ISFAHAN

Opto-electronic Characterization of Perovskite Thin Films & Solar Cells

Never Stand Still | Faculty of Engineering | School of Photovoltaic and Renewable Energy Engineering

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Supervisors:

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Prof. Gavin Conibeer
Dr. Anita Ho-Baillie
Dr. Murad Tayebjee

22nd June 2017

Outline

- Introduction to organic-inorganic metal halide perovskite semiconductors used in optoelectronic devices,
- Development of luminescence imaging technique for perovskite solar cells :
  - ✓ Investigation of the light stability of perovskite solar cells,
- Investigate the excitonic characteristics of perovskites:
  - ✓ Excitonic binding energy (Ry^*) and reduced mass (m^*)
  - ✓ Impact of:
    - Microstructure,
    - Polarons,

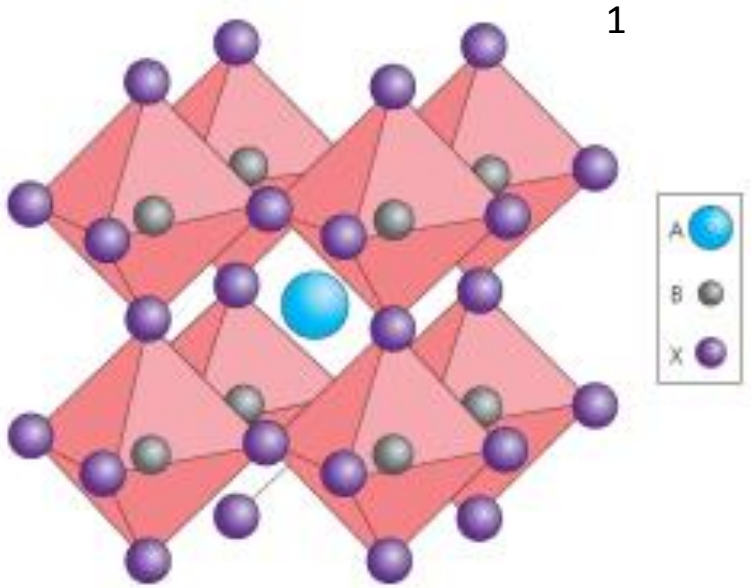
Introduction

Organic-inorganic metal halide perovskite semiconductors:

- General formula ABX_3:

  A = $CH_3NH_3^+$, $H_2N\text{-}CH{=}NH_2^+$, Cs^+, Rb^+; B = Pb^{2+},Sn^{2+}; X = I^-, Br^-;

- Applications:
  - ✓ Photo-detectors,
  - ✓ Light-emitting diodes,
  - ✓ **Photovoltaics,**



[1]

[1]**Martin Green** *et al, Nat. Photonics* (**2014**)

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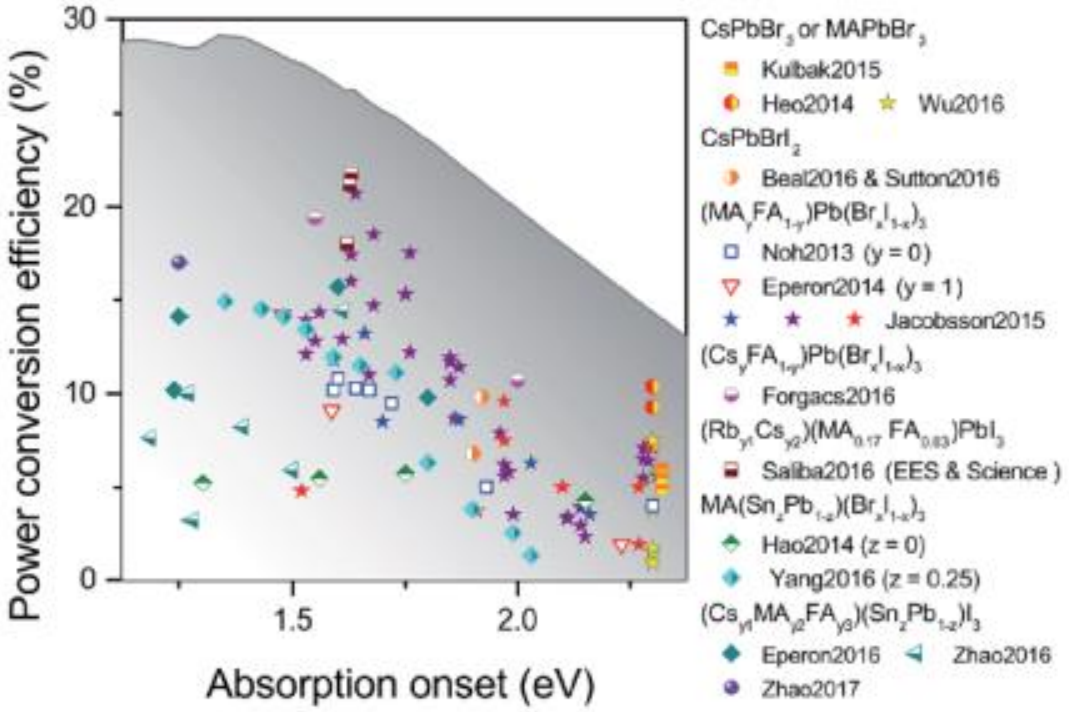
    - Pros:
      - Bandgap tunability[2],



[2]**Eva Unger** et al, *Material Chemistry A* (**2017**)

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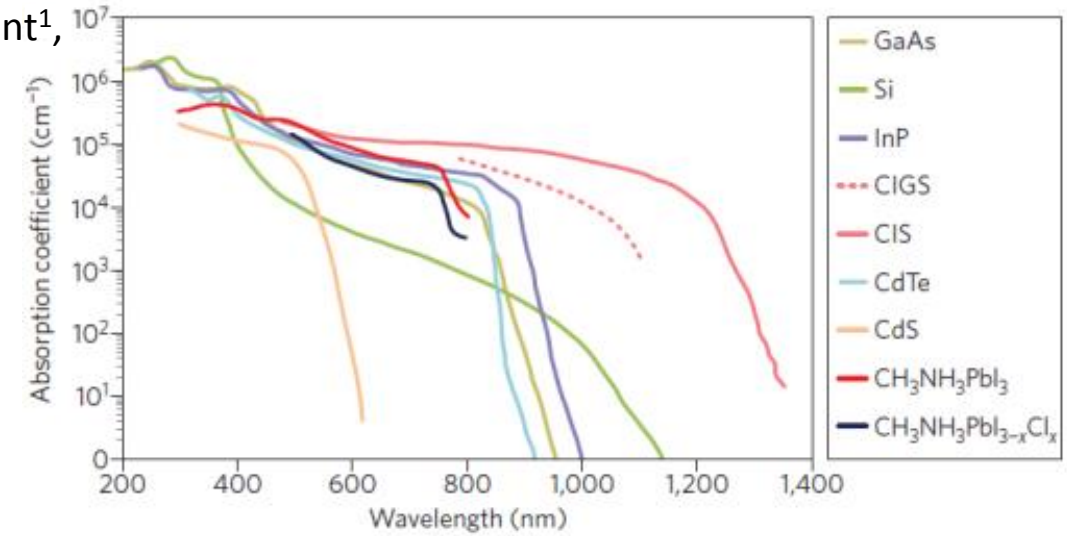

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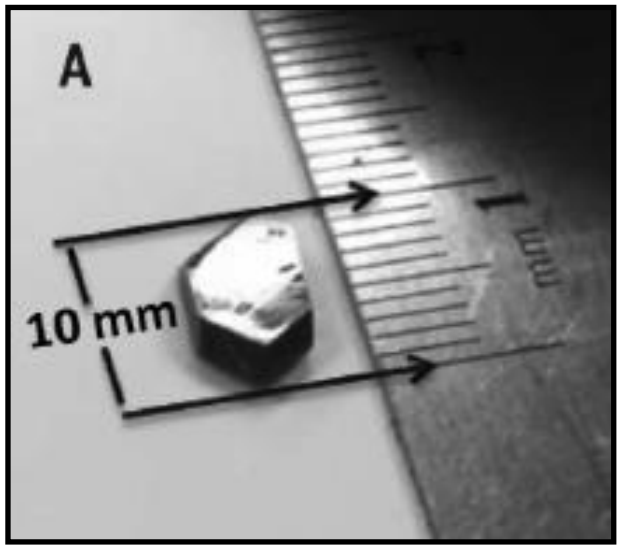

[3]**Qingfeng Dong** *et al, Science* (**2015**)

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      - High absorption coefficient,
      - Long charge-carrier diffusion length (> 175 µm in single crystal)
      - Low exciton binding energy,

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- Applications:
  - ✓ Photo-detectors,
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    - **Cons:**
      - Charge-carrier non-radiative recombination losses[4],

      Polycrystalline perovskite ~ 10^{15}-10^{17} cm^{-3}

      CIGS ~ 10^{13} cm^{-3}

      Single crystal perovskite ~ 10^{9}-10^{12} cm^{-3}

[4]**Samuel Stranks**, *ACS Energy Letters* (**2017**)

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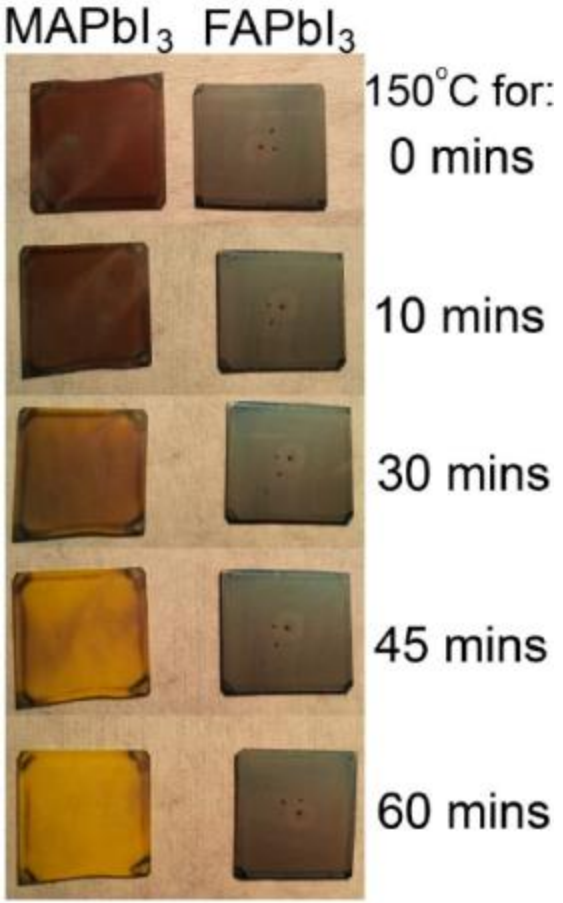

[5]**Eperon** *et al, Energy & Environ. Sci.* (**2014**)

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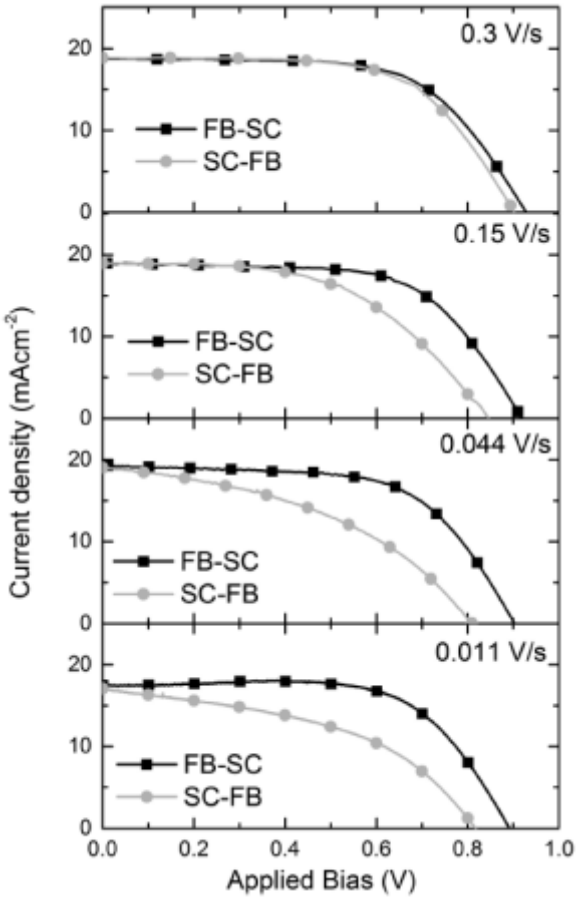
      - Photo-current hysteresis in *J-V* (voltage range, sweep rate and sweep direction)[6],



[6]**Snaith** *et al, J. Phys. Chem. Letters* (**2014**)

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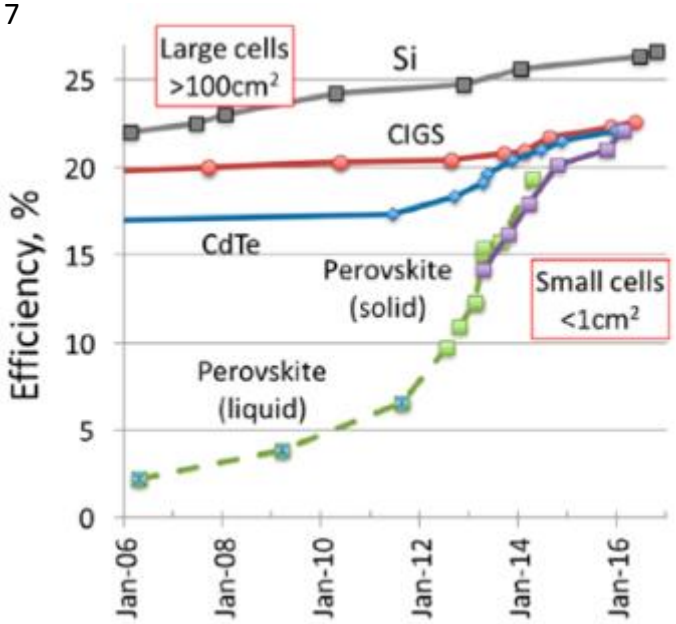
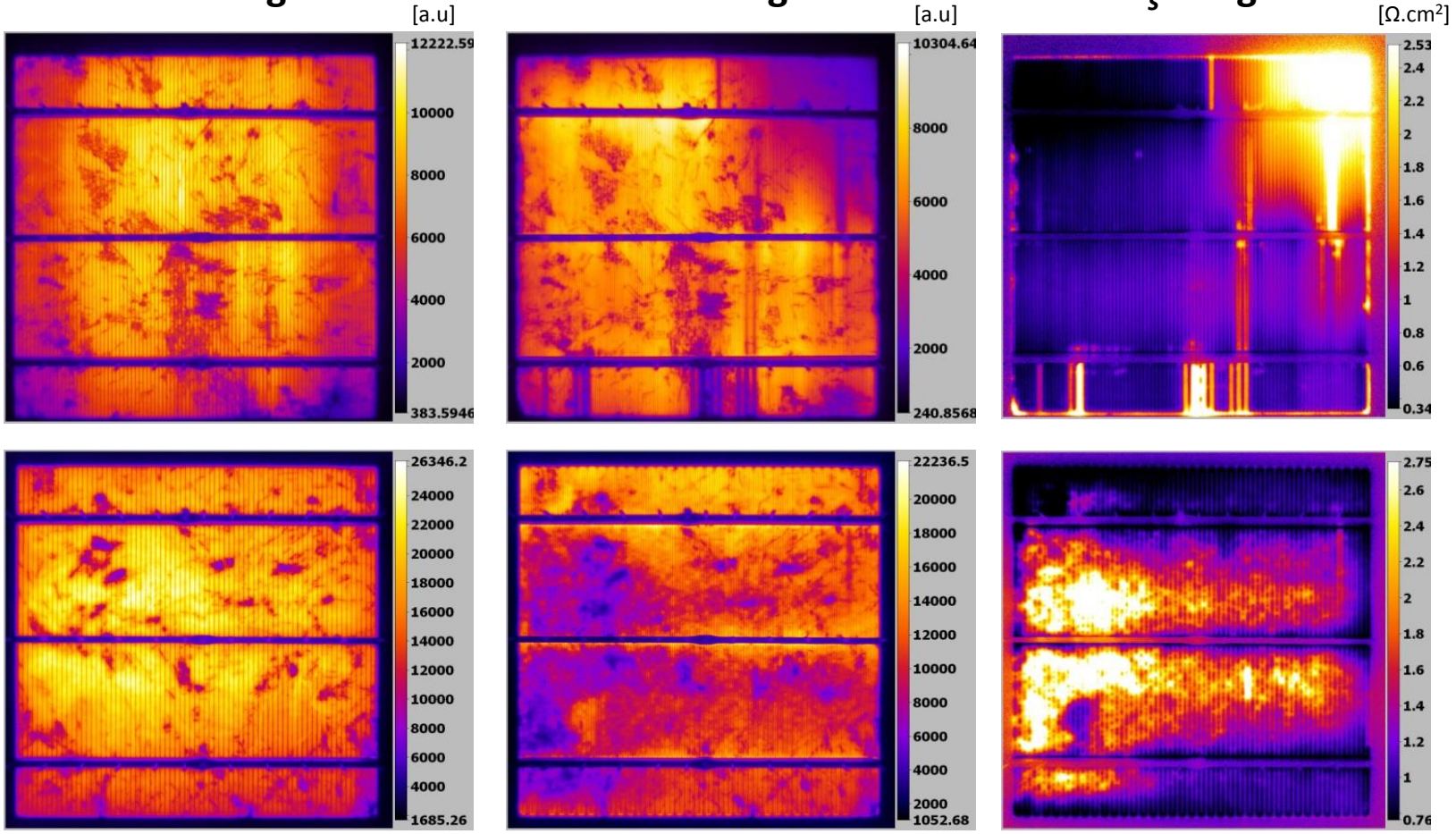


[7]**Green & Ho-Baillie**, *ACS Energy Letters* (**2017**)

Luminescence Imaging Studies

- Photoluminescence (PL) and electroluminescence (EL) imaging have been widely and successfully being used in the silicon PV community.

PL Image | **EL Image** | **R_s Image**



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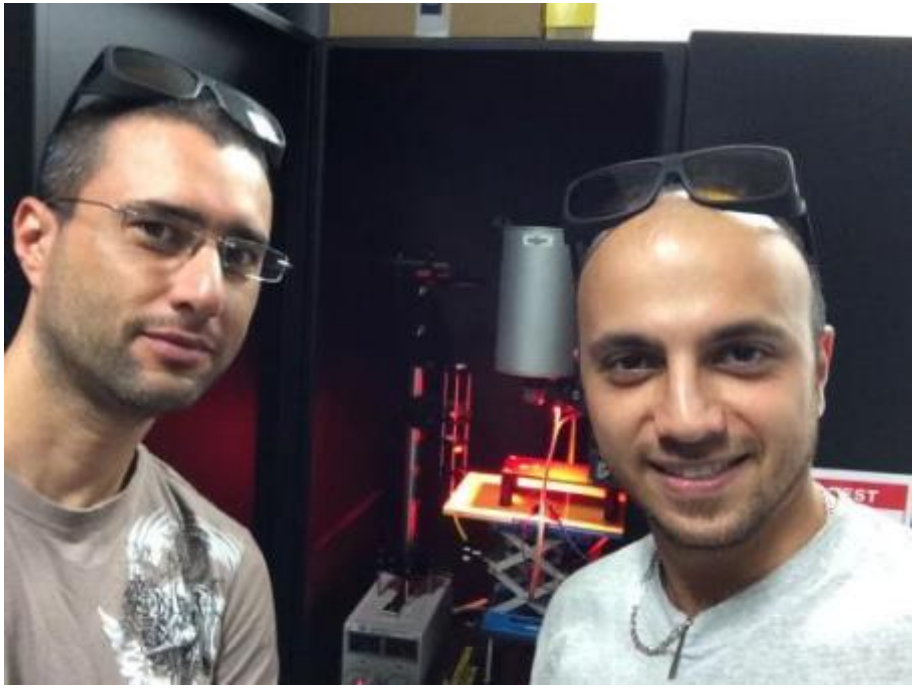


Luminescence Imaging Studies

- Photoluminescence (PL) and electroluminescence (EL) imaging has been widely and successfully being used in the silicon PV community.
- Luminescence imaging speeds up reliable characterization and inspection of solar cell.
- For the first time, the validity of the Planck's generalized emission law was investigated for perovskite solar cells through PL and EL imaging.[8]
- The impact of pre-treatment of the device such as *light-soaking* was examined on the Planck's law.[8]
- Degradation in dark investigated and *J-V* performance was assessed using imaging.[9]
- **Luminescence imaging is also used to investigate the:**[10]
  - ✓ **Immediate** device response to light current-voltage and light-soaking measurements.
  - ✓ **Long-term** device response to light current-voltage and light-soaking measurements.

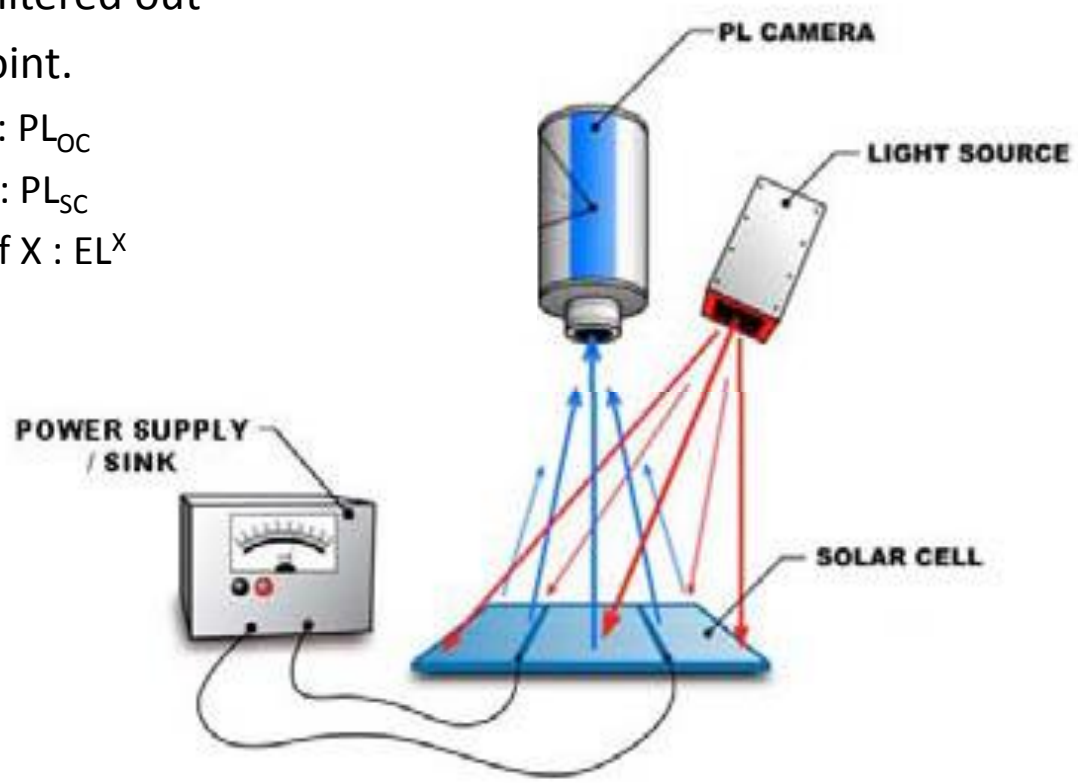
[8]Ziv Hameiri, **Arman Mahboubi Soufiani** *et al*, *PIP* **23**,1697 (**2015**)
[9]**Arman Mahboubi Soufiani** *et al*, *JAP* **120**, 035702 (**2016**)
[10]**Arman Mahboubi Soufiani** *et al*, *Adv. Energy Mat.* **7**, 1602111 (**2016**)

Luminescence Imaging Measurement Setup

- Excitation source: 635 nm light emitting diode (LED).
- Detection system: Silicon charge-coupled device (CCD) camera with 100 milliseconds resolution.
- LED tail spectrum is filtered out using SP filters.
- Reflection from the device is filtered out

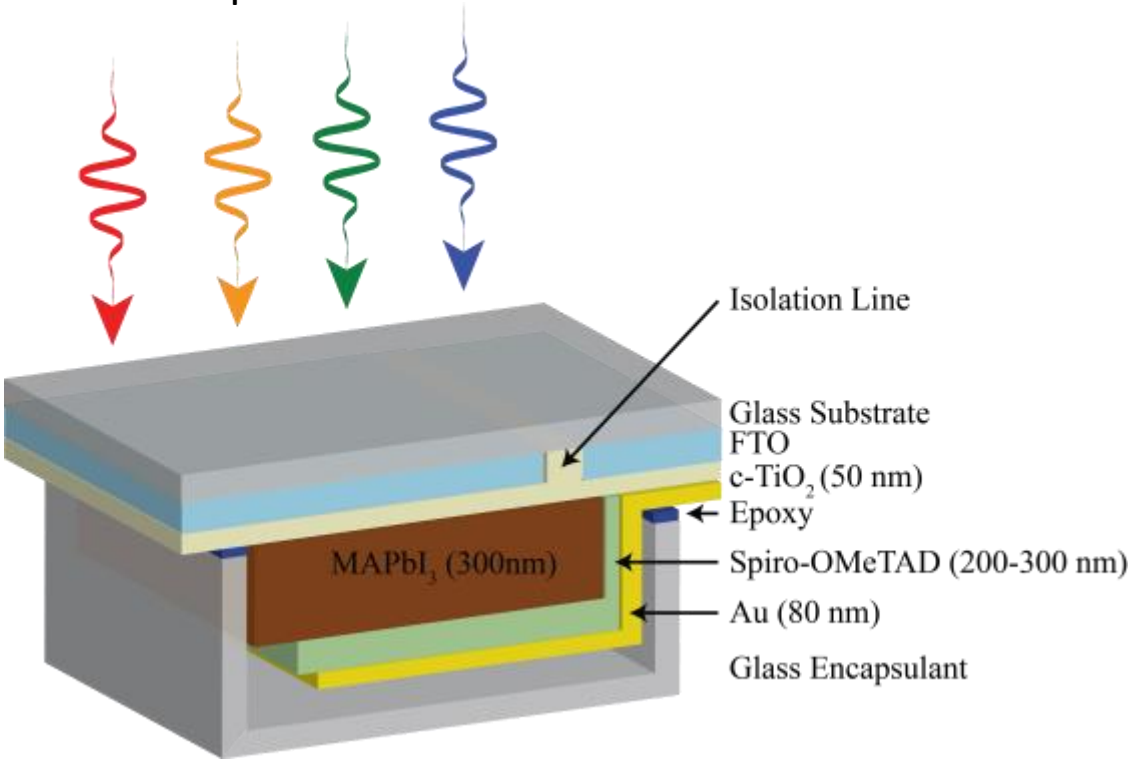
using LP filters at the detection point.

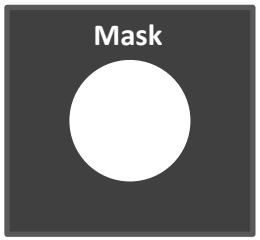
- ✓ PL at open-circuit condition : PL_{OC}
- ✓ PL at short-circuit condition : PL_{SC}
- ✓ EL at terminal voltage bias of X : EL^{X}

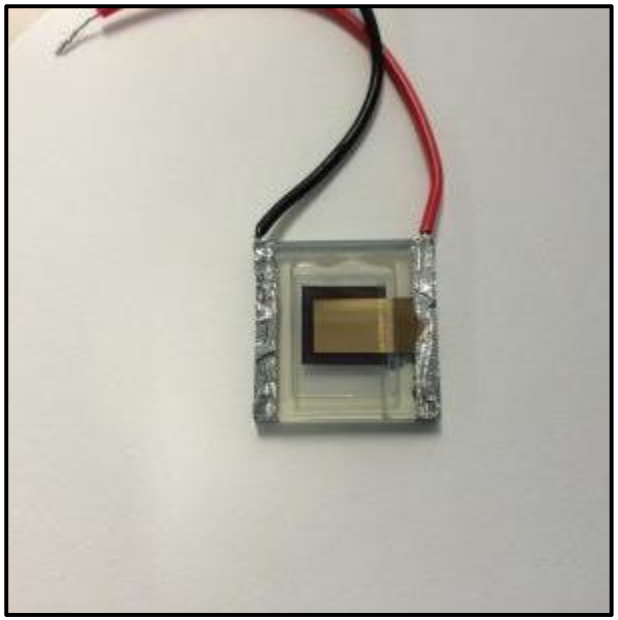


Device Structure

- Planar $CH_3NH_3PbI_3$ based solar cells fabricated via *gas-assisted* technique.[10]
- *c-*TiO_2 as the electron selective and *Spiro-OMeTAD* as the hole selective contacts.
- Device active area ≈ 8 x 8 mm^2
- Aperture Diameter = 4.5 mm

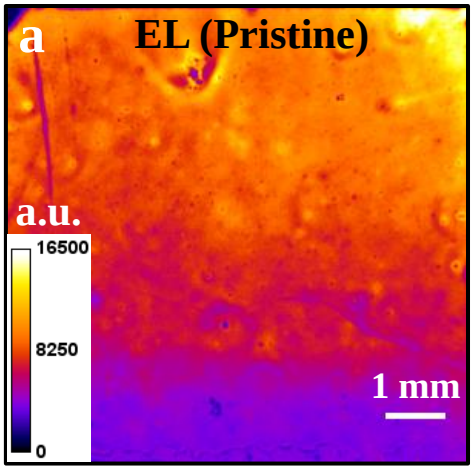


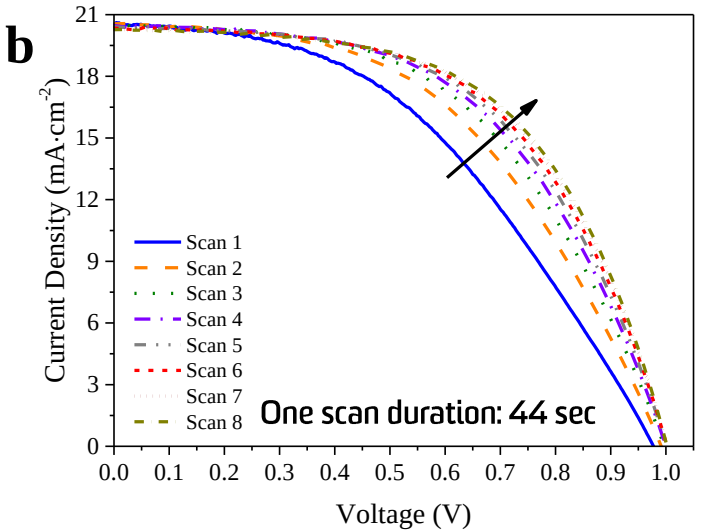




[10]**Arman Mahboubi Soufiani** *et al, Adv. Energy Mat.* **7**, 1602111 (2016)

Effect of Prolonged Illumination





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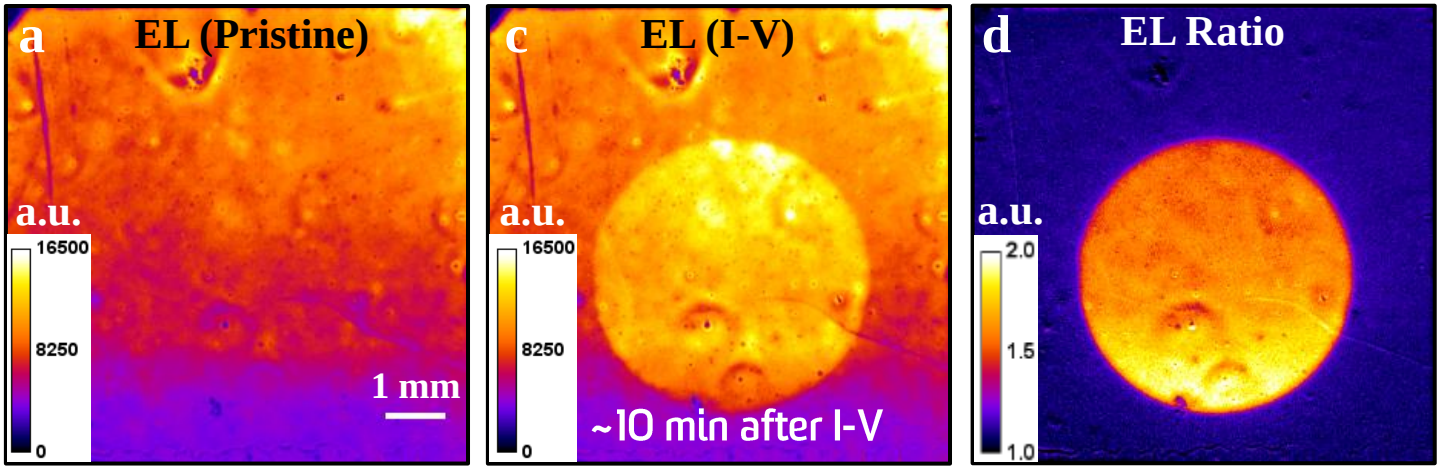
Initial Observations after I-V Measurements: EL and PL_{OC}



$$\phi_{em}(E) \propto EQE_{PV}(E)\exp\left(\frac{V_j}{V_{th}}\right)$$

ϕ_{em} : EL intensity

EQE_{PV} : Photovoltaic external quantum efficiency

V_j : Junction voltage

E : Energy

V_{th} : Thermal voltage

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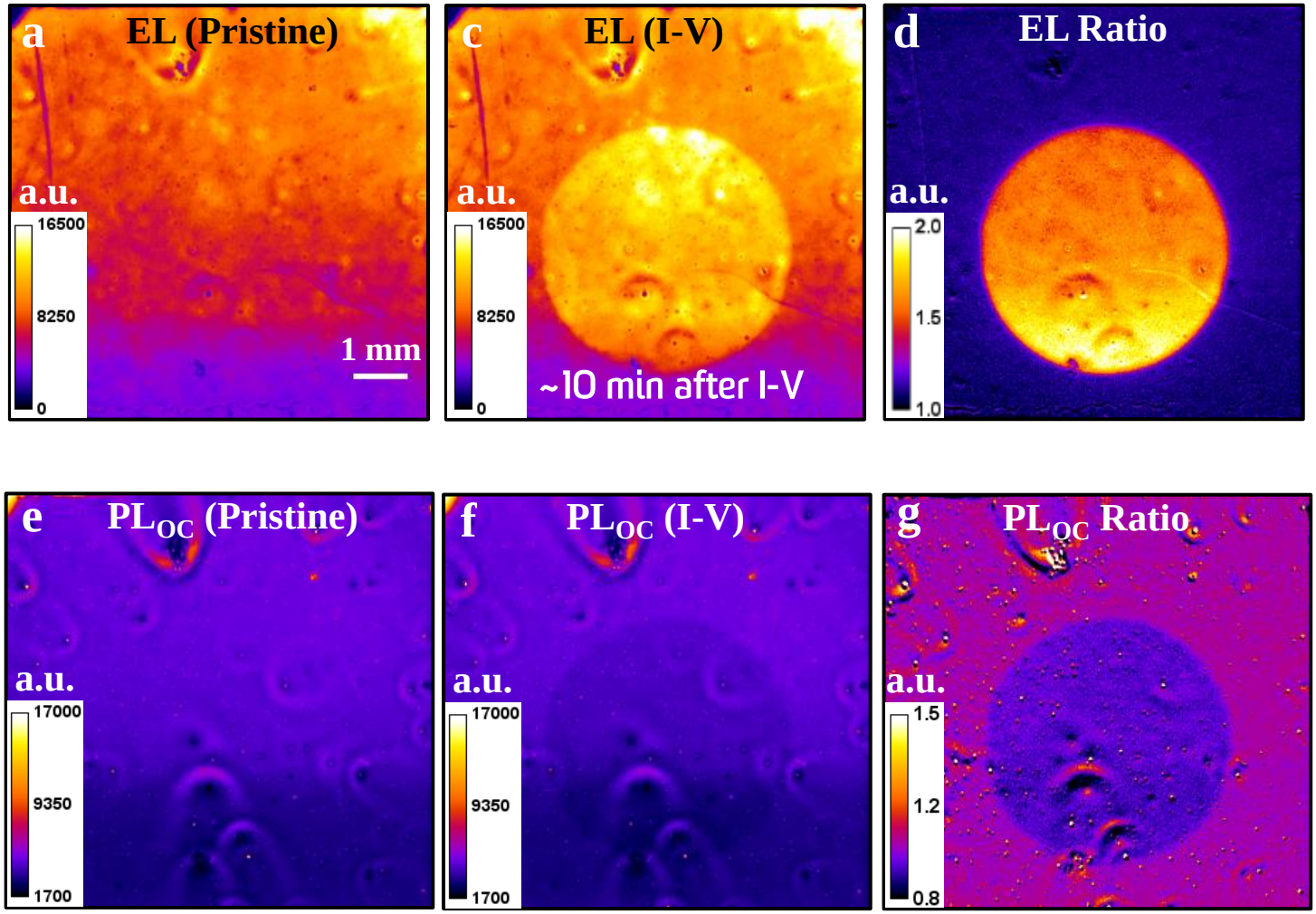

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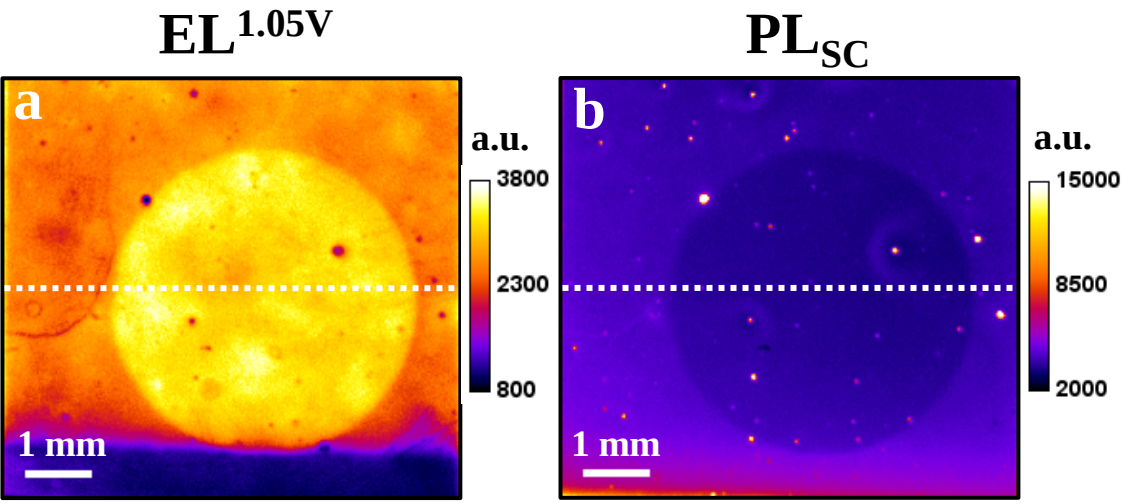

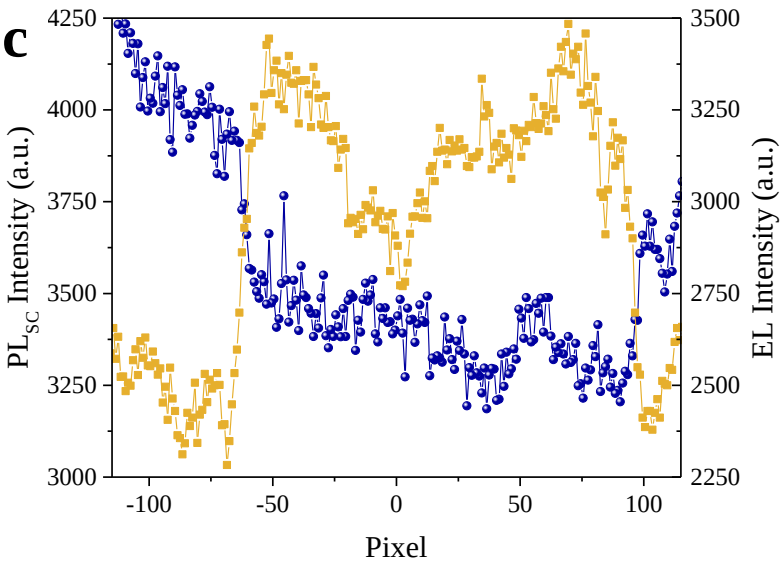

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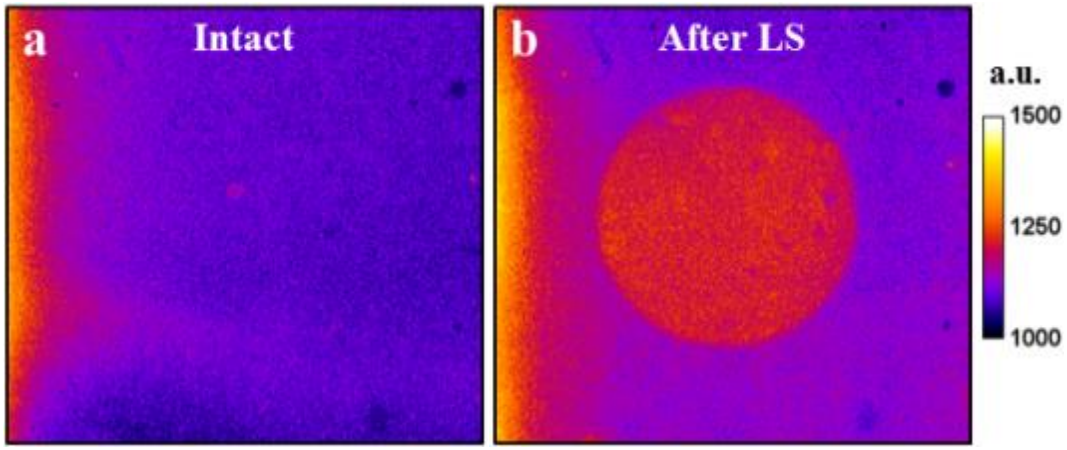
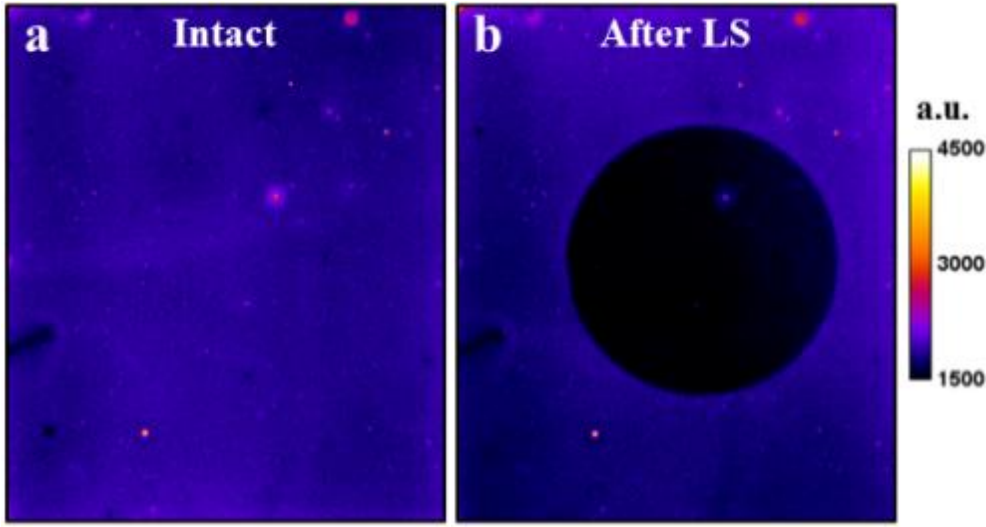
Light-soaked Bilayers: PL_{OC}

$MAPbI_3$/Spiro-OMeTAD



Light-soaking duration: 30min

$c\text{-}TiO_2/MAPbI_3$



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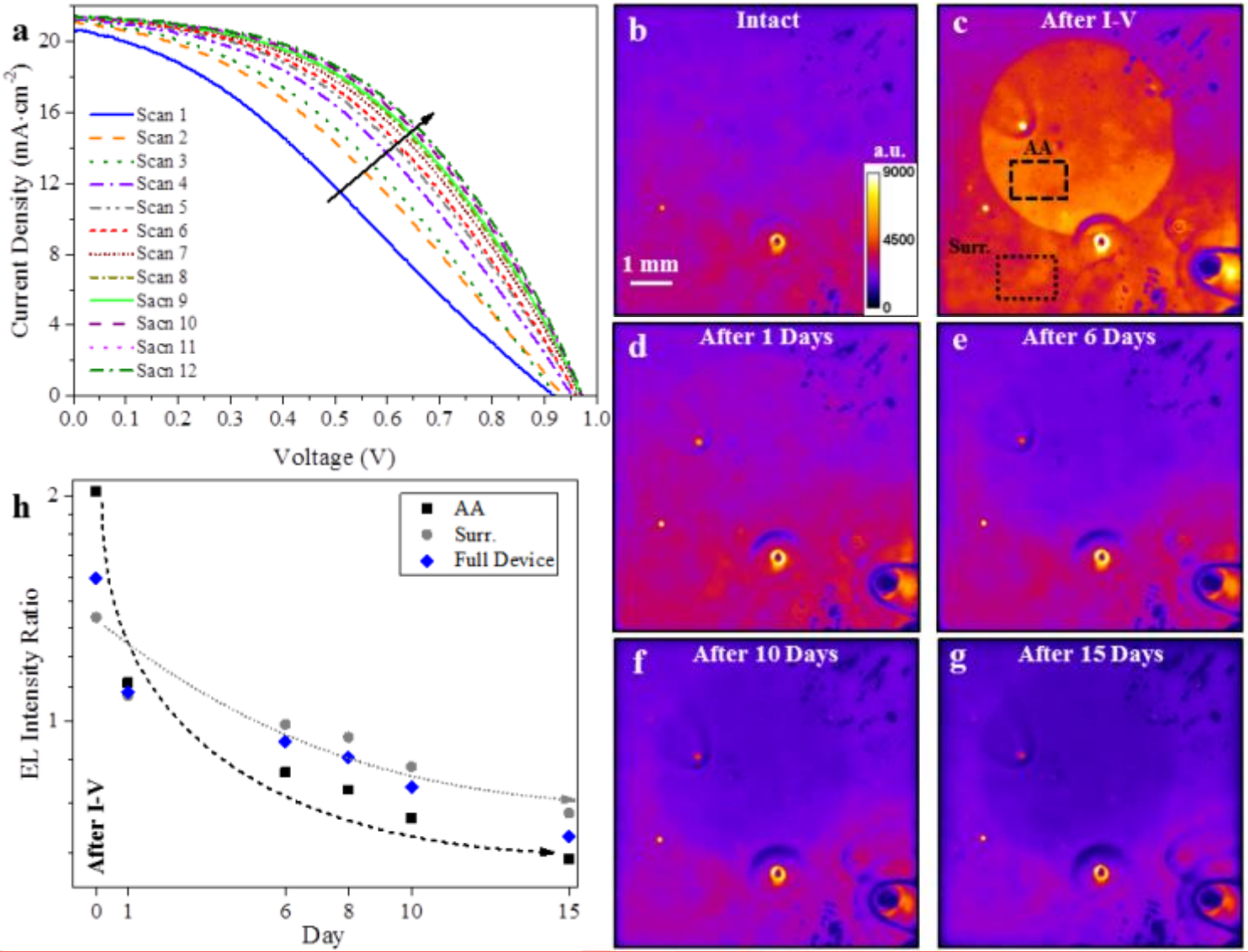
Immediate Observations after I-V Measurements

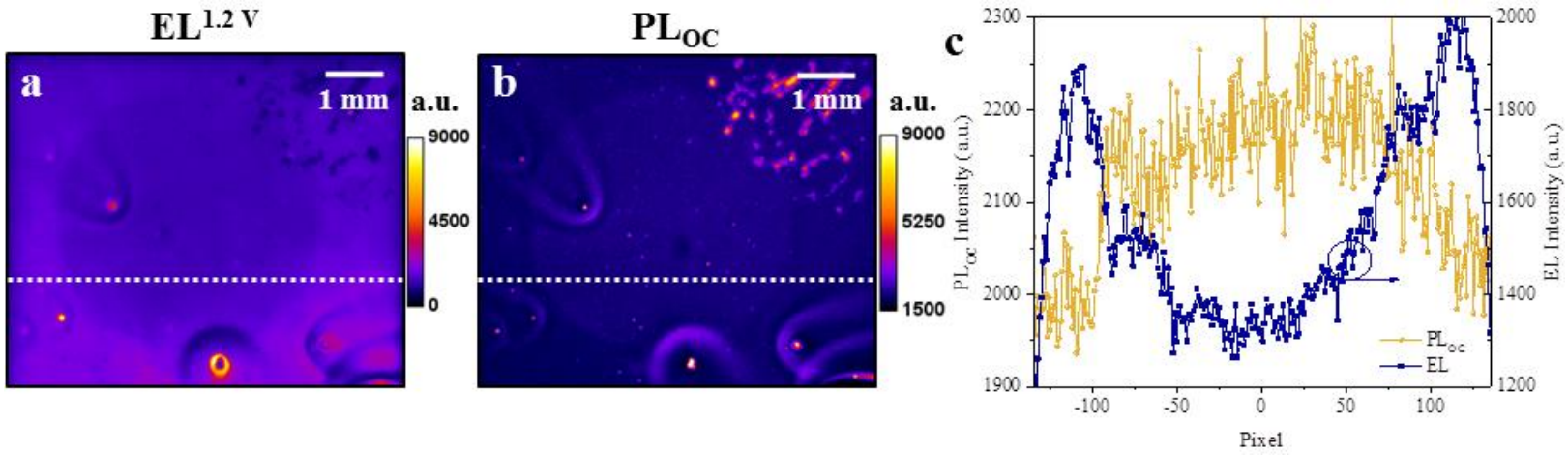
- Series resistance (interfacial): **Improved.**
- Bulk non-radiative recombination: **Possibly Reduced.**
- Front surface non-radiative recombination: **Increased.**
- Back surface non-radiative recombination: **Possibly Increased?**

[10]**Arman Mahboubi Soufiani** *et al, Adv. Energy Mat.* **7**, 1602111 (2016)

Long-term Evolution of EL



Long-term Evolution of PL_{OC}



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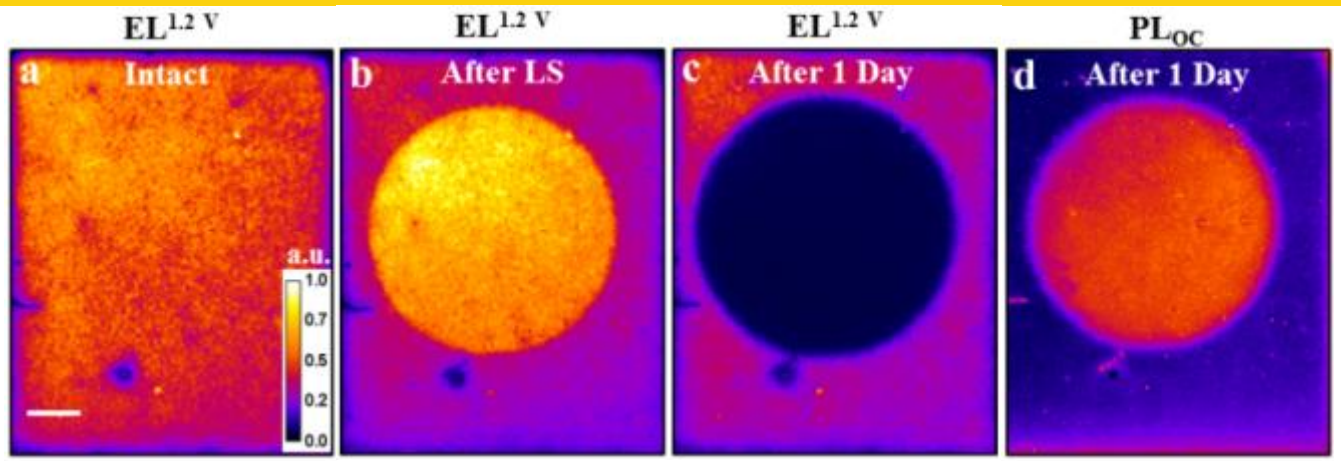
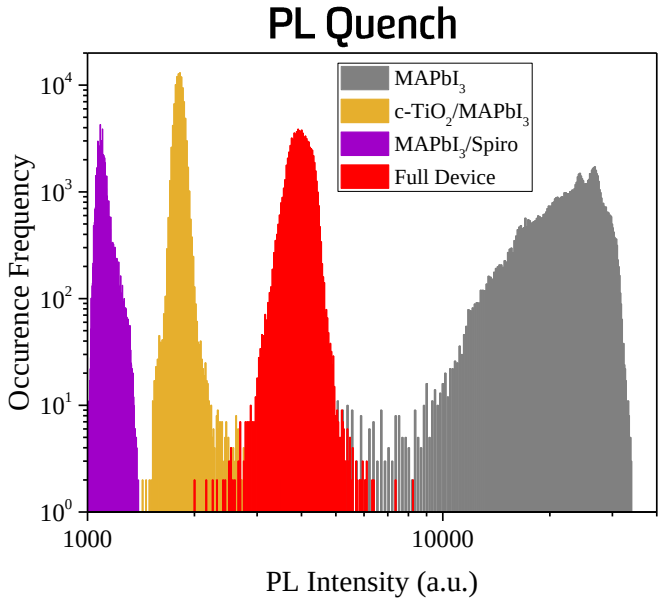
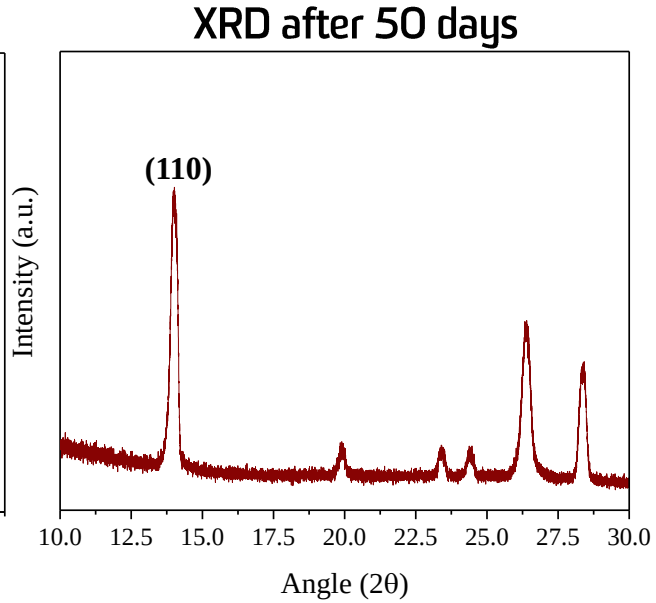
Light-soaking at Open-circuit







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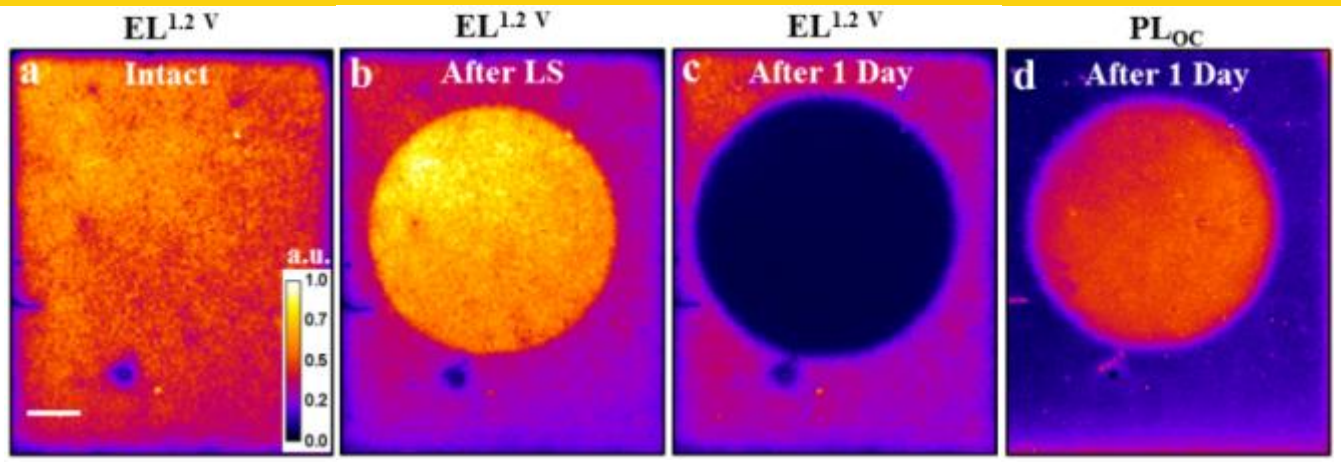
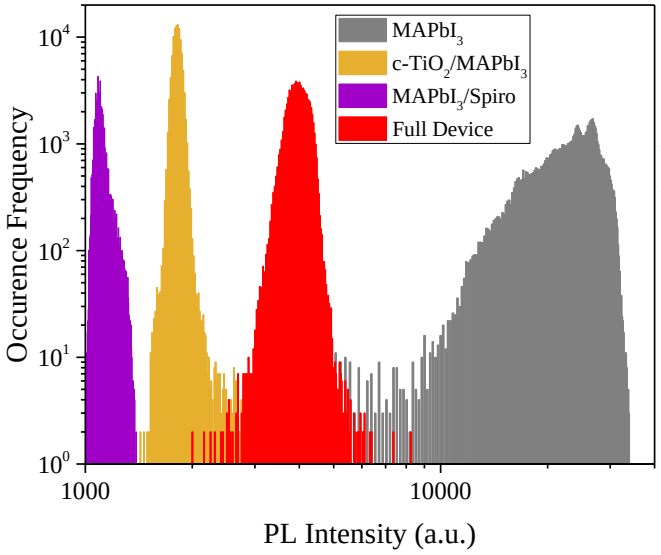
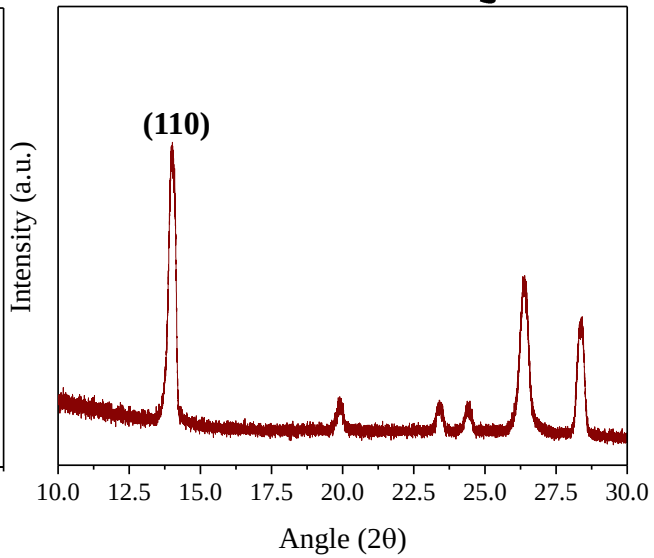


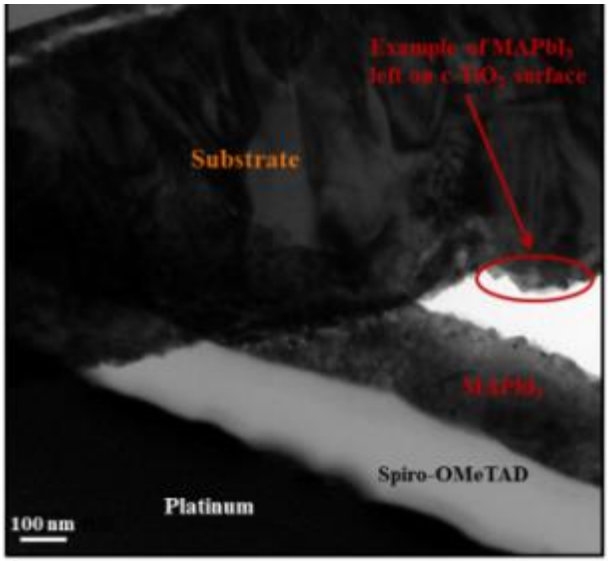
PL Quench



XRD after 50 days



Cross-sectional TEM



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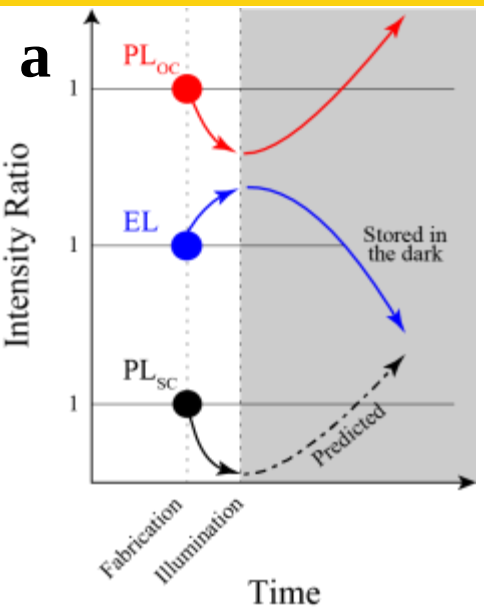
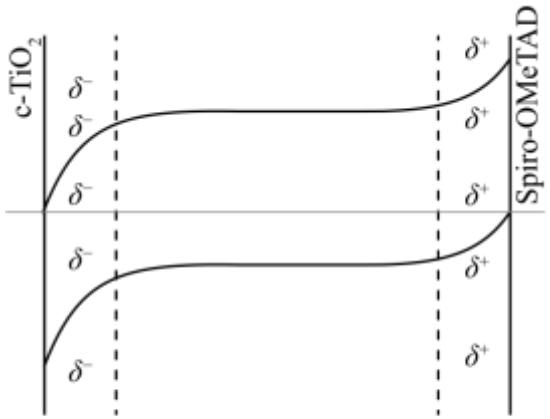
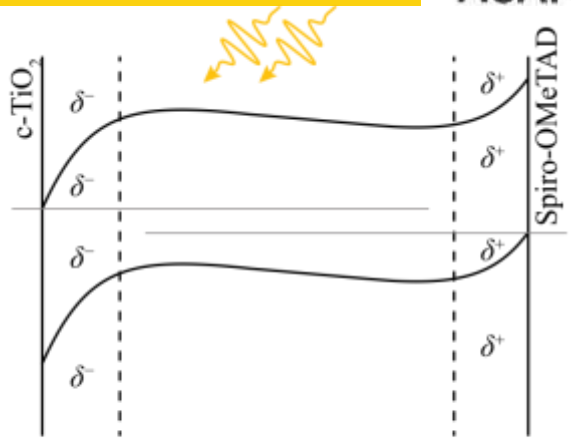
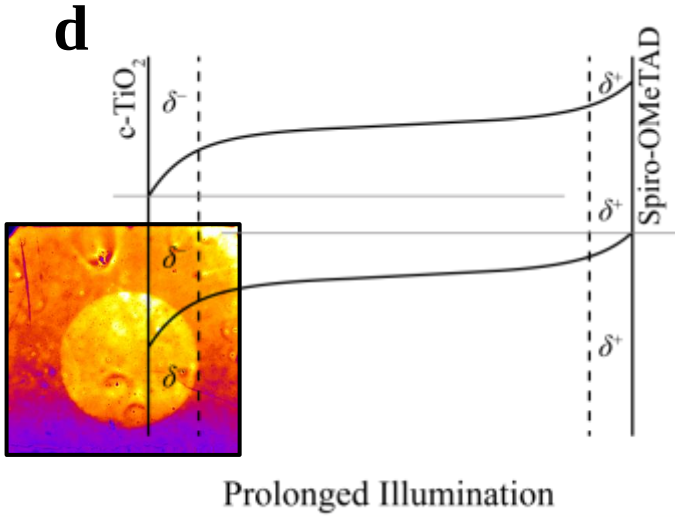
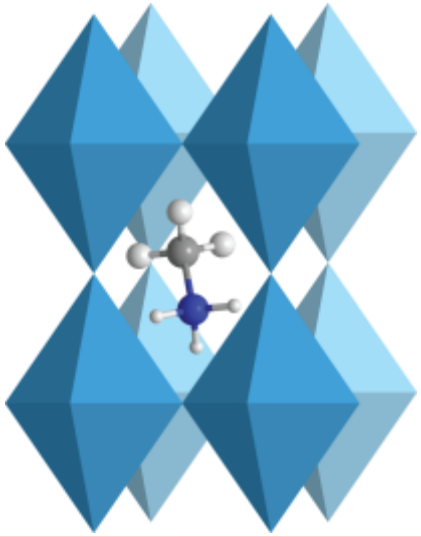
Proposed Mechanism





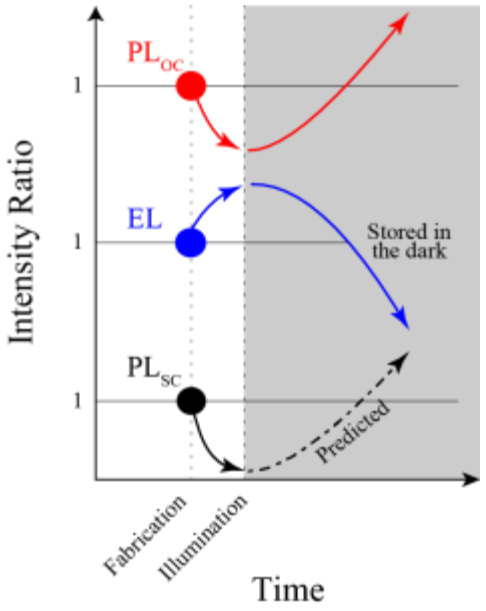






Conclusions

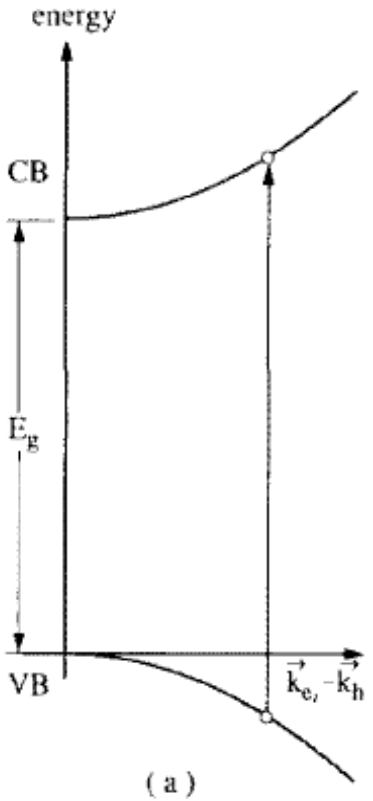
- Interfacial decoupling at $TiO_2/CH_3NH_3PbI_3$ was demonstrated for devices exposed to prolonged illumination.
- This has implications for credible solar cell degradation investigation.
- Experimental observations are explained based on ionic transport characteristics of organic-inorganic metal halide perovskites.[10]

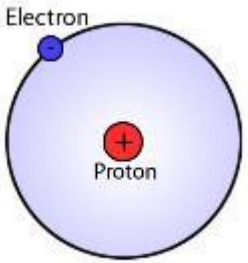


[10]**Arman Mahboubi Soufiani** *et al, Adv. Energy Mat.* **7**, 1602111 (2016)

Introduction to Excitons in Polar Semiconductors

- **Exciton:**
  - **Effective mass approximation**
  - **Hydrogen-like system**





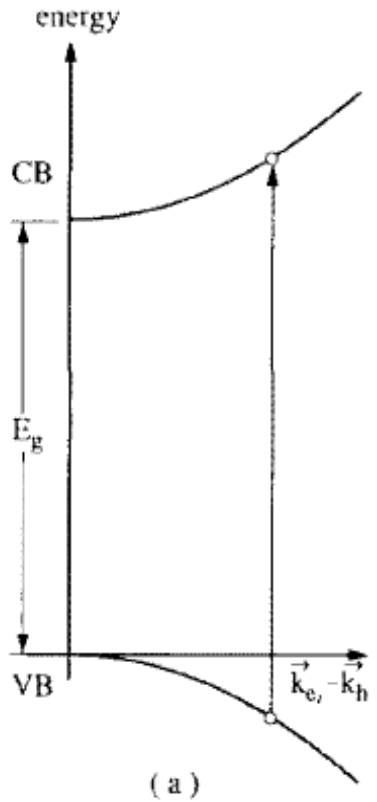
$$Ry^* = \frac{m^*}{\varepsilon^2}\frac{13.6}{m_0}$$

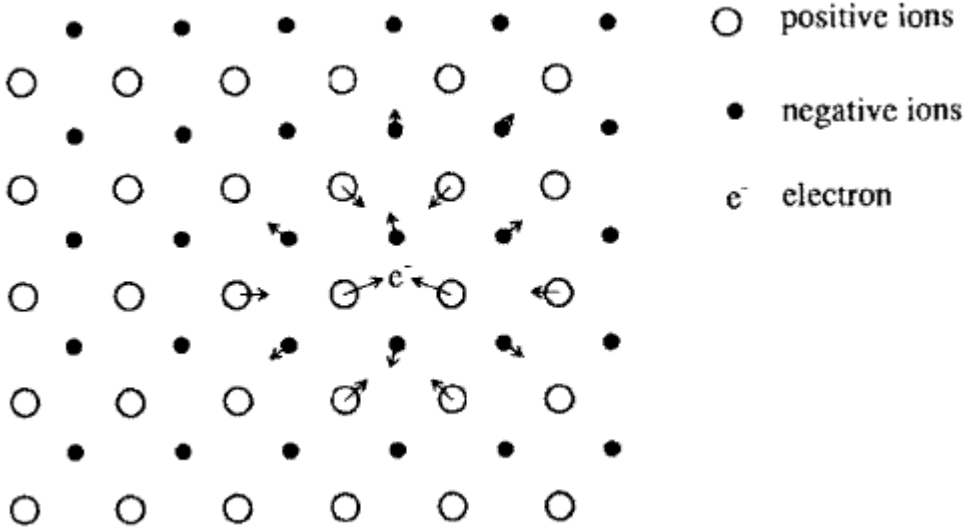
$$E_n = E_g - Ry^*/n^2$$

[11]**Klingshern**, Semiconductor Optics (**2012**)

Introduction to Excitons in Polar Semiconductors

- **Exciton:**
  - **Effective mass approximation**
  - **Hydrogen-like system**





- **Polaron:**
  - **Organic-inorganic lead halides have ionic bonds**
  - **Renormalizations due to polarons:**
    - **Increase in carrier effective mass,**
    - **Lowers the band gap,**

[11]**Klingshern**, Semiconductor Optics (**2012**)

Excitonic Properties (why is it important?)

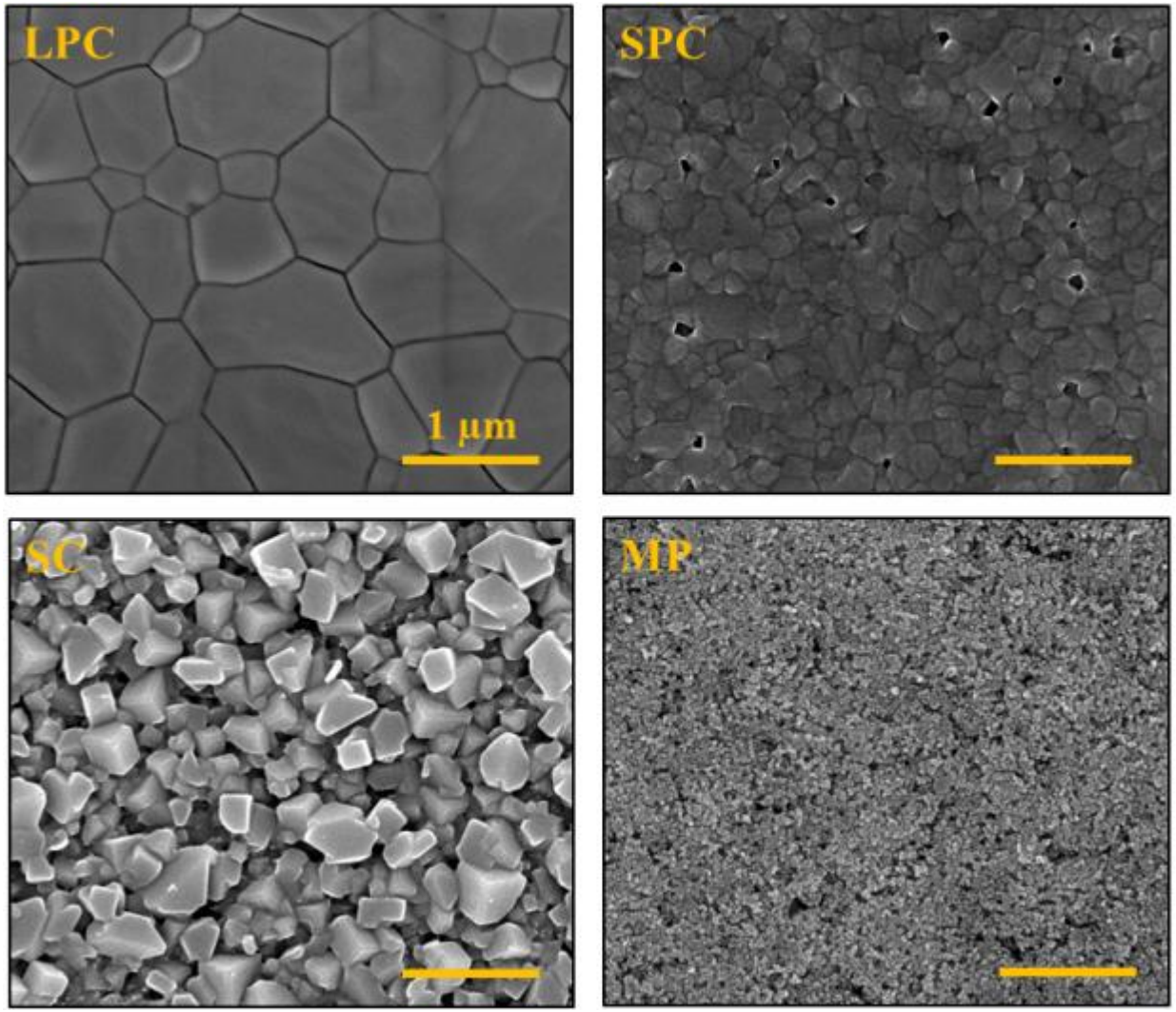
The knowledge of excitonic binding energy is important:

- Determines the nature of the – majority of – photo-generated species,
- Device design optimization:
  - ✓ Large binding energies require an additional mechanism for exciton dissociation into free carriers through which they can readily contribute to the photocurrent,
- In OPV, large binding energy can result in extra loss in open-circuit voltage with respect to the bandgap,
- Influences PL response of the semiconductor,

The knowledge of excitonic reduced mass is important:

- In determination of the charge-carrier mobility $\propto 1/m^*$

$MAPbI_3$ Morphologies



LPC: Large Polycrystalline

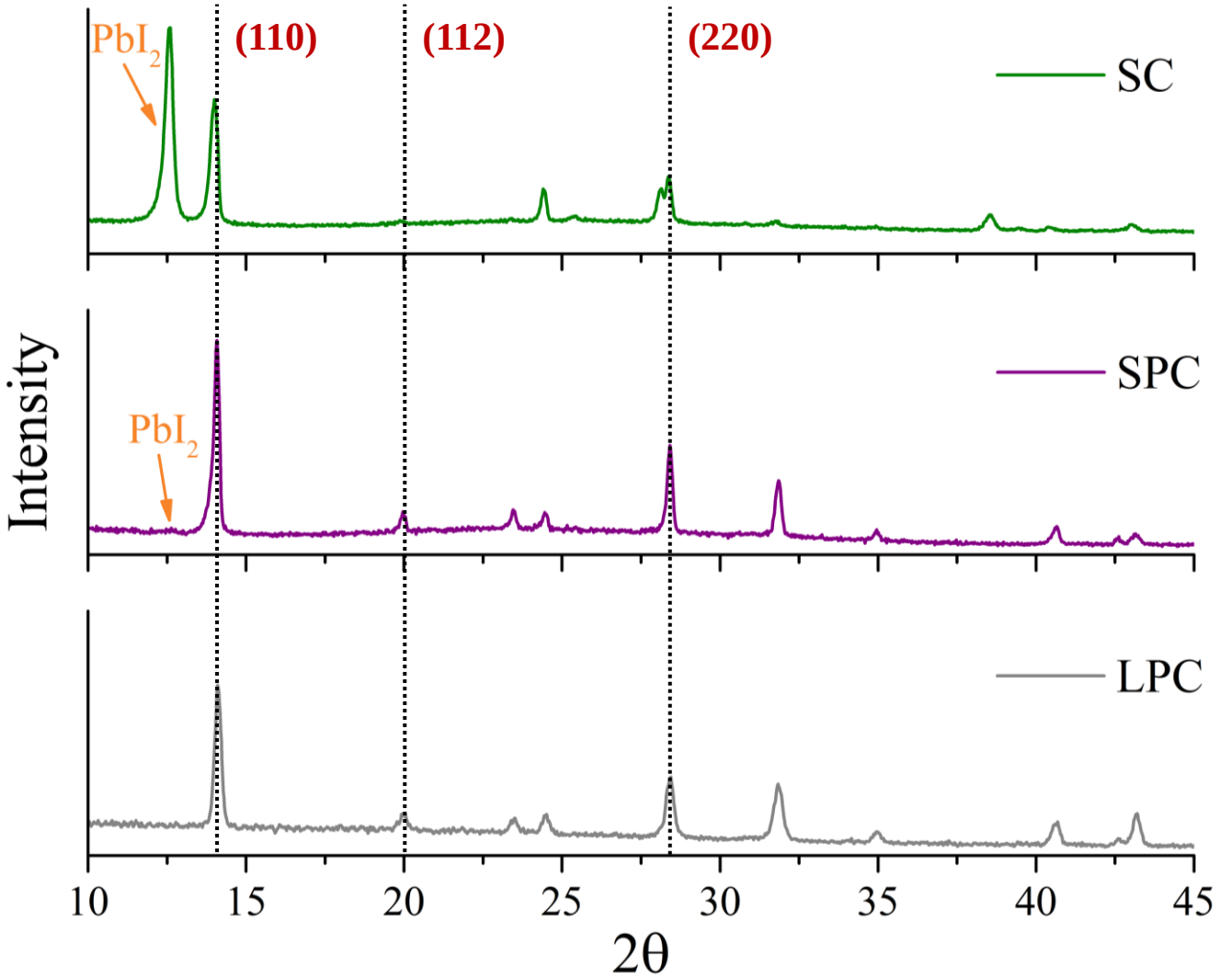
SPC: Small Polycrystalline

SC: Small Crystal

MP: Mesoporous Al_2O_3

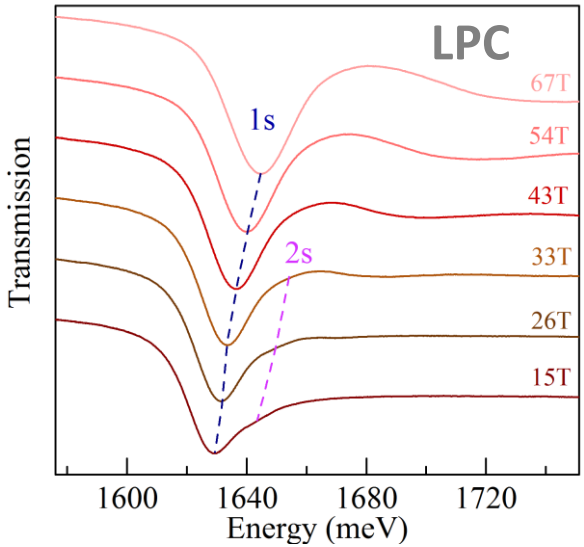
[12]**Arman Mahboubi Soufiani** *et al, Energy Environ. Science* **10**, 1358 (**2017**)

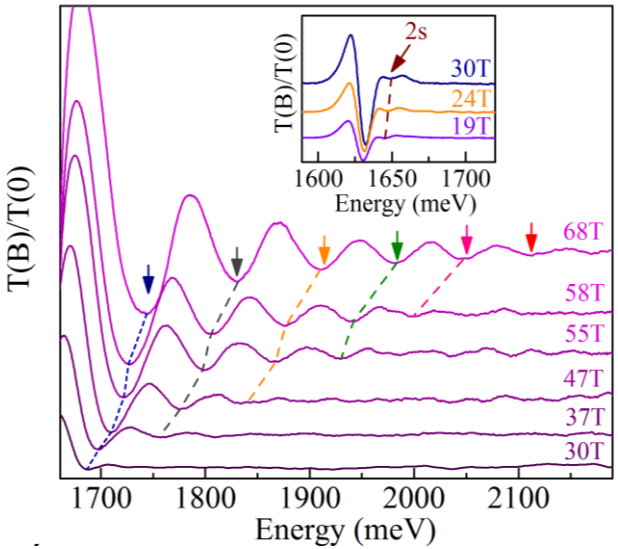
Structural Examination of $MAPbI_3$ (X-ray Diffraction)



[12]**Arman Mahboubi Soufiani** *et al, Energy Environ. Science* **10**, 1358 (**2017**)

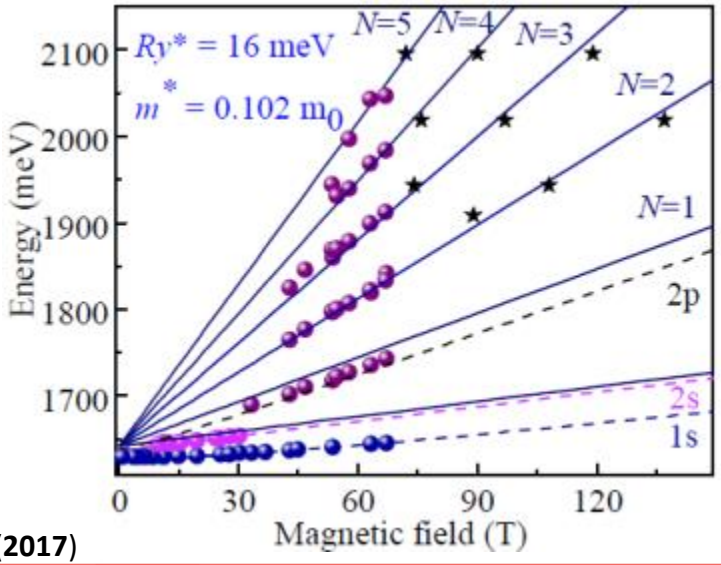
LPC $MAPbI_3$ Magneto-optic Response





- Landau levels (i.e. free carrier states): Quantization of the free particle motion in the plane perpendicular to the magnetic field direction.
- Landau level transitions are described by:

$$E(B) = E_g + (N + 1/2)\hbar\omega_c$$
$$\hbar\omega_c = \hbar eB/m^*$$



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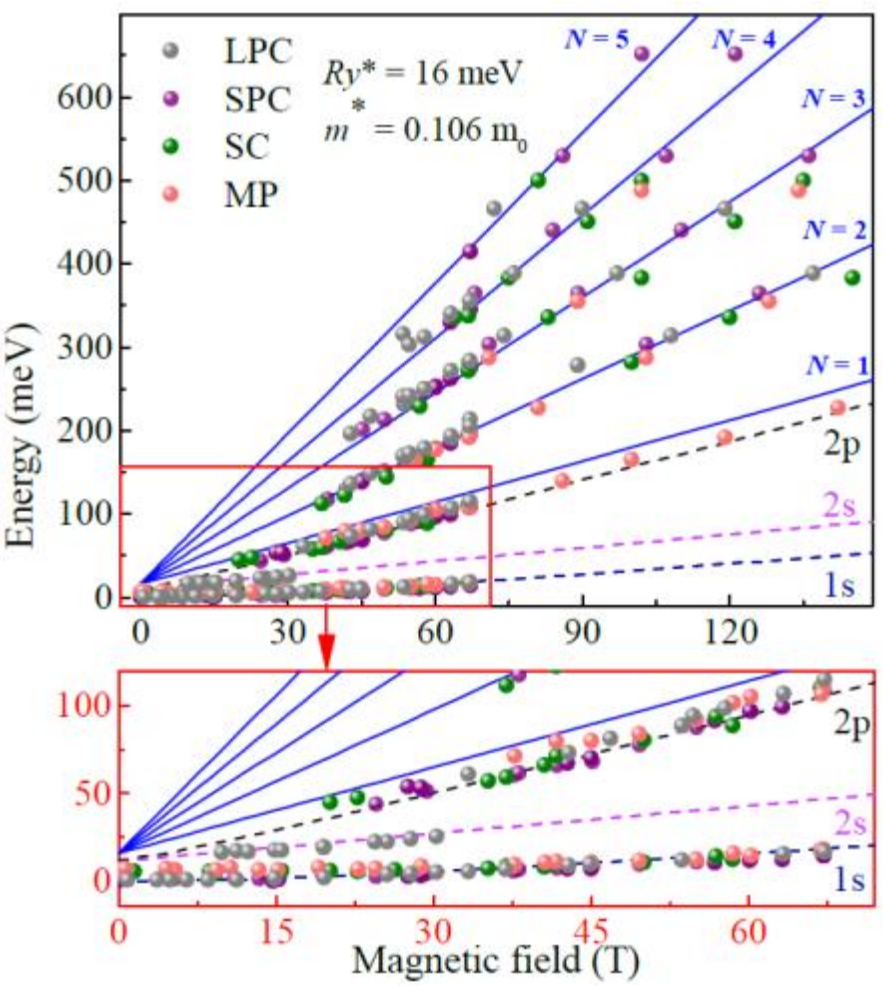
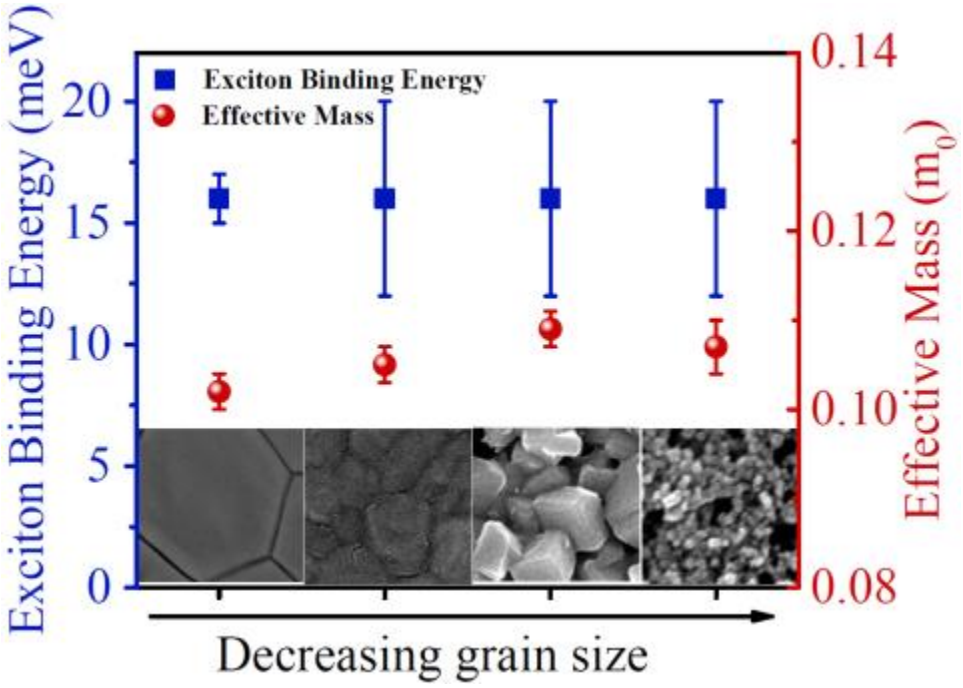
$MAPbI_3$ Magneto-optic Responses

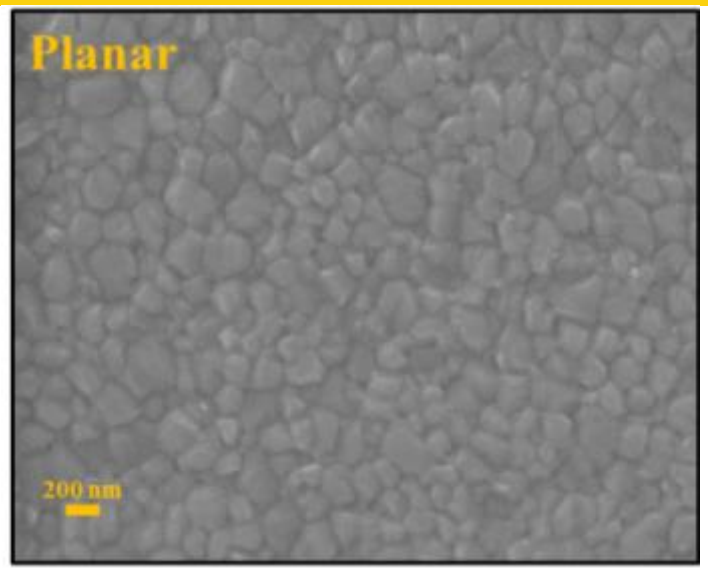


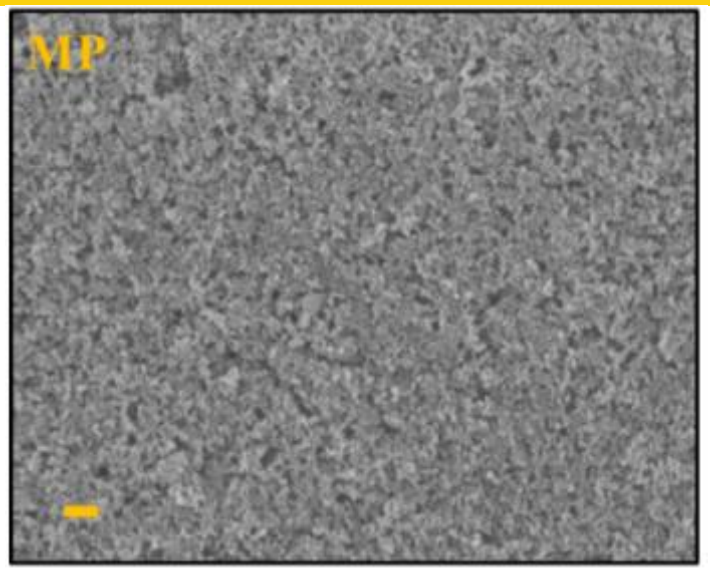
	Size Distribution (nm)	E_g (meV)	m^* (m_0)	Ry^* (meV)
Large Polycrystalline	772(227)	1642(2)	0.102(0.002)	16(1)
Small Polycrystalline	214(57)	1643(2)	0.105(0.002)	16(4)
Small Crystal	291(64)	1639(2)	0.109(0.002)	16(4)
Mesoporous	<50	1638(2)	0.107(0.003)	16(4)

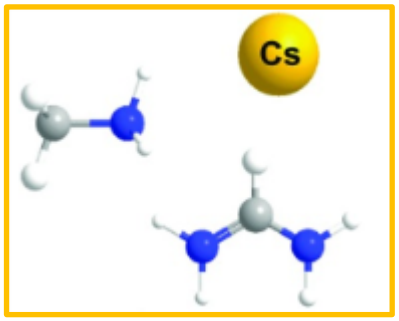


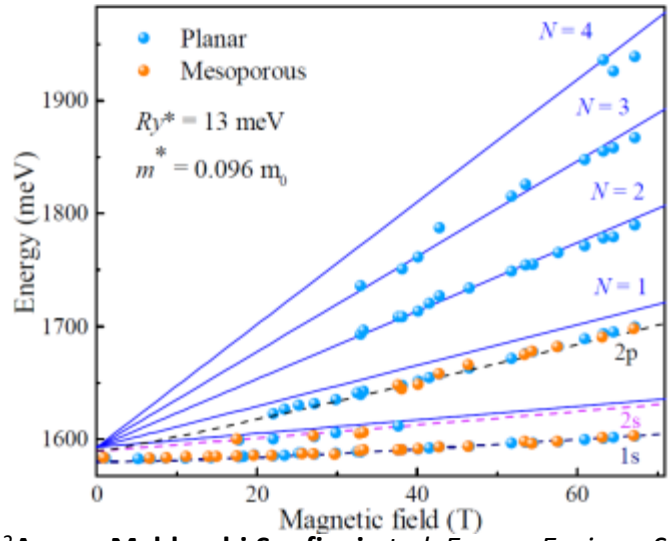
[12]**Arman Mahboubi Soufiani** *et al, Energy Environ. Science* **10**, 1358 (**2017**)

$Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{0.83}Br_{0.17})_3$ Morphologies









	E_g (meV)	m^* (m_0)	Ry^* (meV)
Planar	1593(2)	0.096(0.002)	13(2)
Mesoporous	1594(2)	0.096(0.008)	13(2)

[12]**Arman Mahboubi Soufiani** *et al, Energy Environ. Science* **10**, 1358 (**2017**)

Exciton-polaron Interaction

$$Ry^* = \frac{m^*}{\varepsilon^2}\frac{e^4}{2\hbar^2(4\pi\varepsilon_0)^2};$$

$$a_{e,h} = \left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_s}\right)\frac{e^2}{2\hbar\omega_{LO}}\sqrt{\frac{2m_{e,h}\omega_{LO}}{\hbar}}$$

$$m_{e,h}^p \approx m_{e,h}(1+\frac{a}{6}+\frac{a^2}{40}+...) \qquad \frac{1}{m^*} = \frac{1}{m_e^p} + \frac{1}{m_h^p}$$

[13] **Arman Mahboubi Soufiani**, *PhD Thesis* (**2017**)

Conclusions

- Excitons truly play a negligible role in the operation of organic cation-based perovskites regardless of the thin film deposition technique and final morphology.
  - ✓ Universal values for **$CH_3NH_3PbI_3$** at 2 K:
    - Ry^*: **15-16 meV**
    - μ: **0.102-0.109m_0**
  - ✓ Universal values for **$Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{0.83}Br_{0.17})_3$** at 2 K:
    - Ry^*: **13±2 meV**
    - μ: **0.096±0.008m_0**
- The electronic structure of the inorganic cage (e.g. PbI_3^- in $CH_3NH_3PbI_3$) is likely to have the greatest contribution to the excitonic properties of the perovskite semiconductors rather than the degree of poly-crystallinity and the order of dipolar organic-cation domains.
- Negligible influence of microstructure on the reduced mass implies that:
  - ✓ Polaron coupling constant (α) is only minimally influenced by the variation in microstructure.

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Khaju Bridge (Persian: پل خواجو Pol-e Khāju)
Thank You!