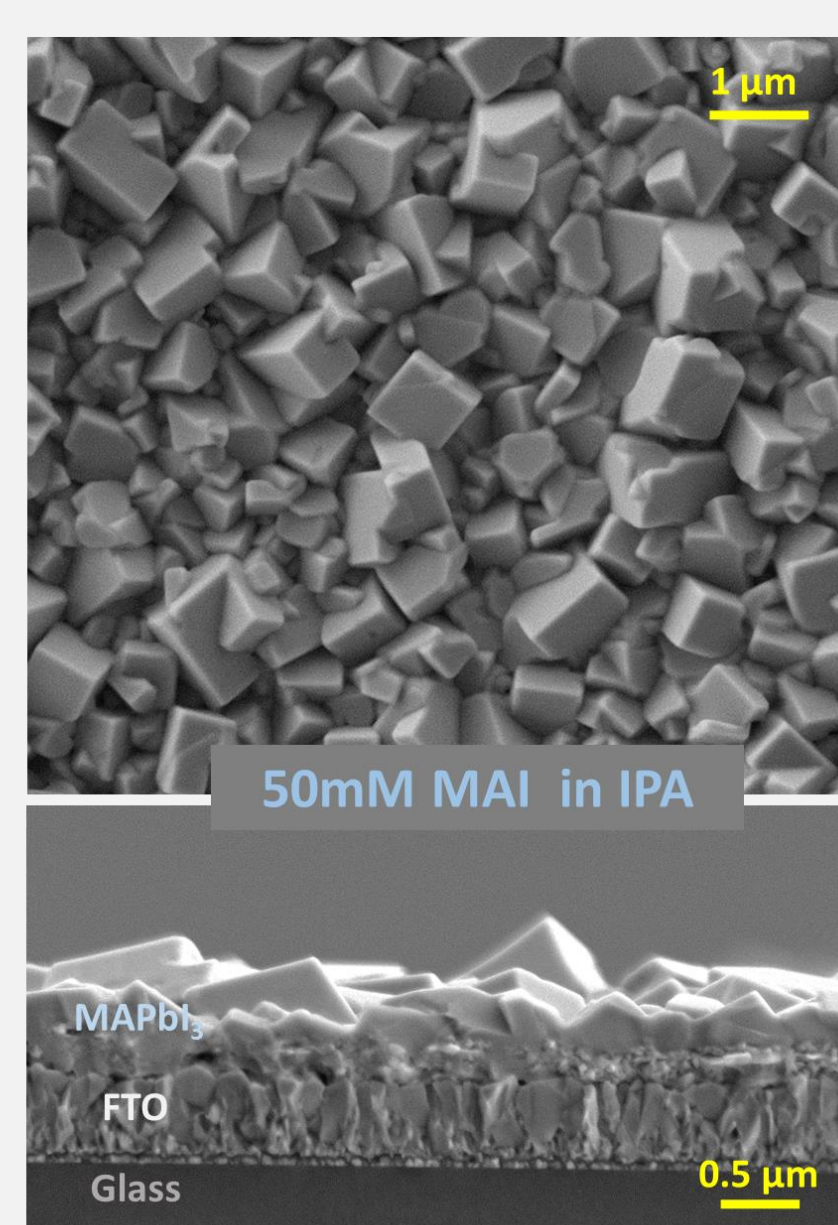
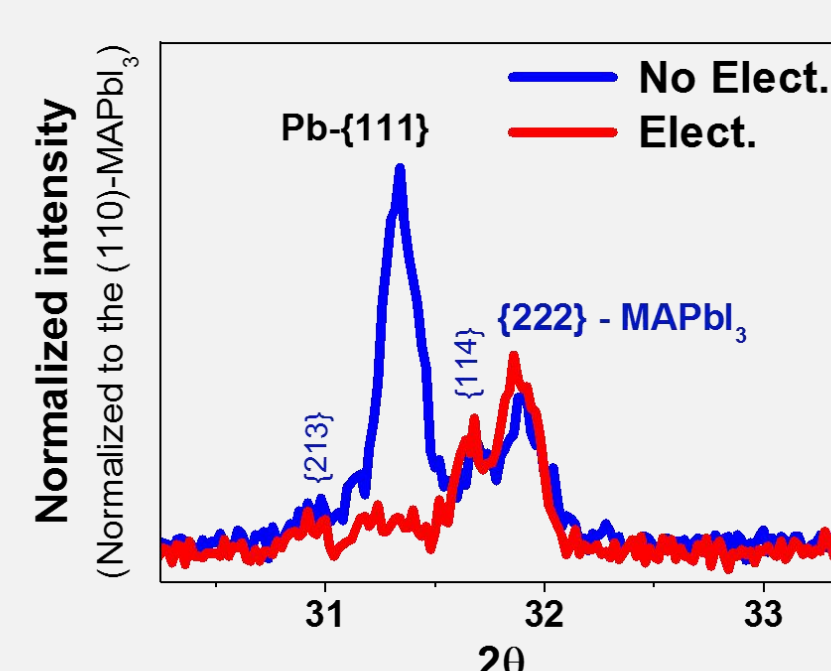
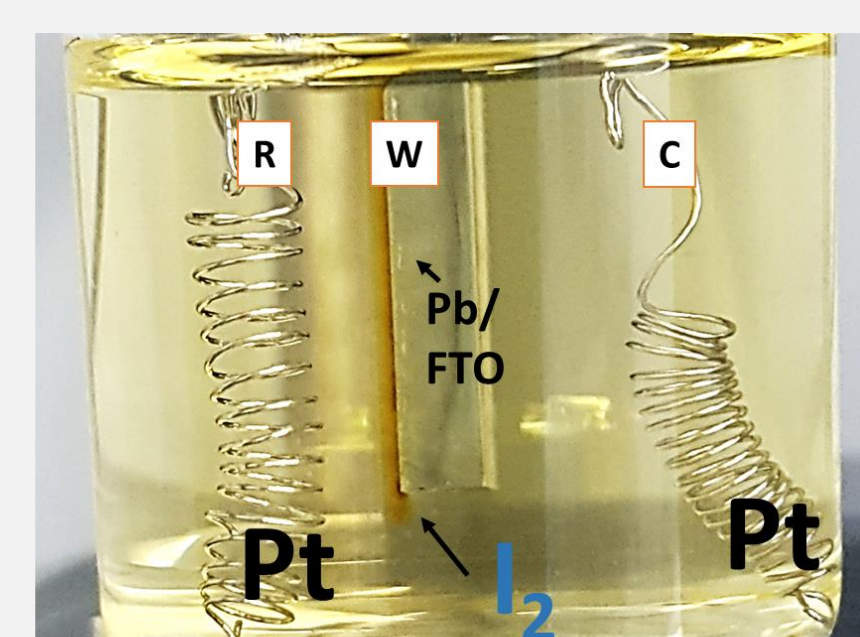
Morphological tunability

MAI Concentration:



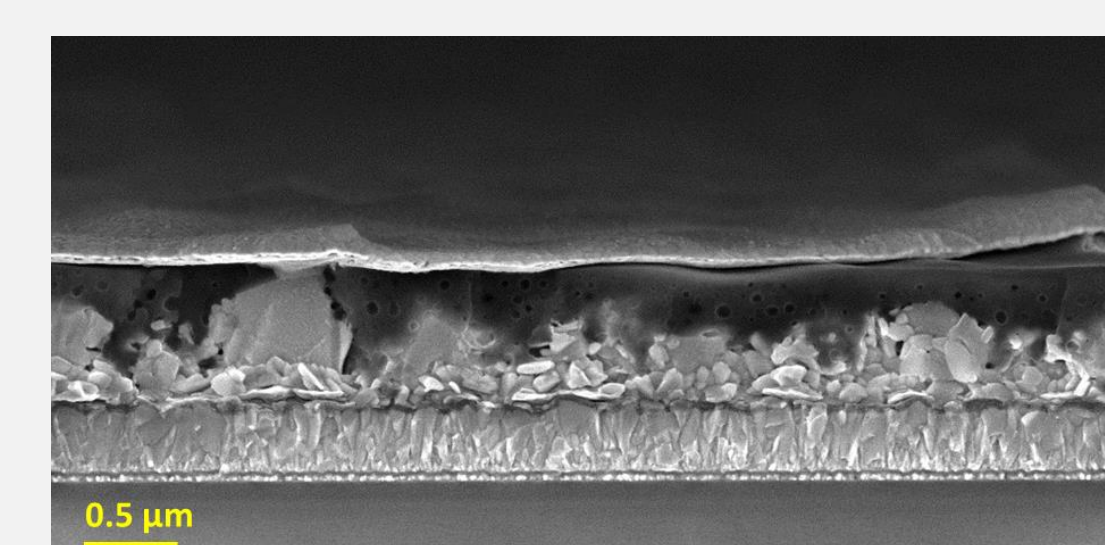
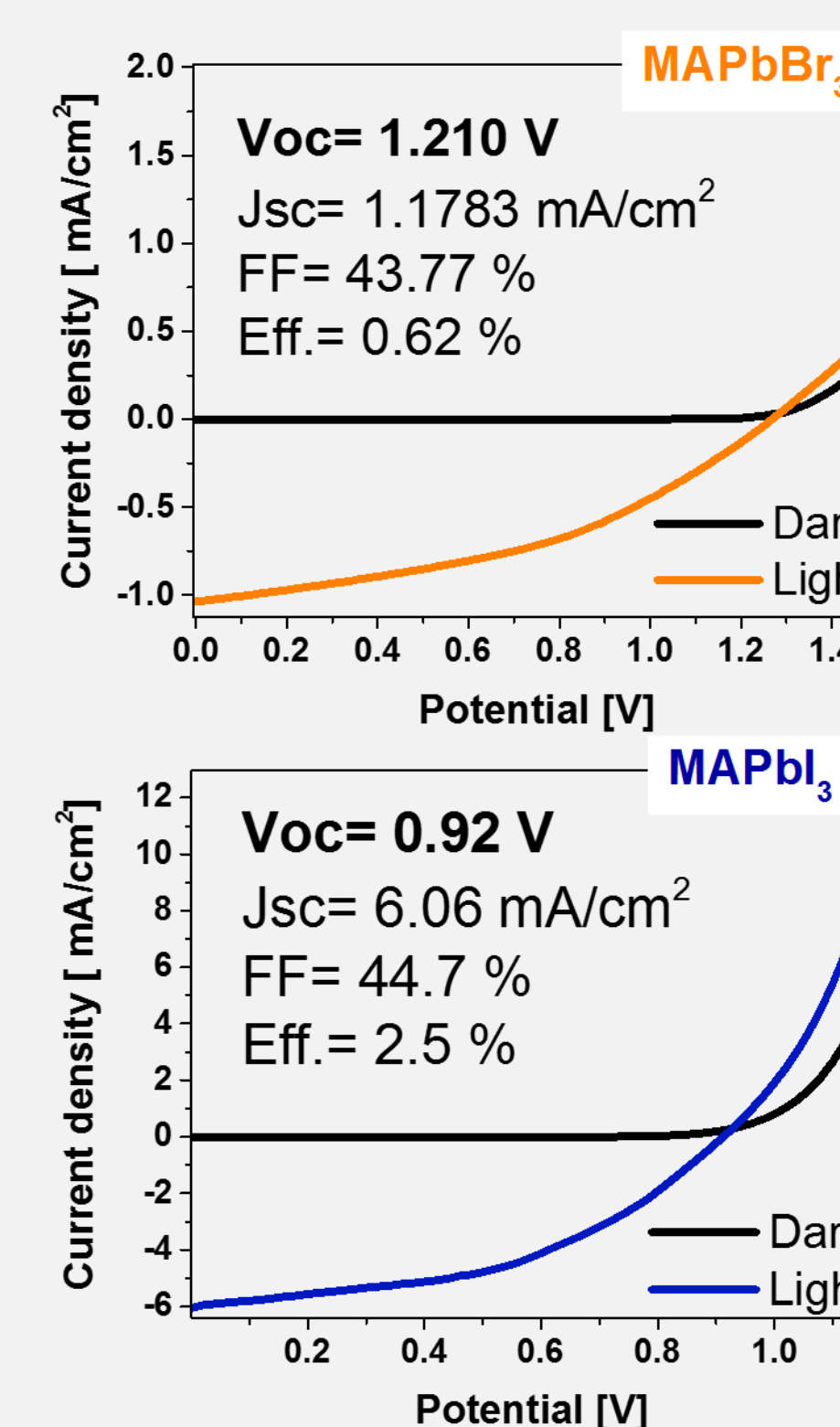
Electrochemically accelerated (hours to minutes)

Electrochemically-assisted Pb (~ 150 nm on FTO) transformation to MAPbI₃ in 50 mM MAI in IPA solution. Left - (top) photograph of the reaction system about 1 min after applying 0.75 V. 'R', 'W' and 'C' correspond to 'Reference' (Pt), Working (Pb film) and 'Counter' (Pt) electrodes. (Bottom) - XRD pattern or 1 hr reaction proves acceleration. Right - SEM views after electrochemically-assisted reaction.



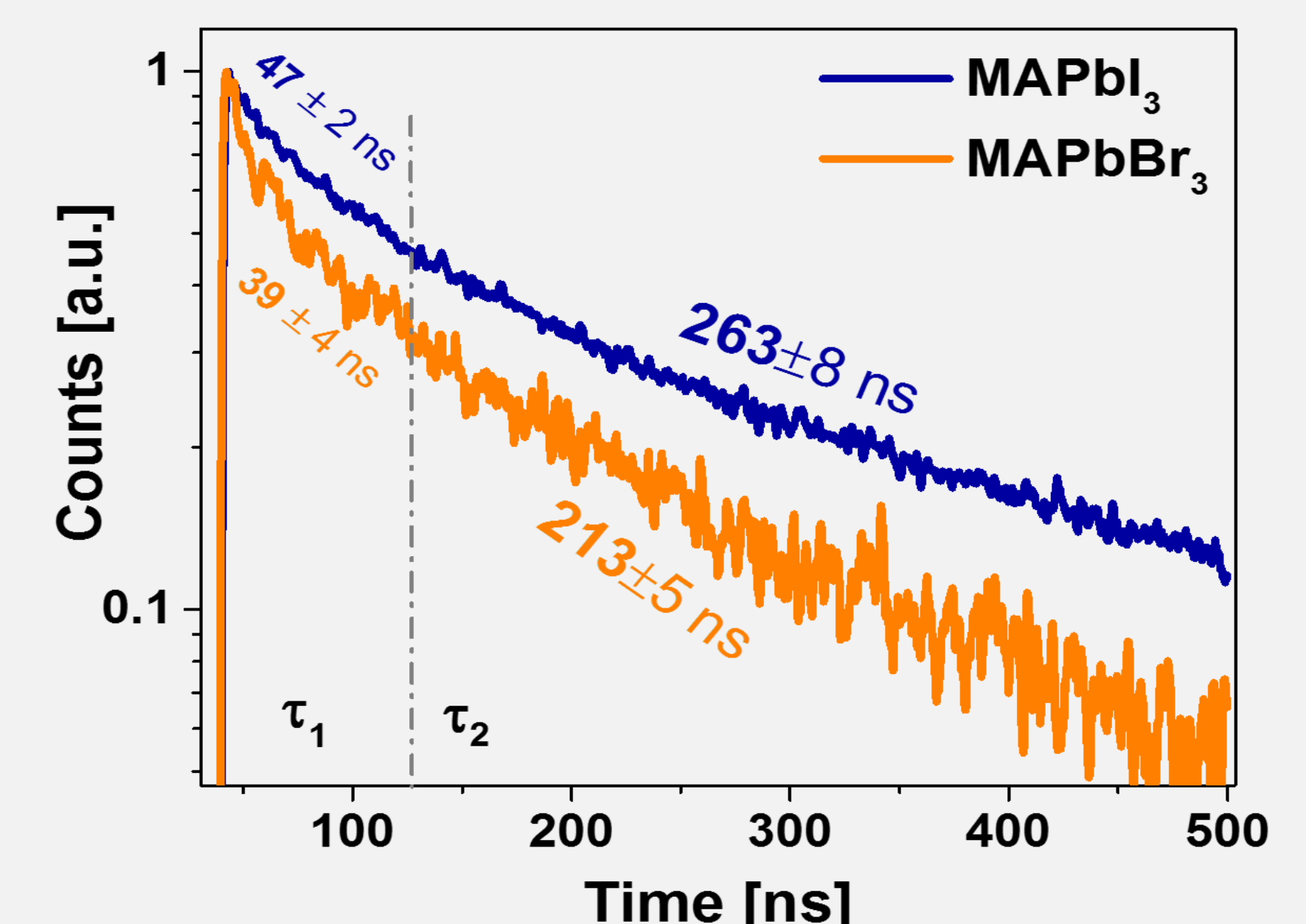
Photovoltaic-related characterizations

Photovoltaic performance



Cross-section SEM image of a MAPbI₃ solar cell.

Time-Resolved Photoluminescence (TRPL) is comparable to that of single crystals



as a starter...

Prepared by YR. YR thanks Igal LEVIN and Arava ZOHAR for fruitful discussions.