

Supporting Information

Tailoring the Nucleation and Grain Growth by Precursor Phase Ratio for Efficient Organic Lead Halide Perovskite Optoelectronic Devices

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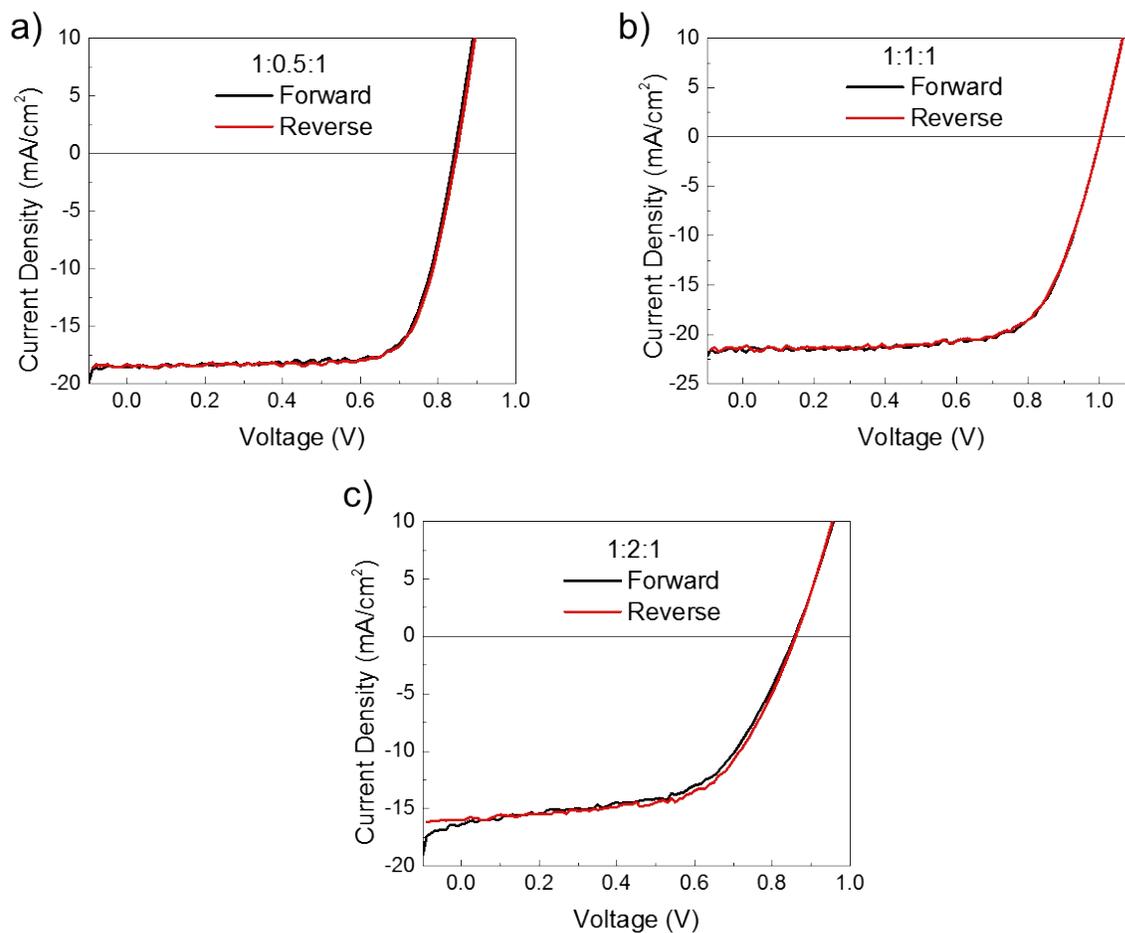


Figure S1. Current density vs voltage plot under forward (short circuit \rightarrow open circuit) and reverse (open circuit \rightarrow short circuit) scan conditions of a) 1:0.5:1, b) 1:1:1 and c) 1:2:1 solar cells

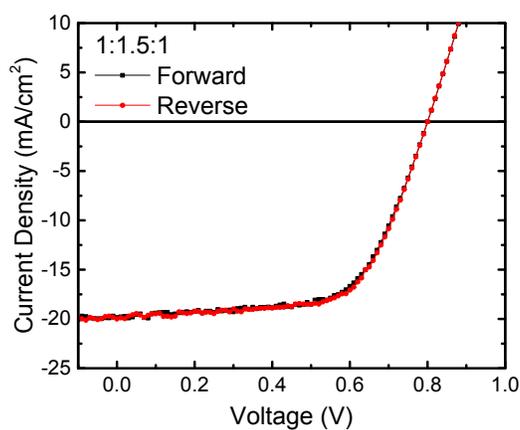


Figure S2. Current density vs voltage plot under forward and reverse scan conditions of 1:1.5:1 ratio solar cell.

Table S1. Photovoltaic parameters derived from Figure S1 and Figure S2 under forward and reverse scan conditions for solar cells derived from different precursor ratios

Precursor ratio	J_{sc} (mA/cm ²)		V_{oc} (V)		FF		PCE (%)	
	Forward	Reverse	Forward	Reverse	Forward	Reverse	Forward	Reverse
1:0.5:1	18.58	18.29	0.84	0.85	74.21	75.69	11.61	11.74
1:1:1	21.66	21.34	1.00	1.00	69.10	69.39	15.01	14.85
1:1.5:1	22.06	19.85	0.79	0.8	63.26	64.3	11.16	10.29
1:2:1	16.36	16.31	0.85	0.86	57.20	58.08	8.00	8.11

Table S2. Solar cell performances with generic architecture “transparent electrode/PEDOT:PSS/perovskite/ETL/metal electrode” for different perovskite deposition techniques.

Deposition method	Device architecture	V_{oc} , V	J_{sc} , mA/cm ²	FF, %	PCE, %	Refer ence
PbCl ₂ precursor	ITO/PEDOT:PSS/ CH ₃ NH ₃ PbI _{3-x} Cl _x /PC ₆₁ BM)/C ₆₀ /Ag	0.92	17.5	73	11.8	¹
PbAc ₂ precursor	ITO/PEDOT:PSS/CH ₃ NH ₃ PbI ₃ /PCBM/B a-Ag	0.954	18.8	69.7	12.5	²
Two step with polar solvent additive	ITO/PEDOT:PSS/ CH ₃ NH ₃ PbI _x Cl _{3-x} /PC ₆₁ BM/BCP/Ag	1.03	23.4	79.6	19.2	³
Solvent engineering	ITO/PEDOT:PSS/ CH ₃ NH ₃ PbI ₃ /PCBM/Al	0.86	20.1	60.8 7	10.44	⁴
Anti-solvent	ITO/PEDOT:PSS/ CH ₃ NH ₃ PbI ₃ /ETL/Ag	0.84	17.11	75	9.88	⁵
Hot casting	FTO/PEDOT:PSS/perovskite/PCBM/Al	-	-	-	~18	⁶
MAAC precursor (1:1:1)	ITO/PEDOT:PSS/CH ₃ NH ₃ PbI ₃ /C ₆₀ /BCP/ Al	1.00	21.7	69.1	15.0	this work

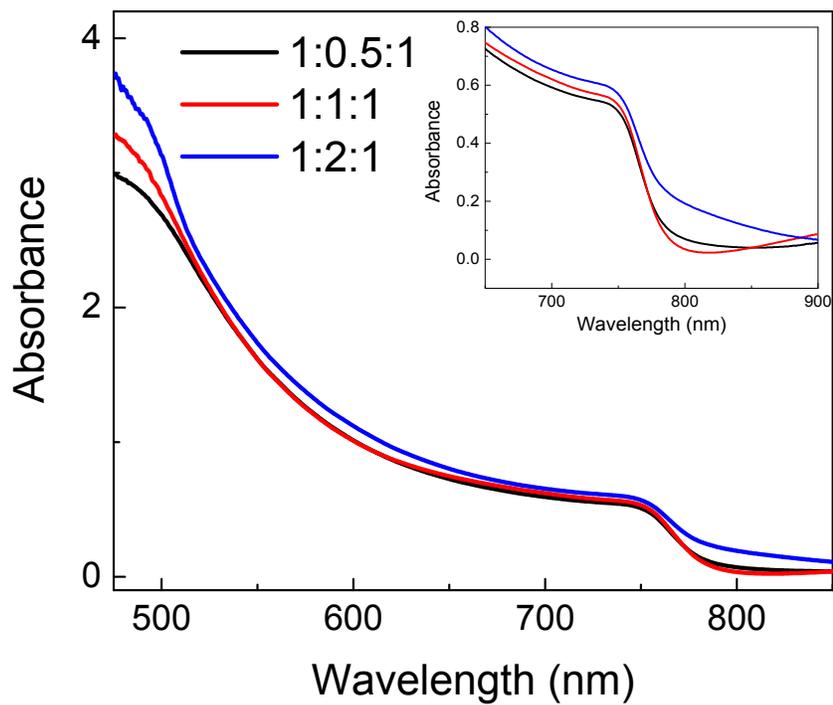


Figure S3. UV-Visible absorption spectra of perovskite films coated from different precursor ratios. Inset is showing the magnified view of absorbance for wavelength range 650nm – 900 nm.

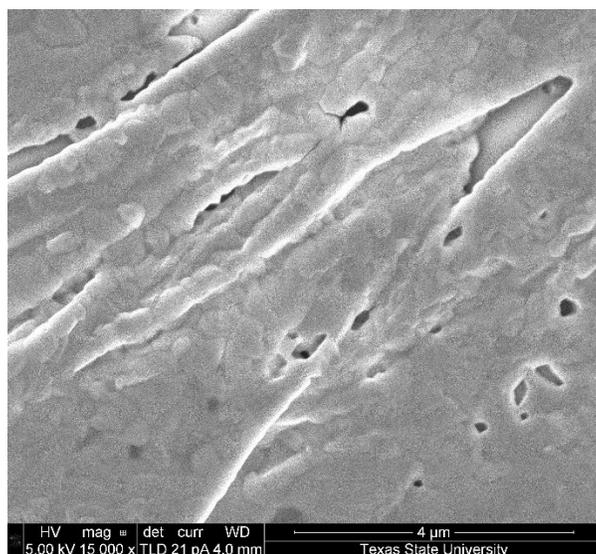


Figure S4. SEM images of perovskite synthesized with precursor ratio $\text{PbI}_2:\text{MAI}=1:1$, no MAAC is used.

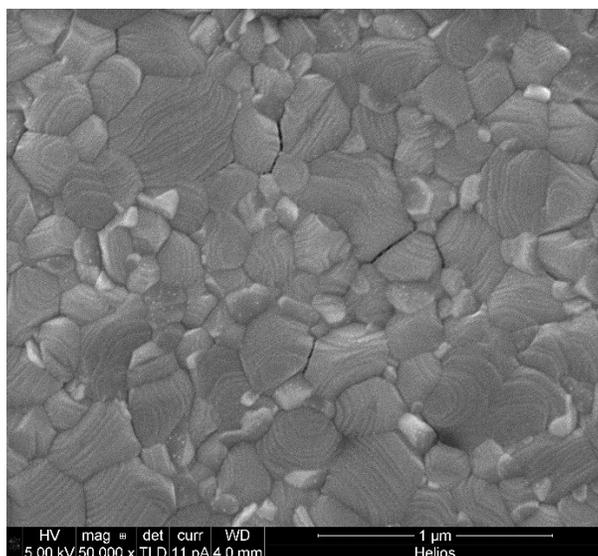


Figure S5. SEM images of perovskite synthesized with precursor ratio $\text{PbI}_2:\text{MAAc}:\text{MAI}=1:1.5:1$.

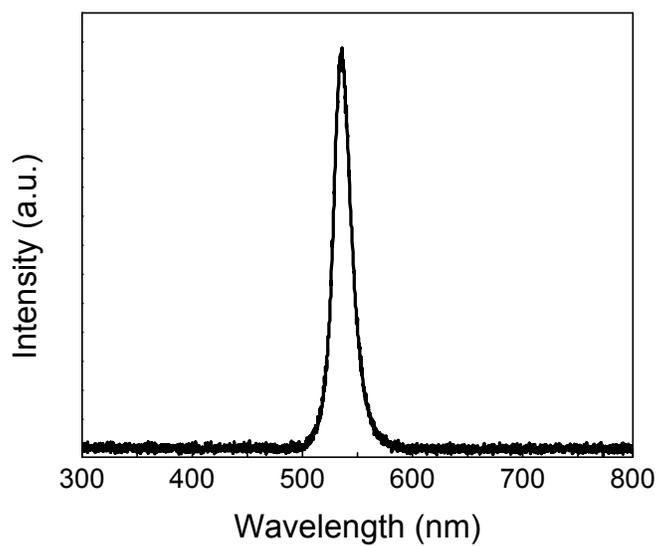


Figure S6. Electroluminescence spectra of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite light emitting diodes.

Perovskite LED versus current commercial LED

The highest EQE reported for $\text{CH}_3\text{NH}_3\text{PbBr}_3$ based PeLED is 8.53%, whereas, the value is less or equal to 0.48% for the device architecture similar to our device structure. Like solar cell devices some optimized composite halide perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$) LED reported to have higher EQE ⁷. We point out, however, that PeLED research has started just recently in 2014. So modest values reported so far do not necessarily adequately reflect fundamental limitation of the materials itself. As for the benchmark, currently, III- Nitrides are the most promising materials for LED fabrication as of today. Bandgap of III-Nitride materials can be tuned from 0.7eV to 6.2eV by suitable alloy composition of AlGaInN system. Hence, this family of materials covers the entire UV and visible ranges of spectrum ⁸. Likewise, emerging organic-inorganic hybrid perovskite can be chemically tuned by suitable precursor composition of the solution. The band gaps of MAPbI_3 and MAPbBr_3 were reported as 1.5eV and 2.3 eV respectively. The bandgap of $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ can be engineered for almost entire visible range by changing halide composition in room temperature ⁹. While both III-Nitrides and hybrid perovskites have the flexibility of the bandgap tuning, the process of tuning is much easier for perovskites. For III-Nitrides it requires very sophisticated control of MOCVD and/or MBE. On the other hand, for hybrid perovskite, mixing of precursor salts in the desired ratio into a solvent is sufficient in most case. This solution can be spin casted on a substrate to get active perovskite layer. In addition to that, substrate for growth of III-Nitrides is very important. GaN based semiconductors, LED, can be grown on sapphire, silicon, metal (e.g. Mo, Ni, Ag, Cu and Fe), and unconventional oxide surface ⁸. All individual substrate has pros and cons related to cost and growth of material i.e. lattice mismatch, coefficient of thermal expansion, reaction at the interface between GaN and substrate etc. ¹⁰. Fabrication of a typical GaN based LED requires the growth of several buffer layers on sapphire to reduce the lattice mismatch between GaN and sapphire followed by undoped GaN, n-type doped GaN, several layers of InGaN/GaN multiple quantum well, electron blocking layer, p-type GaN and a transparent conductive film. This entire process demands critical control of multiple variables in MOCVD or MBE. The architecture of perovskite based LED is quite simpler. An active emission layer of perovskite is sandwiched between an electron and a hole transport layers which in turn can be amorphous organic semiconductors that do not require lattice match. These transport layers as well as perovskite itself can either be printed (spin casted) or deposited by thermal vacuum deposition on virtually any substrate including flexible foils. Two electrodes are also required for external contact on two side of the sandwich and can be either metals or transparent oxides. Thus, PeLED can be easily fabricated on far less expensive pre-patterned ITO substrate (e.g. glass or PET foils) without any critical issue unlike GaN based LED. In summary despite its limited early reported performance, fabrication complexity and material cost of PeLED is much less than that of current III-Nitride based LEDs.

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