Improved Colloidal stability of Precursor solution by a novel HI acid controlled route of Methylammonium Iodide synthesis for efficacious solar cells

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Introduction

Perovskite film formation and in turn photovoltaic performance of solar cells made with these materials exhibit large dependence on the colloidal chemistry occuring in the perovskite precursor solution[1]

It was shown that the purity of methylammonium iodide (MAI) can have a large influence on the perovskite film formation. Particularly, the presence of trace amounts of different phosphate salts (for example methylammonium hypophosphite MAH_2PO_2), was detected in MAI powder and shown to affect the colloidal size in perovskite precursor solution and overall crystallization process of perovskite films[2],[3]

MAI is conventionally synthesized from methylamine and hydroiodic acid (HI) which has to be stabilised with hypophosphorus acid (HPA), a reducing agent. HPA is the source of phosphorus-containing salts in MAI.

Here, we present methylammonium lead iodide ($MAPbI_3$) perovskite films with:
no HI as reagent, ultra pure MAI, no phosphorus traces leading to superior perovskite layers leading to higher PV performances.

The reactions involved are as follows:

1. $CH_3NH_3^{\oplus} I^{\ominus} + I_2 \longrightarrow CH_3NH_3^{\oplus} I_3^{\ominus}$
2. $CH_3NH_3^{\oplus} I_3^{\ominus} + HCOOH \longrightarrow CH_3NH_3^{\oplus} I^{\ominus} + 2\,H^{\oplus} I^{\ominus} + CO_2$
3. $CH_3NH_2 + H^{\oplus} I^{\ominus} \longrightarrow CH_3NH_3^{\oplus} I^{\ominus}$

Summary:

4. $2\,CH_3NH_2 + I_2 + HCOOH \longrightarrow 2\,CH_3NH_3^{\oplus} I^{\ominus} + CO_2$

Materials, methods and device architecture

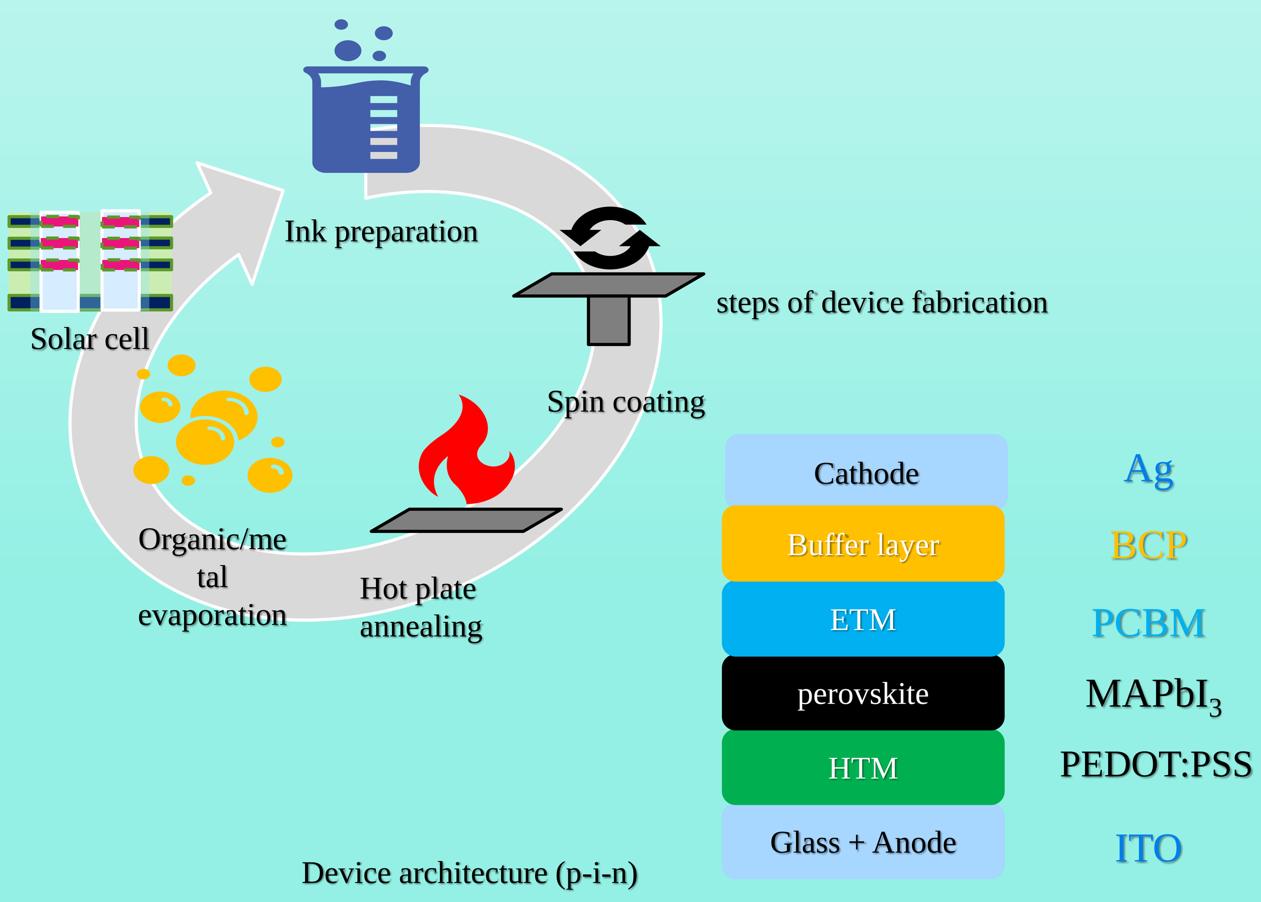
In this work five perovskite films were prepared for devices with three different MAI's

The samples were labelled as :

'old MAI' : *HI based route with no MAH_2PO_2 additive*

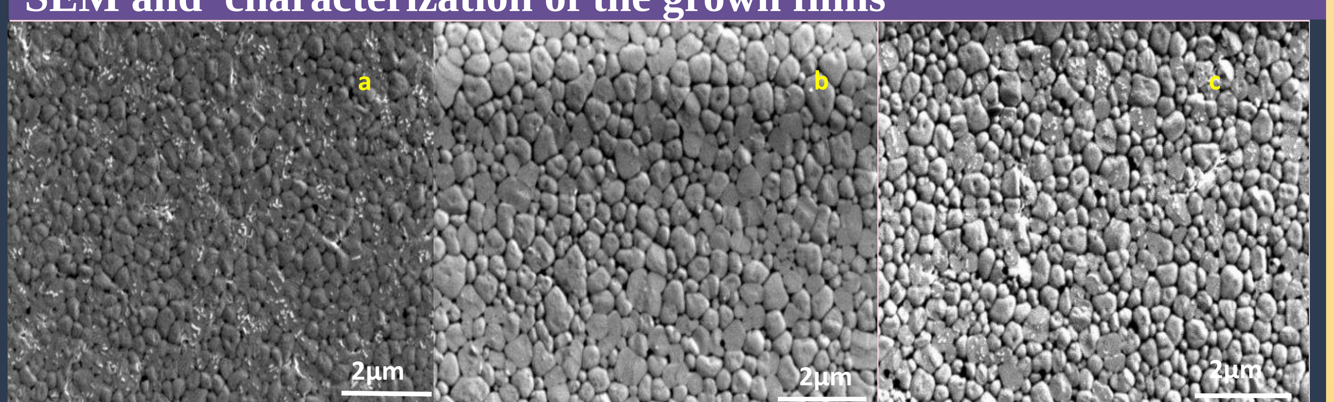
'new MAI+add': *HI free route with MAH_2PO_2 additive*

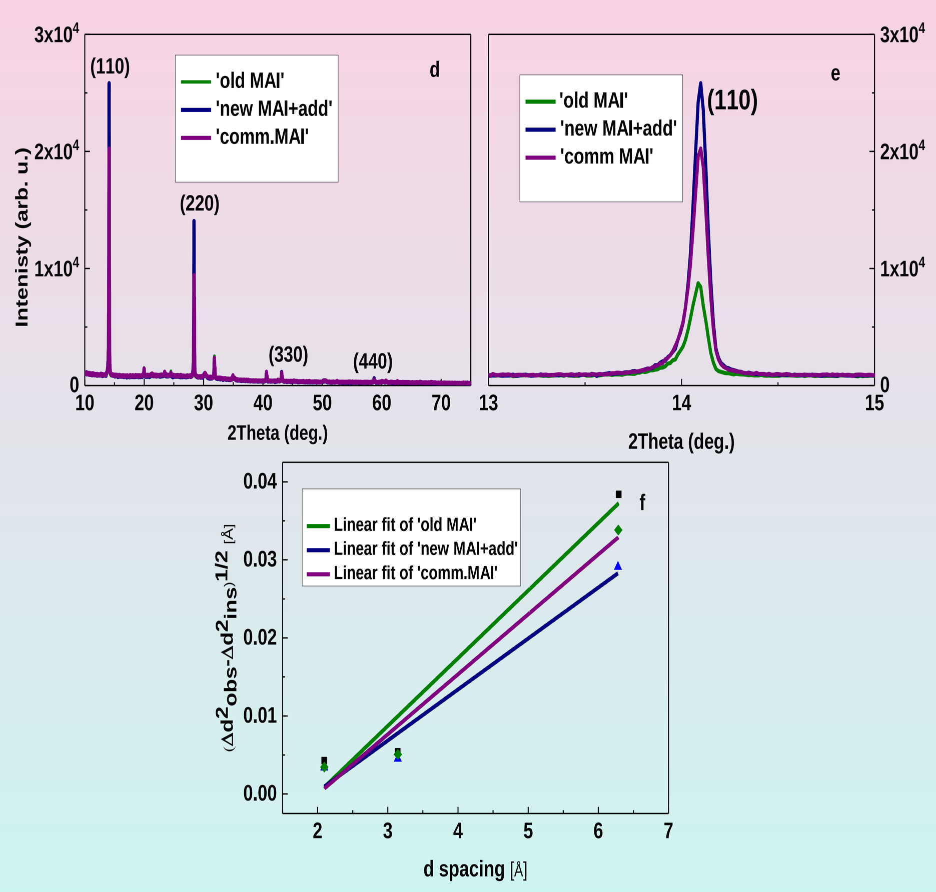
'comm.MAI': *HI based route with no MAH_2PO_2 additiv*



Device architecture (p-i-n)

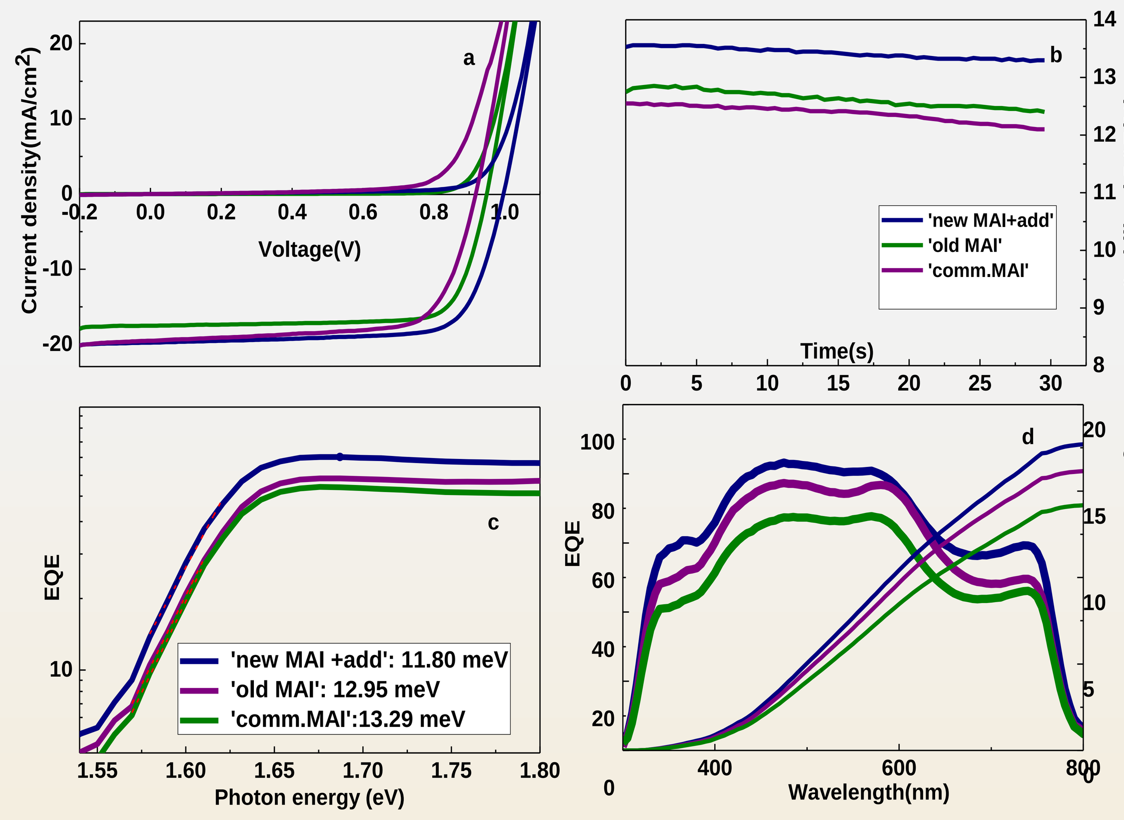
SEM and characterization of the grown films





SEM top-view images displaying morphologies of $MAPbI_3$ perovskite layers, processed from different precursor solutions: a) 'old MAI', b) 'new MAI+add.', c) 'comm. MAI'; d) X-ray diffractograms of the same films, and e) zoom-in at the (110) reflection peak of these diffractograms. f)The $\{\Delta d^2_{obs} - d^2_{ins}\}^{1/2}$ versus d (P, T) plot.

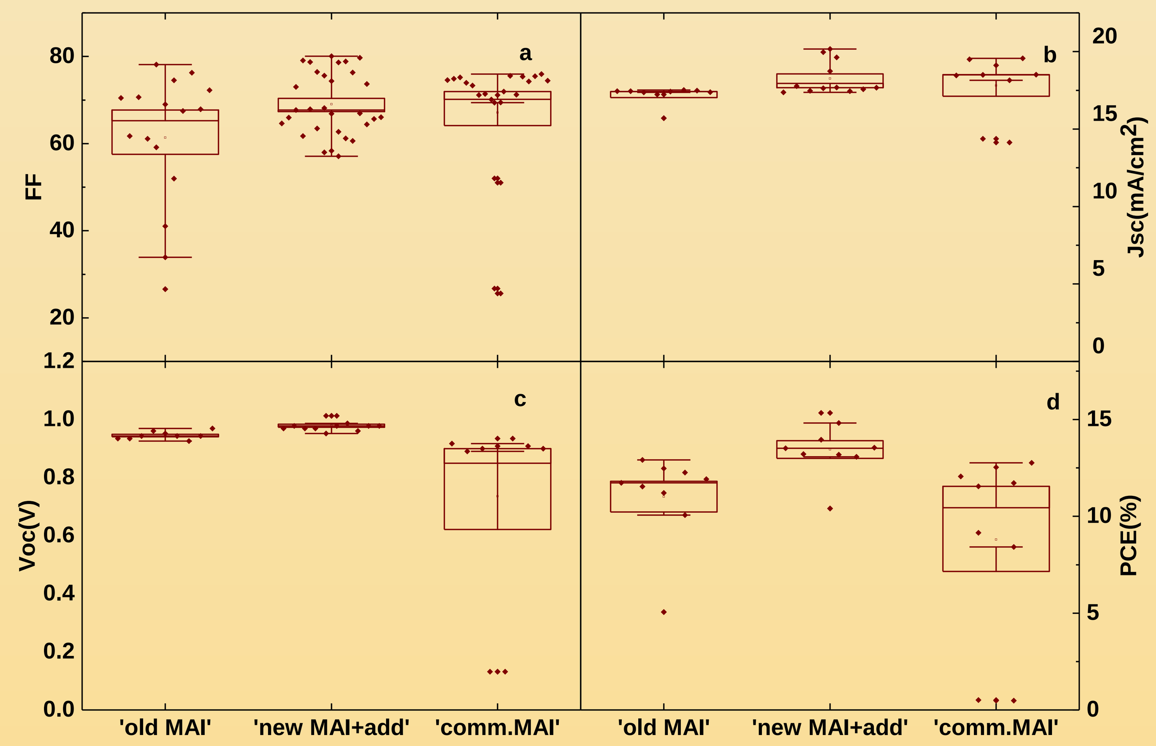
Electrical Characterizations



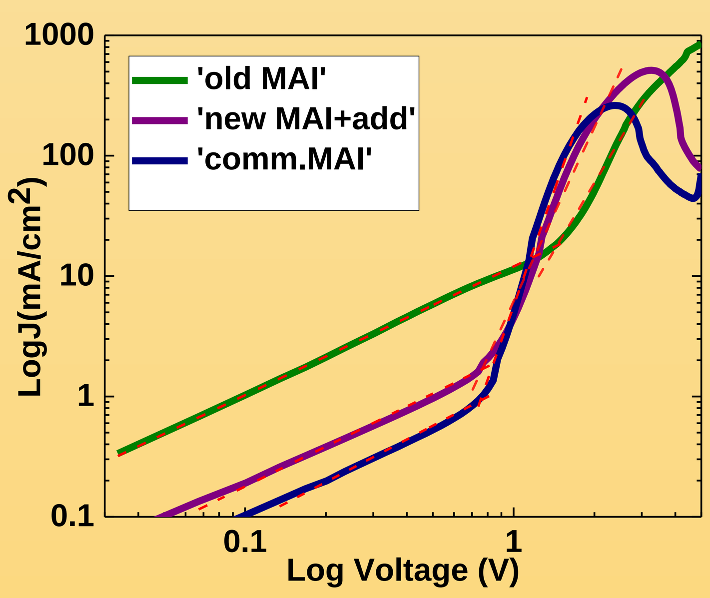
a:J-V plots of solar cell devices fabricated from thin film layers from precursor solutions with different MAI synthesis routes namely 'old MAI','new MAI+add' and 'comm.MAI' under illuminated and dark conditions in forward scans-b: Stabilized Power Output curves of solar cell devices fabricated from thin film layers from precursor solutions with different MAI routes at a given Voltage maximum power point(V_{MPP}),c: Semi-log plot for Urbach tail calculation from EQE for respective samples.d:EQE and extracted Jsc plots for respective samples.

Sample	J_{SC} best (J_{SC} average ± SD) [mA/cm²]	V_{OC} best (V_{OC} average ± SD) [V]	FF best (FF average ± SD) [%]	PCE best (PCE average ± SD) [%]	SPO best [%]
'old MAI'	17.52 (17.22±0.57)	0.94 (0.94±0.01)	78.14 (61.38±15.4)	12.91 (11.01±2.37)	12.6±0.13
'new MAI+add'	19.98 (18.25 ±1.06)	1.01 (0.97±0.01)	75.60 (69.05±7.32)	15.30 (13.45±1.38)	13.62±0.09
'comm.MAI'	19.50 (17.81±2.07)	0.91(0.73 ±0.34)	71.40 (67.13±14.47)	12.76 (8.79±4.93)	12.37±0.13

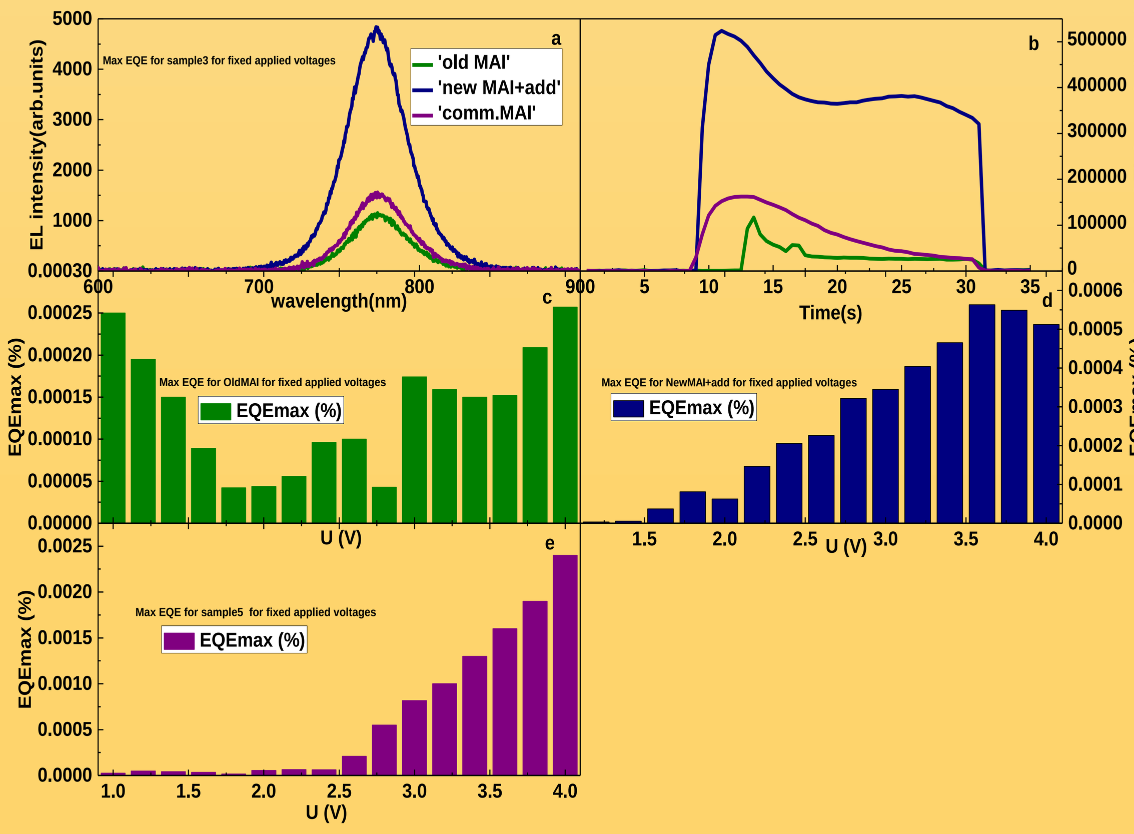
Table displaying different parameters of the solar cells fabricated from precursor solutions with different MAI synthesis routes namely 'old MAI', 'new MAI+add' and 'comm.MAI' at forward scans on a pixel size of $0.06cm^2$



Statistical data displaying the photovoltaic parameters

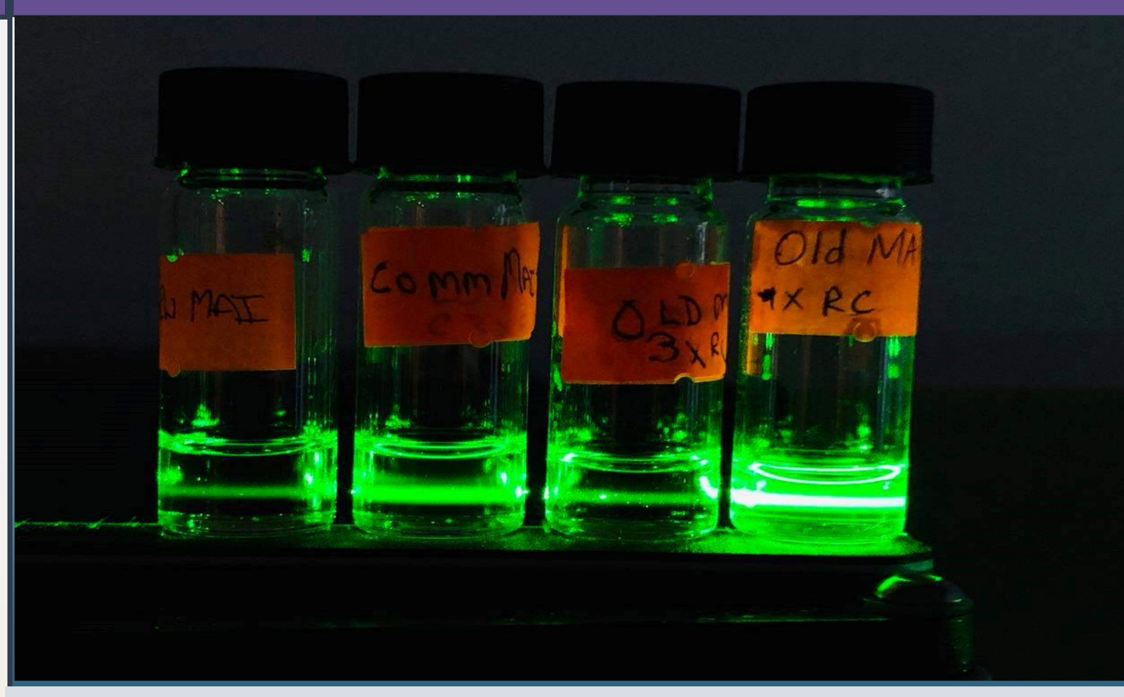


From SCLC studies the density of trap states was lower in devices made from new MAI with additive.The sample hole only architecture wasglass/ito/PEDOT:PSS/perovskite/PTAA/Au



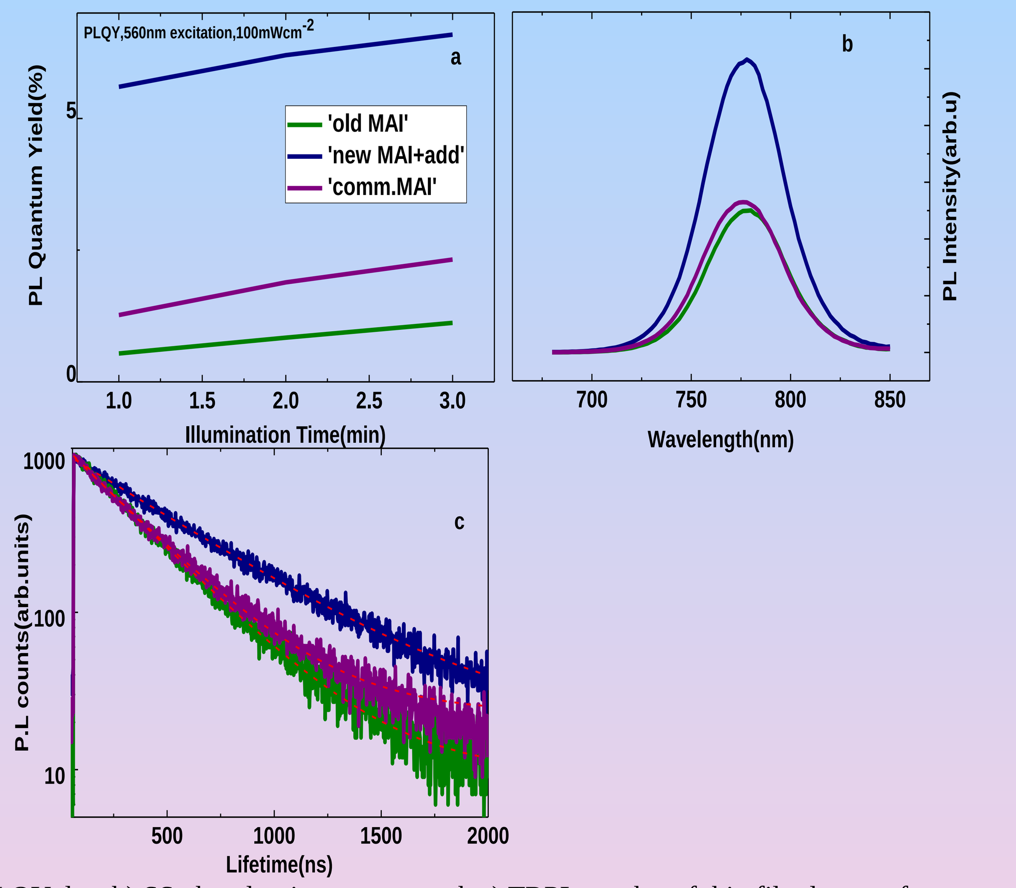
EL intensities as a function of applied voltage of 3V of devices fabricated from thin film layers from precursor solutions with different MAI synthesis routes namely 'old MAI, 'new MAI+add' and 'comm.MAI'.5b: Integrated EL intensities as a function of time at a fixed voltage of 3V for the measured samples.5c,5d and 5e: Maximum ELQE results for a given range of fixed voltages of the measured samples.

Colloidal stability of precursor solutions



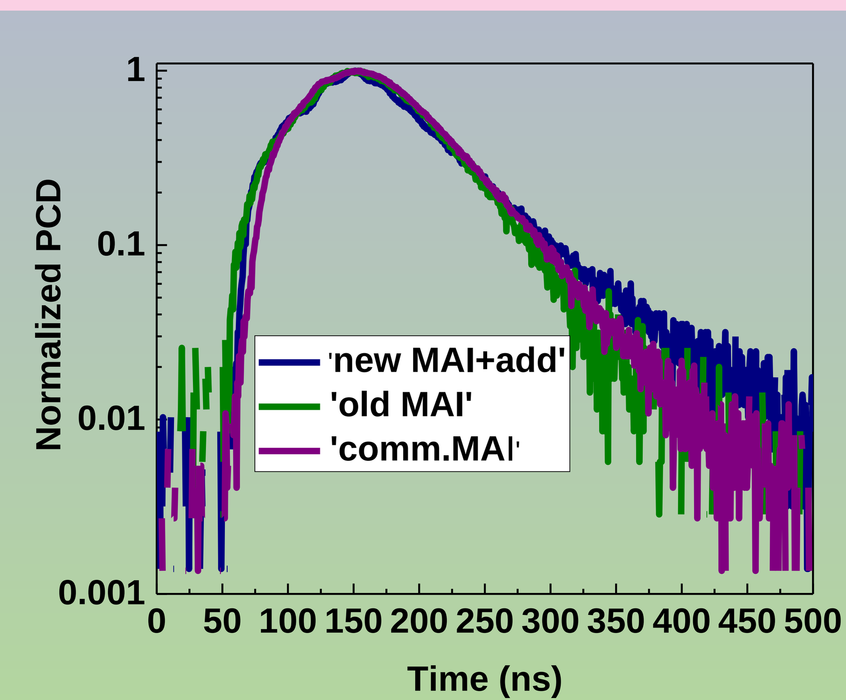
Tyndall effect studies carried on the as labelled perovskite precursor solutions after filtration with a 0.45μm nylon filter, prepared from different MAI powders (as labelled from left to right):'old MAI 1x RC', 'old MAI 3 x RC, 'New MAI no additive(0wt% additive) and 'comm.MAI'

Optoelectronic characterizations



a) PLQY data b) SS photoluminescence graph c) TRPL graphs .of thin film layers of precursor solutions with different MAI synthesis routes namely 'old MAI', 'new MAI+add' and 'comm.MAI'.

Perovskite films from sample 3 displayed best luminescing properties with higher steady state PL intensity and lifetime of nearly 600 nanoseconds.. PLQE is also significantly higher for this sample 3 films asserting less non radiative recombinations in the perovskite layer.



From Microwave reflectance studies of the perovskite films fabricated from different MAI samples,it was observed that sample 3 MAI displayed a higher lifetime indicating higher number of free charge carriers

Conclusions

In this work we report a new synthetic route for makingMAI key precursor component for $MAPbI_3$ perovskite material. This new route is characterized by the lack of HI in the reaction substrates, which leads to high purity MAI material. The reported process leads to:

- Controlled particle size over couple of weeks, which led to the formation of clear perovskite precursor solutions, resulting in perovskite films of higher quality.
- Good reproducibility and better control over the crystallization process as confirmed from well oriented XRD films and SEM images.
- Perovskite films made from these inks display superior optoelectronic properties which results in better photovoltaic performance of constructed solar cells

References

[1] K.Yan et al. ***J. Am. Chem. Soc.*2015, 137, 13, 4460-4468**

[2]Ievgen Levchuk Yi Hou Marco Gruber Marco Brandl Patrick Herre Xiaofeng Tang Florian Hoegl Miroslaw Batentschuk Andres Osvet Rainer Hock Wolfgang Peukert Rik R. Tykwinski Christoph J. Brabec,,***10.1002/admi.210600593***

[3] Xiao et.al , ***Energy Environ. Sci.***, 2016,**9**, 867-872