Photonic Devices and Applications: Perovskite LED and Laser

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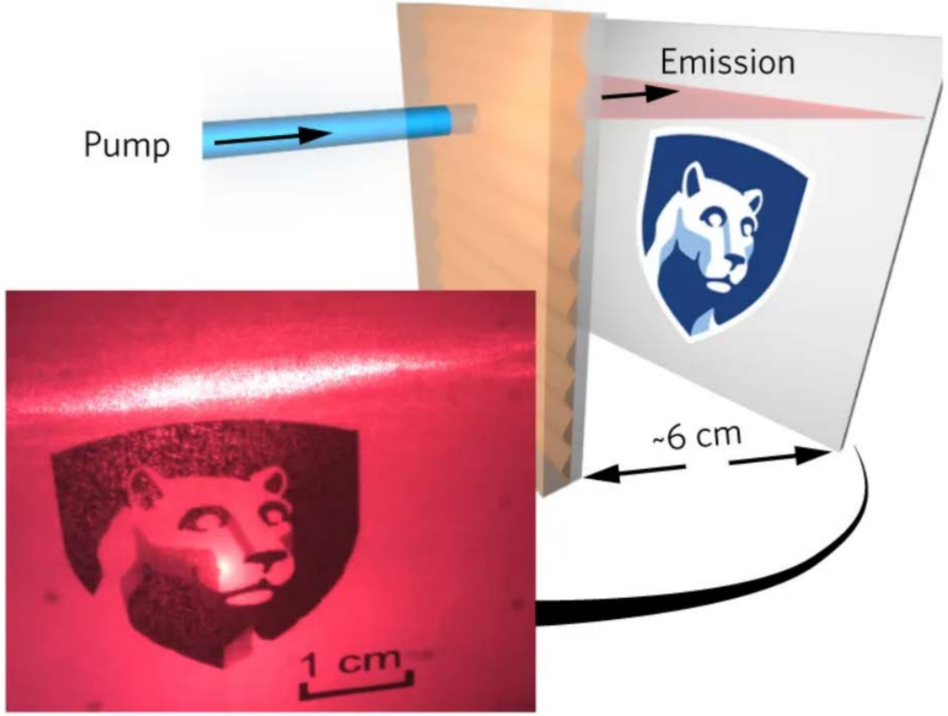
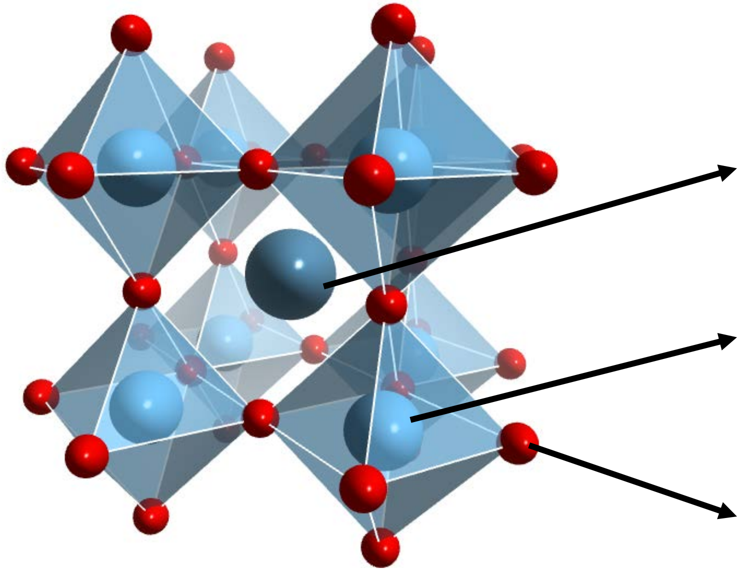
Light Emitting of Perovskites

Perovskite LEDs

Perovskite lasers



Halide Perovskite Composition

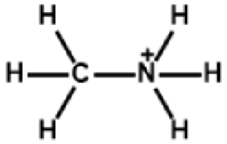


Chemical formula: $\boldsymbol{ABX_3}$

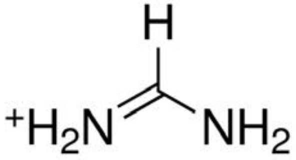
A-site:
methylammonium cation (MA^+), formamidinium cation (FA^+), Cs^+

B-site:
Pb^{2+}, Sn^{2+}

X-site:
Cl^-, Br^-, I^-



MA^+



FA^+

Examples:

- Single composition: $MAPbI_3$, $FAPbI_3$, $CsPbBr_3$
- Mixed composition: $MAPbI_xBr_{3-x}$, $MA_xCs_{1-x}Br_3$
- Lead-free perovskite: $MASnI_3$, $MASnBr_3$

Perovskite Crystal Structure

Tolerance factor: $$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}$$

t	Crystal system
> 1.0	Hexagonal or Tetragonal
0.9 ~ 1.0	Cubic
0.71 ~ 0.9	Orthorhombic/Rhombohedral
< 0.71	Different structures

Composition effect

Composition	Crystal system at RT
$MAPbI_3$	Tetragonal
$MAPbBr_3$	Cubic

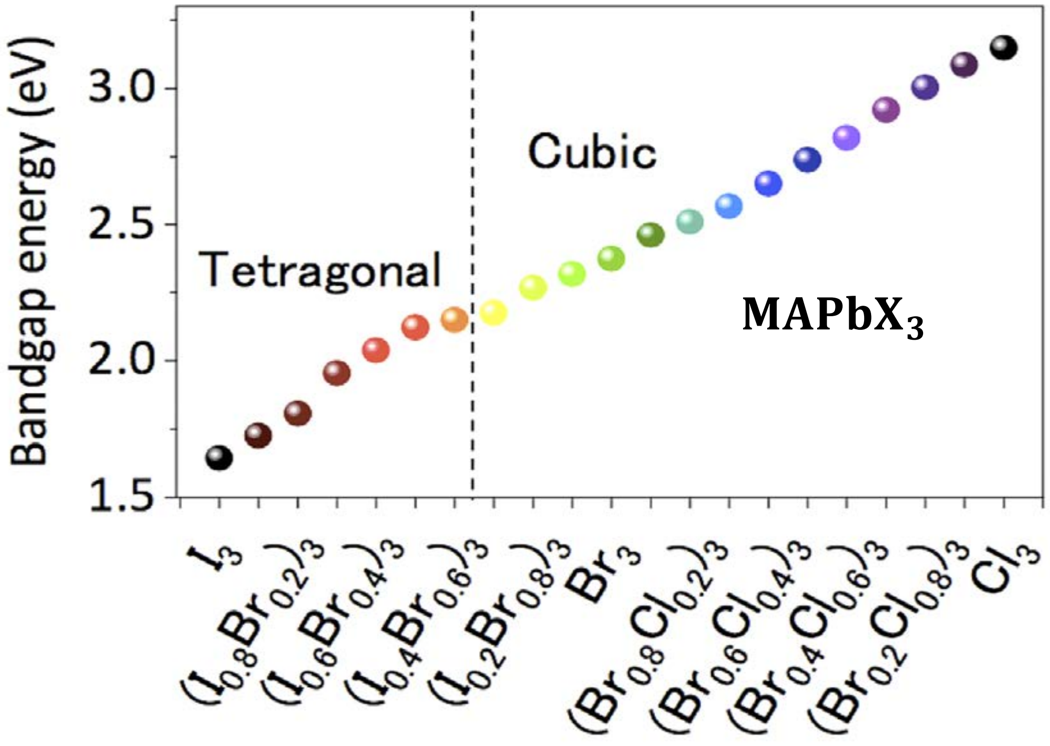
Temperature effect

Temperature	Crystal system of $MAPbI_3$
< 162 K	Orthorhombic
162 K ~ 327 K	Tetragonal
> 327 K	Cubic

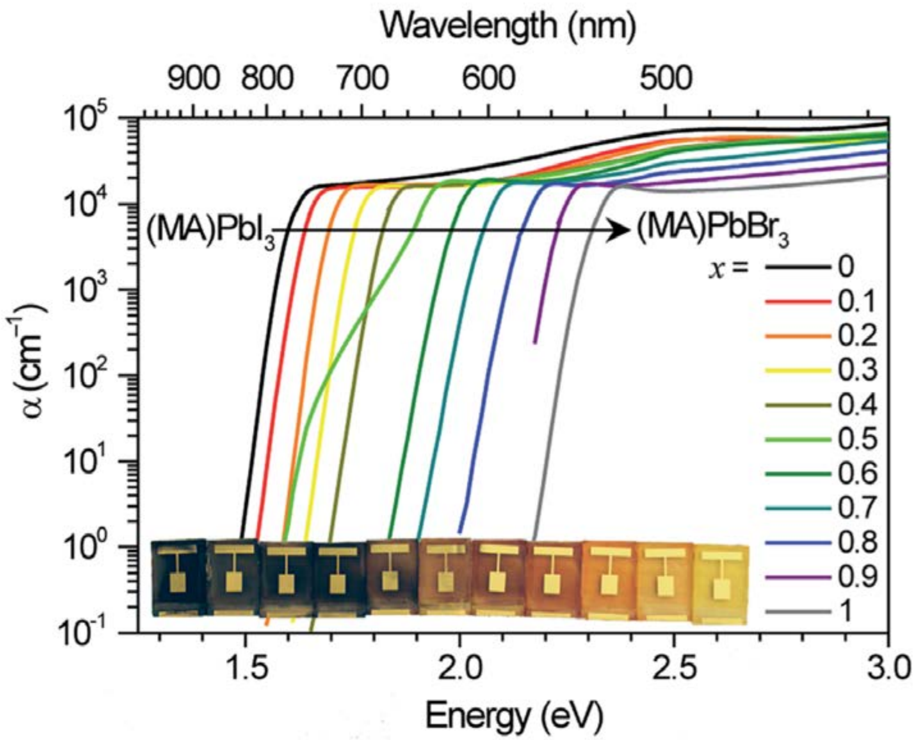
Quarti et al. *Energy Environ. Sci.*, 2016, **9**, 155-163.

Perovskite Properties

A semiconductor with tunable band gap



Pathak *et al. Chem. Mater.*, 2015, **27**, 8066−8075.



Pathak *et al. Chem. Sci.*, 2015, **6**, 613–617.

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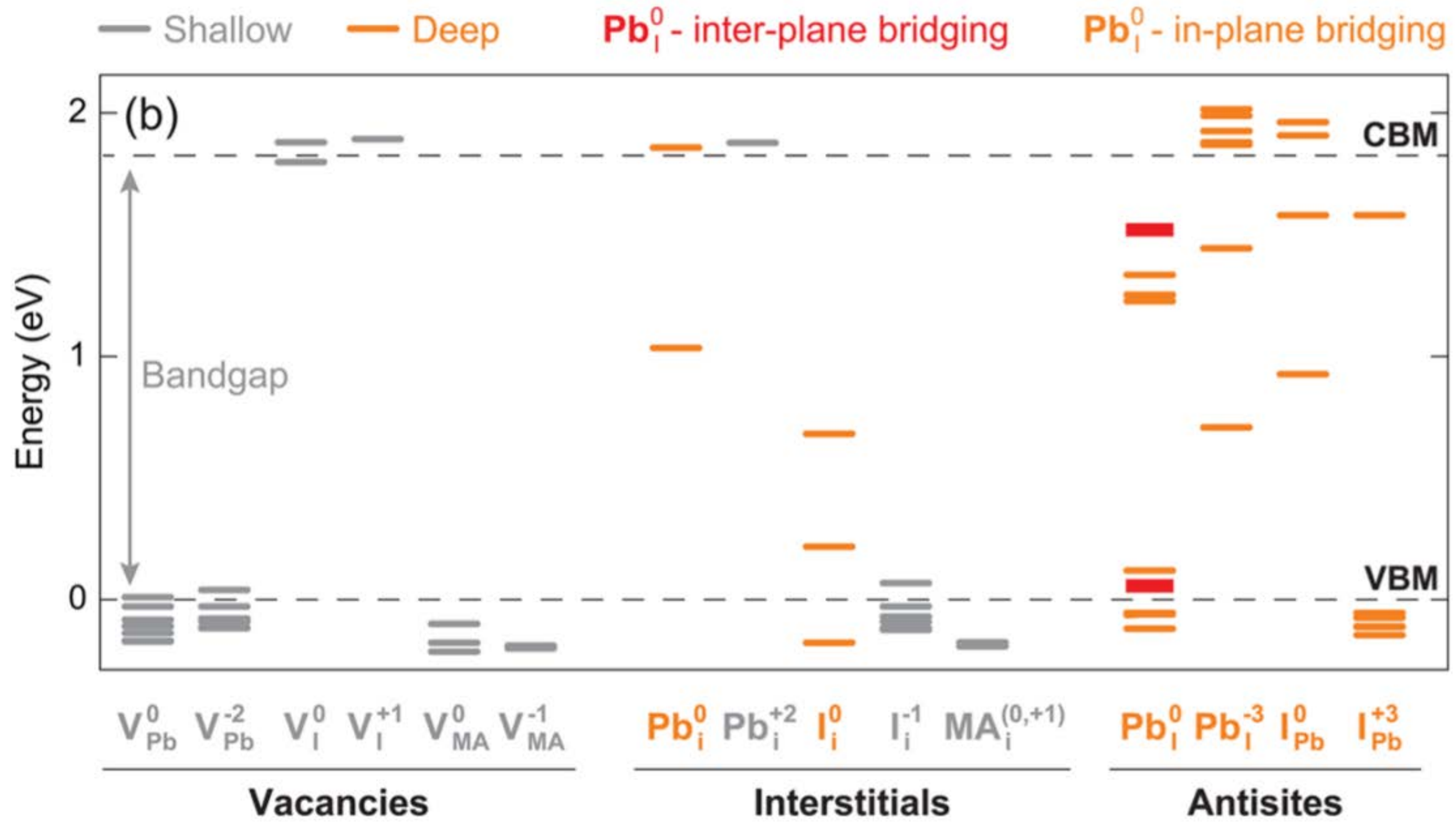
Perovskite Properties

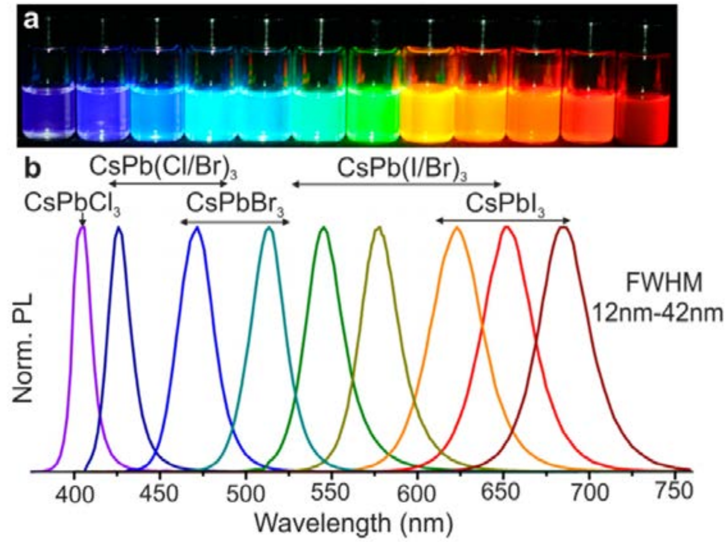
Defect tolerance: Dominant intrinsic defects are mainly shallow defects



Buin *et al.* *Nano Lett.*, 2014, **14**, 6281−6286

Perovskite Properties

- **Narrow Emission linewidth**
- **High PLQY**



PLQY > 90%

Protesescu *et al. Nano Lett.*, 2015, **15**, 3692−3696

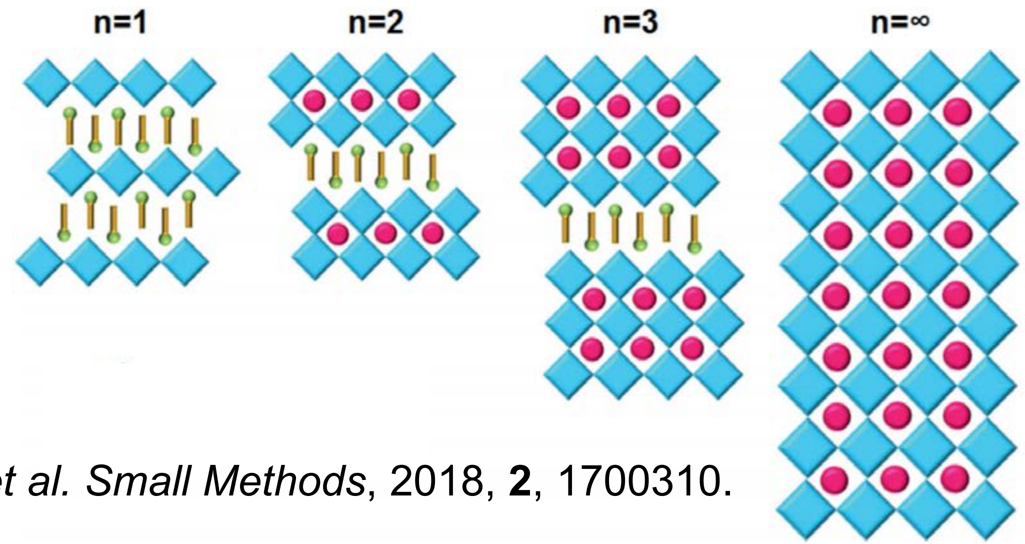
Long carrier diffusion length

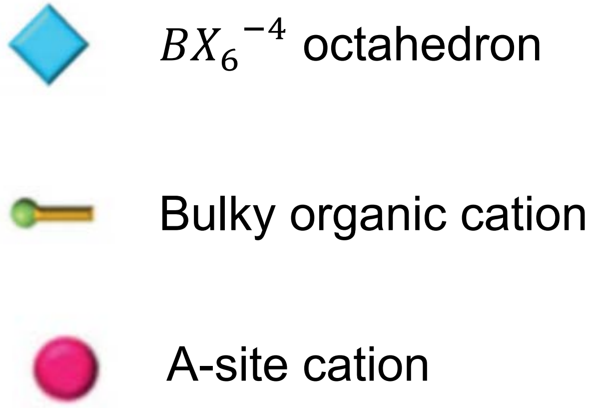
Perovskite	Species	D (cm^2 s^{-1})	L_D (nm)
$CH_3NH_3PbI_{3-x}Cl_x$	Electrons	0.042 ± 0.016	1069 ± 204
	Holes	0.054 ± 0.022	1213 ± 243
$CH_3NH_3PbI_3$	Electrons	0.017 ± 0.011	129 ± 41
	Holes	0.011 ± 0.007	105 ± 32

Stranks *et al. Science*, 2013, **342**, 341-343

Quasi-2D Perovskite

Layered structure



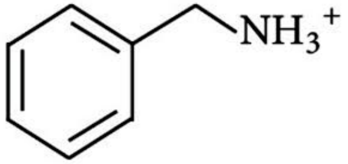


Kim *et al. Small Methods*, 2018, **2**, 1700310.

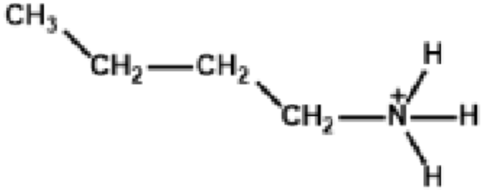
Advantages of quasi-2D perovskite:

- Improved stability (higher formation energy)
- Defect passivation by amine group (high PLQY)

Example of bulky organic cation:

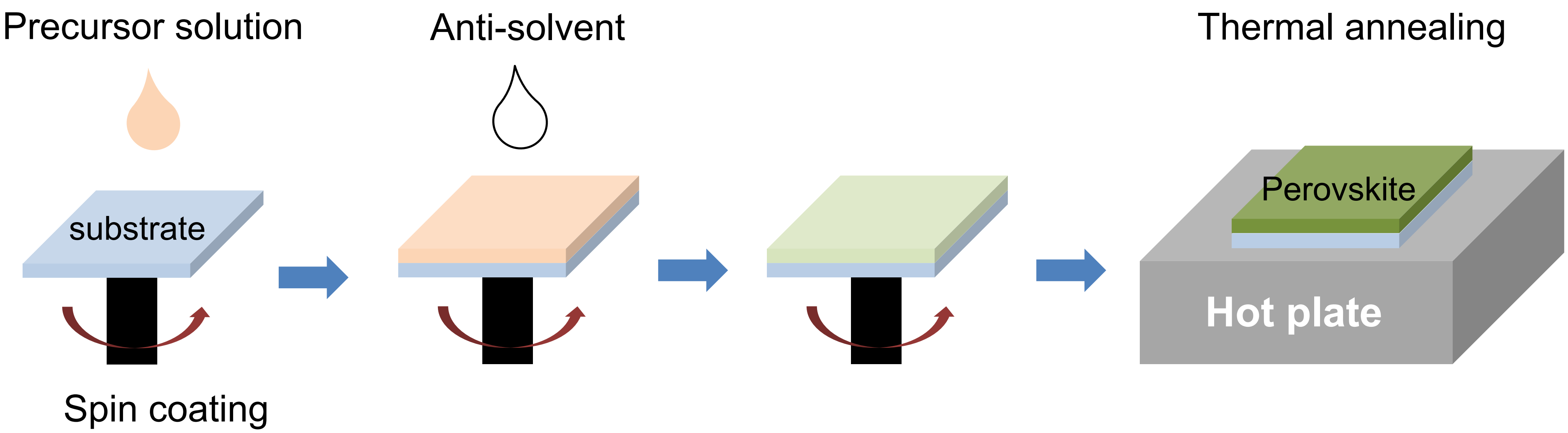


Phenethylammonium (PEA)



n-butylammonium (BA)

Fabrication of Perovskite



Precursor solvents:

Dimethylformamide (DMF), Dimethyl sulfoxide (DMSO), N-Methyl-2-pyrrolidone (NMP)

Antisolvents:

Chlorobenzene (CB), Toluene, Chloroform

Anti-solvent dripping is used to control crystal growth and morphology

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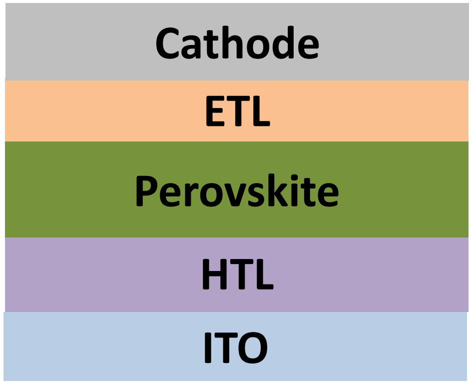
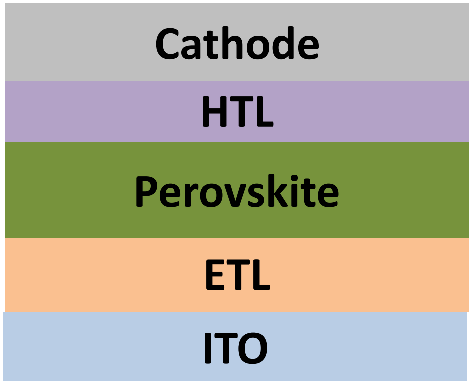
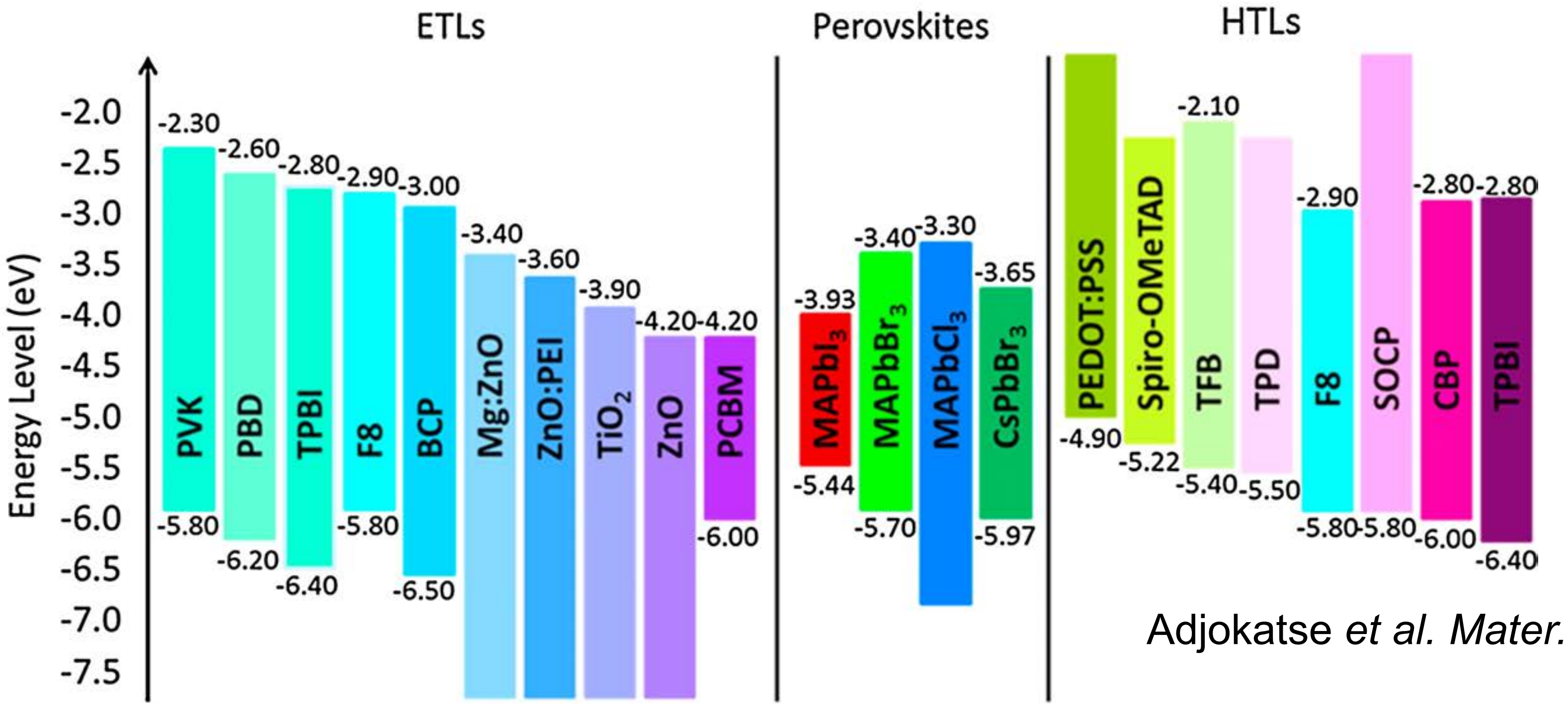
Device Structure of PeLED

Conventional structure



Inverted structure

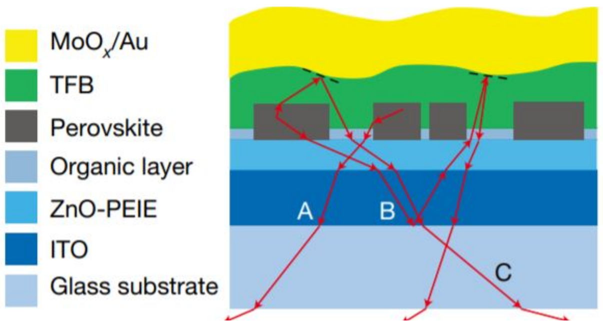


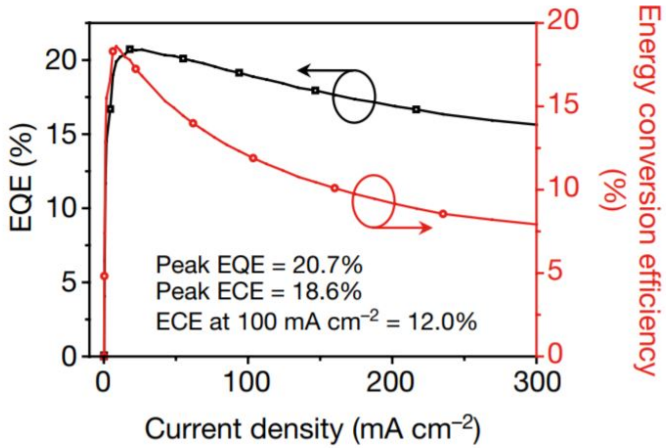


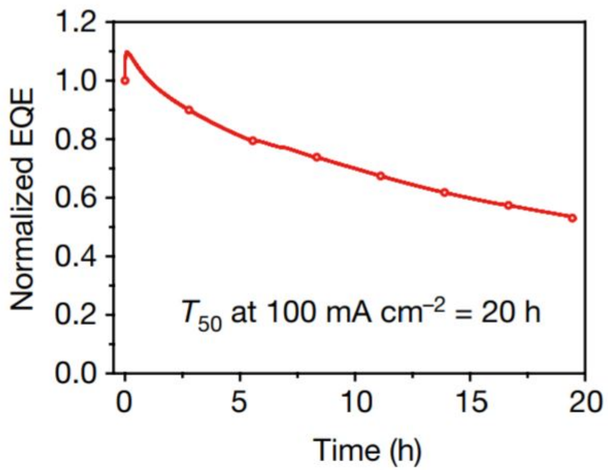
Adjokatse *et al. Mater. Today*, 2017, **20**, 413-424.

Performance of PeLEDs

Red PeLED

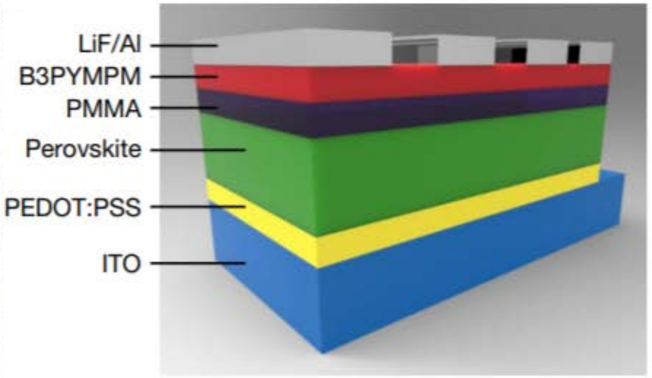


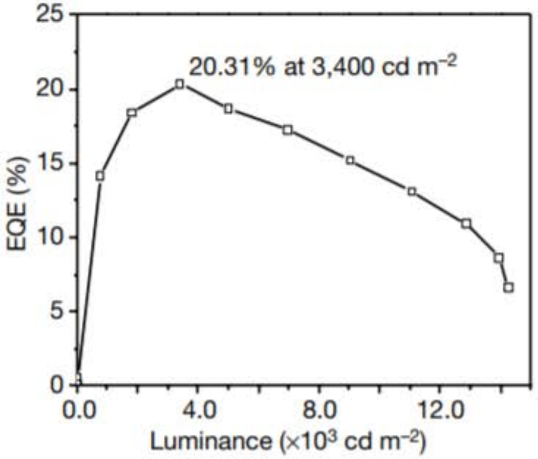


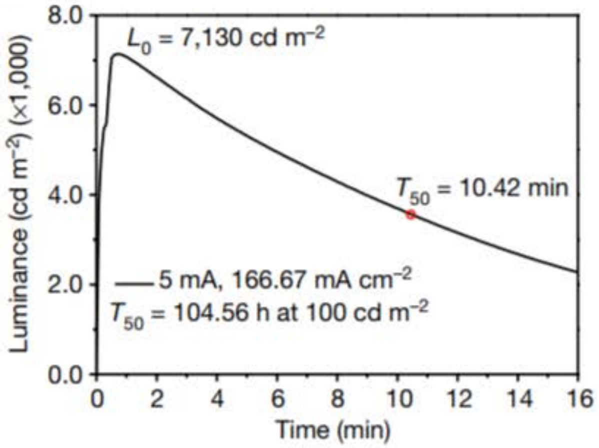


Cao *et al. Nature*, 2018, **562**, 249-253.

Green PeLED



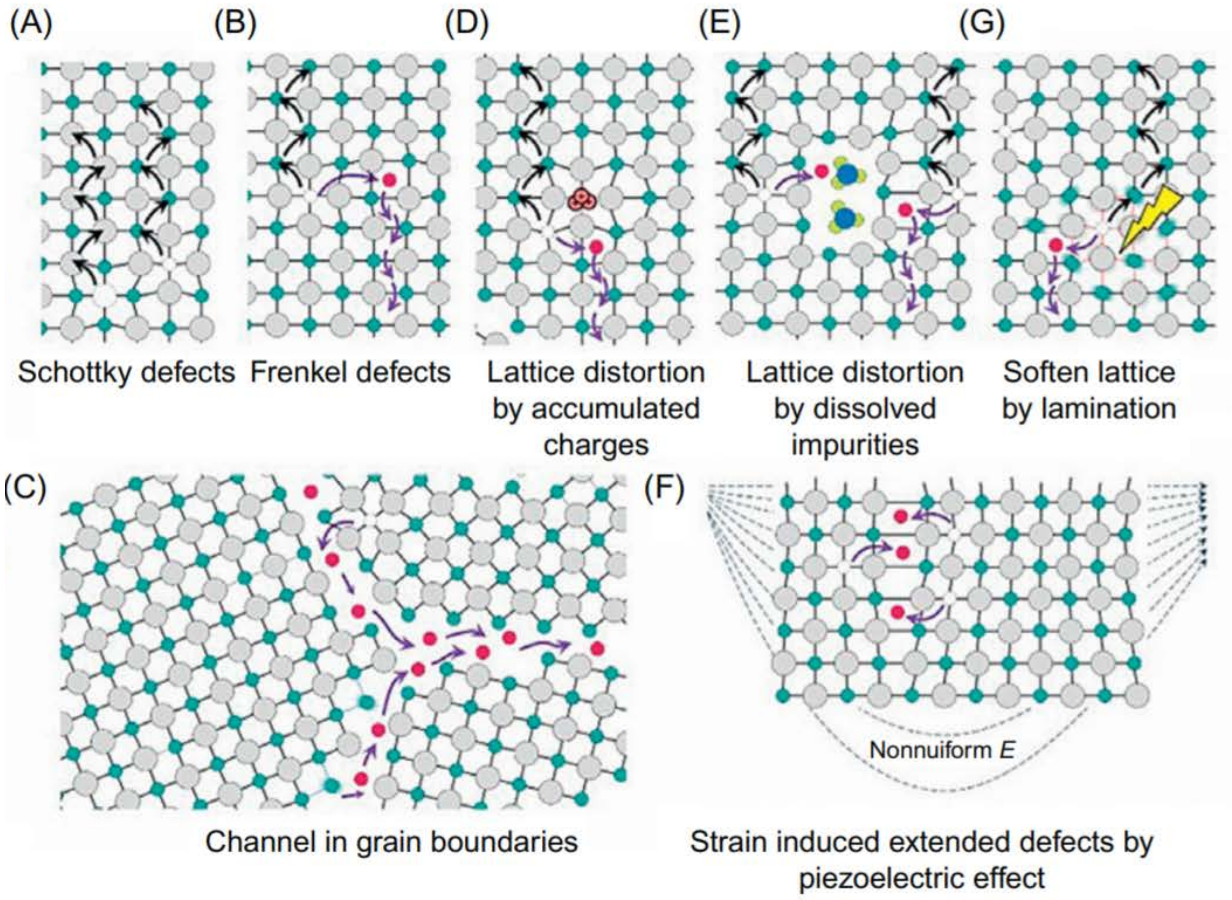




Lin *et al. Nature*, 2018, **562**, 245-248.

Ion Migration in Perovskites

The **short operational lifetime** of PeLED compared to OLED is mainly due to **ion migration**.



Both Halide ion and MA^+ are mobile

Table 1 | Calculated activation energies for ionic migration in $CH_3NH_3PbI_3$.

Migrating vacancy	Defect notation	E_A (eV)
I^-	$V_I^\bullet$	0.58
Pb^{2+}	V''_{Pb}	2.31
$CH_3NH_3^+$ (MA^+)	V'_{MA}	0.84

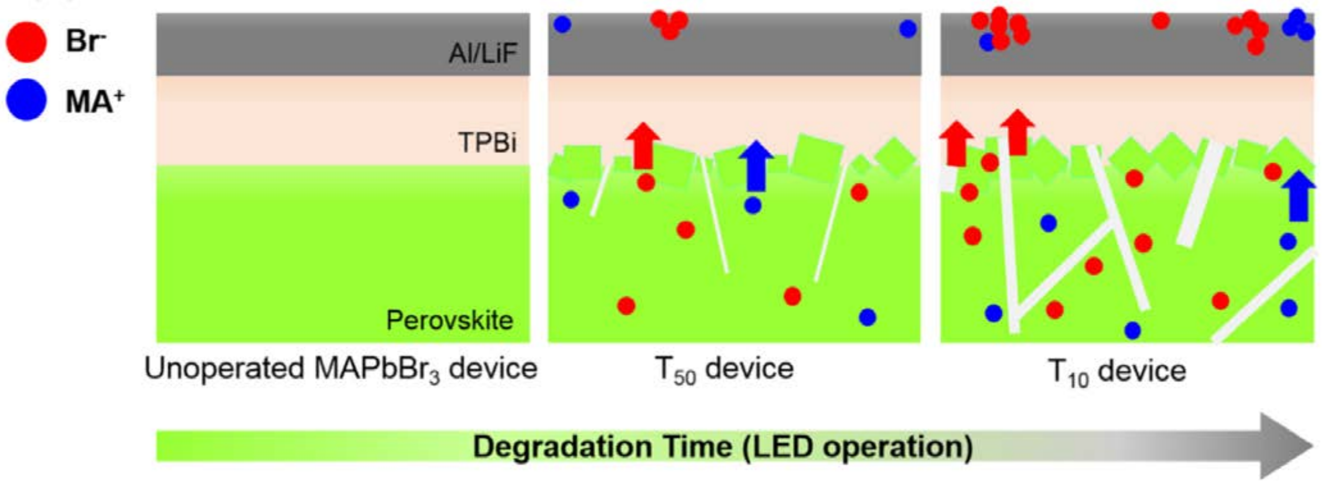
The migration of ion species is mediated by vacancy defects.

Eames *et al. Nat. Commun.*, 2015, **6**, 7497.

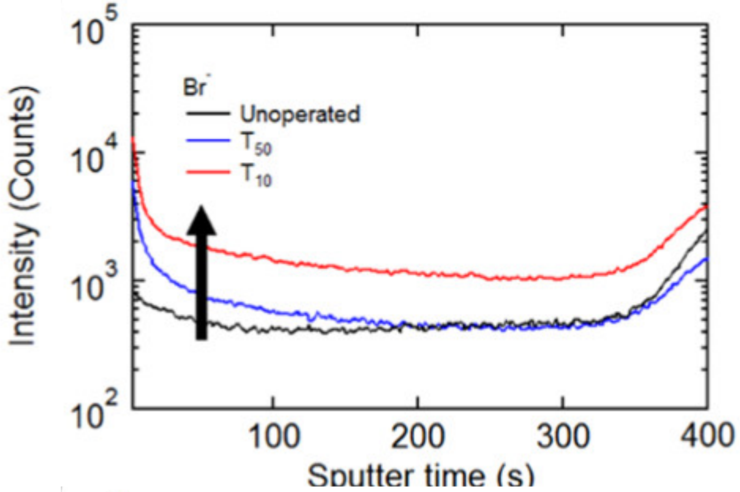
Christie L.C. (2018), *Perovskite photovoltaics (Chapter 6)*. Academic Press.

Degradation Mechanism

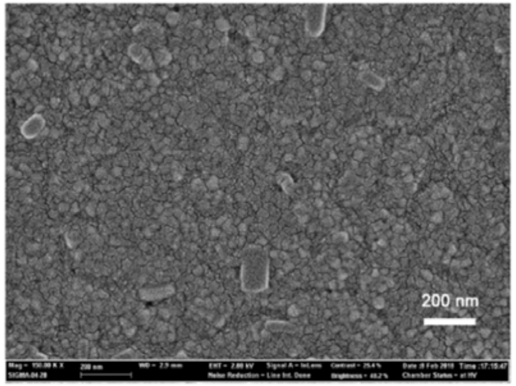
Ion migration is the main reason for device degradation



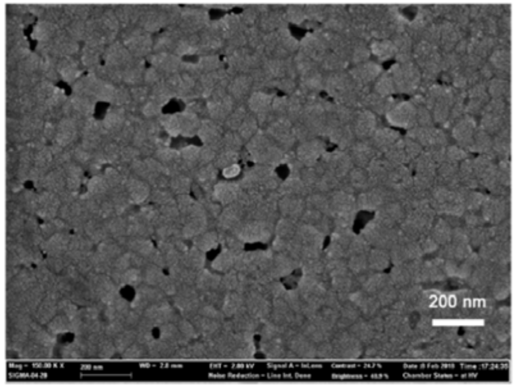
Br^- and MA^+ in Al electrode by SIMS

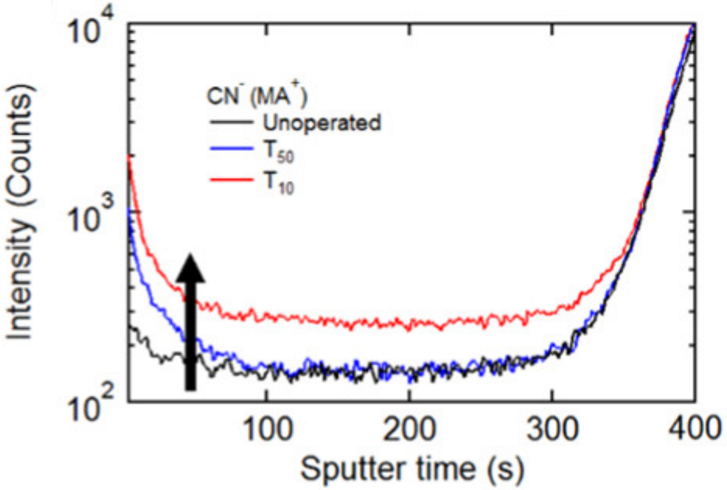


Fresh perovskite



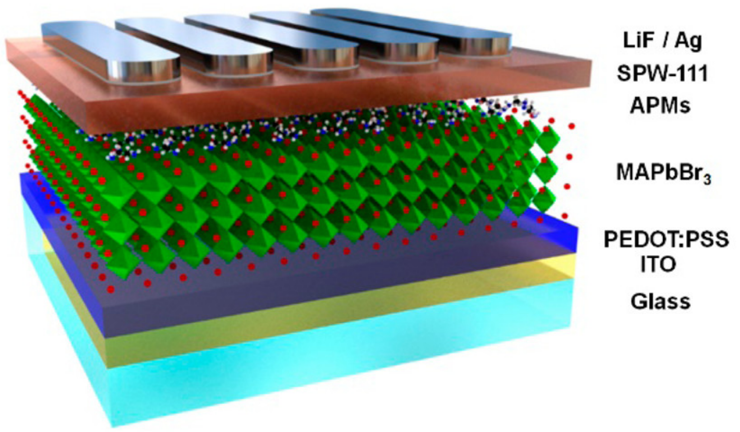
After degradation

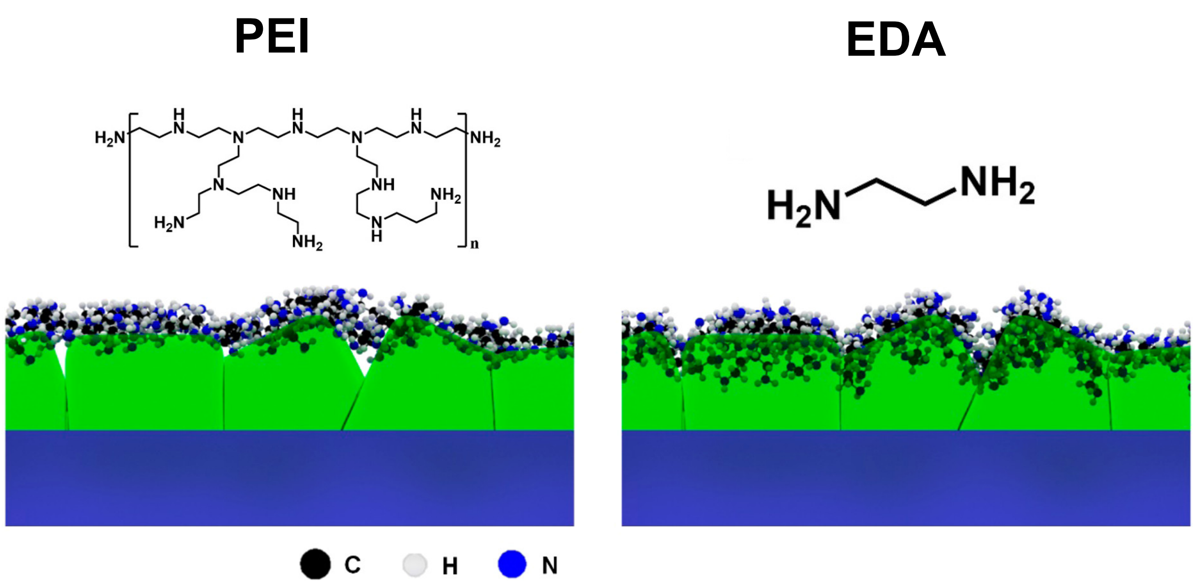




Lee *et al.* *ACS Appl. Mater. Interfaces*, 2019, **11**, 11667−11673.

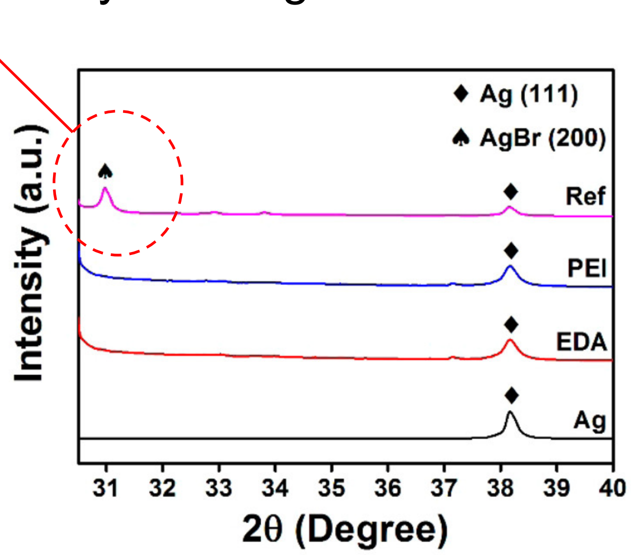
Improve Stability by Passivation

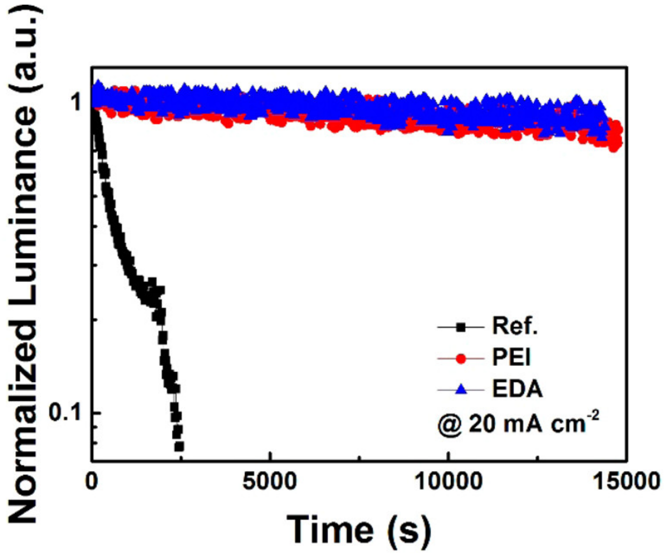




Lee *et al. J. Phys. Chem. Lett.*, 2017, **8**, 1784-1792.

Electrode corrosion by Br^- migration





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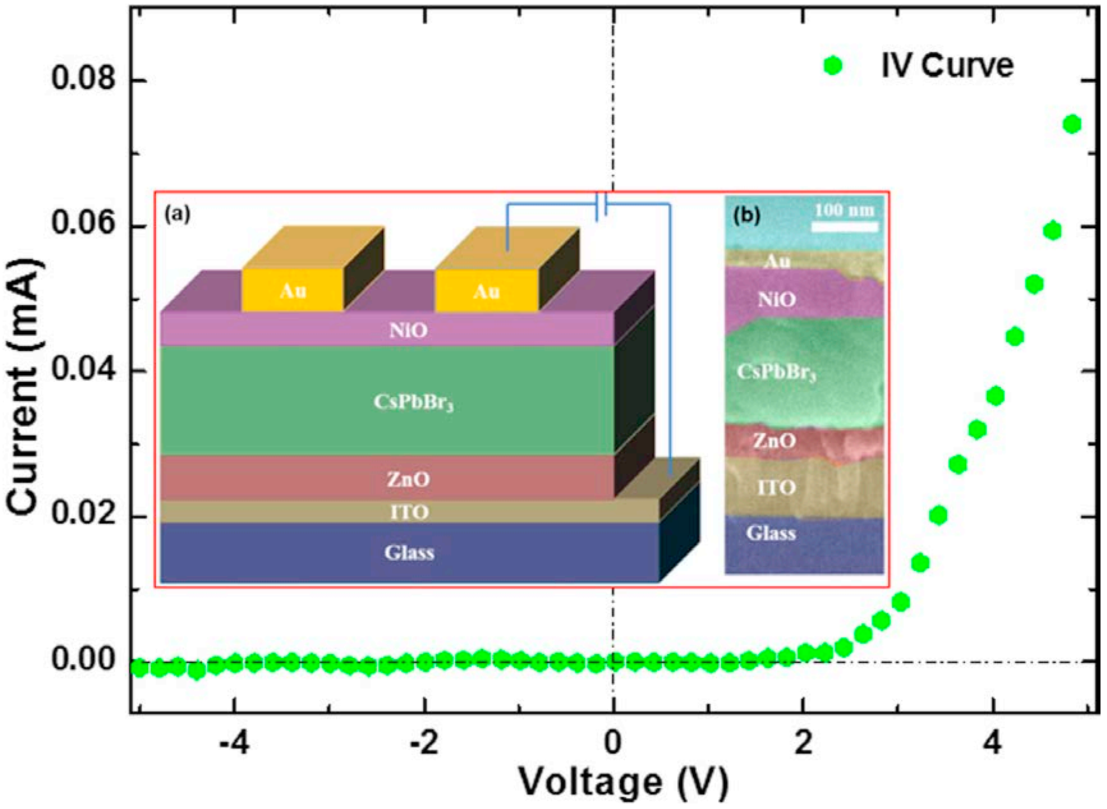
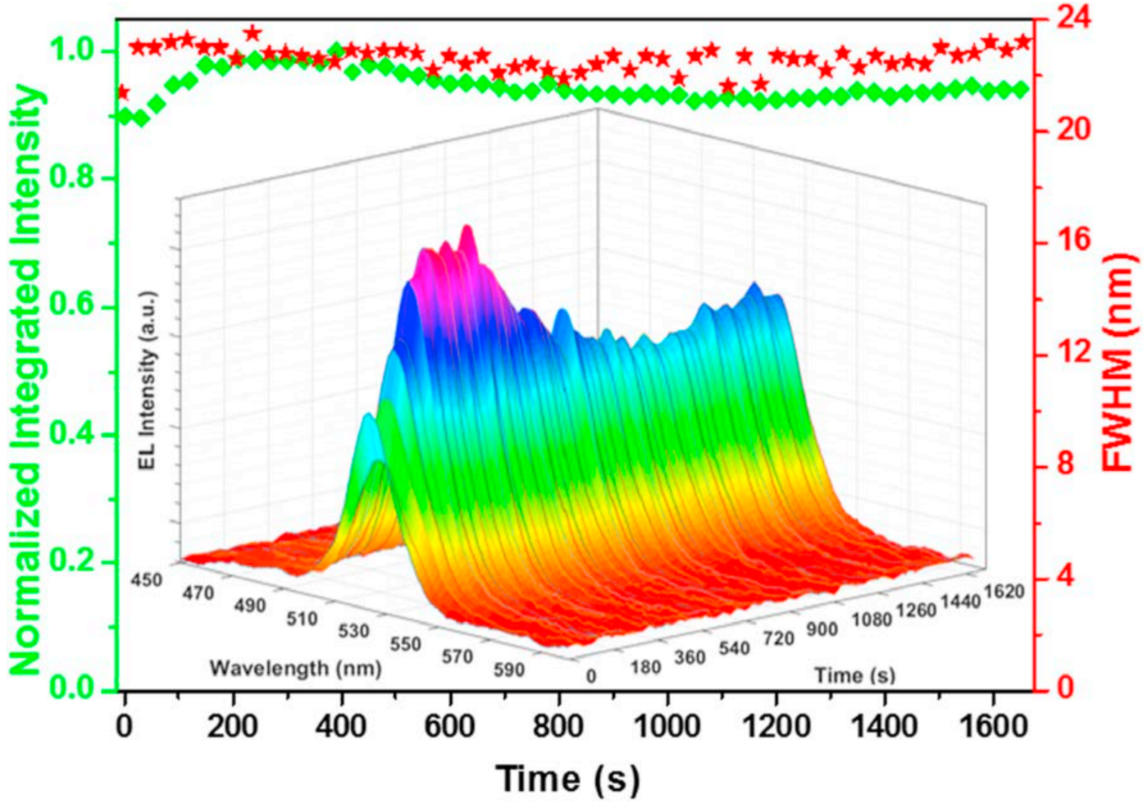
Improve Stability by Ion Blocking Layer





- Metal oxides (ZnO and NiOx) function as ion blocking layer
- Stability of PeLEDs can be improved

Zhuang *et al. Ceram. Int.*, 2018, **44**, 4685-4688.

Perovskite Lasers

Light **A**mplification by **S**timulated **E**mission of **R**adiation (LASER)

General properties of laser:

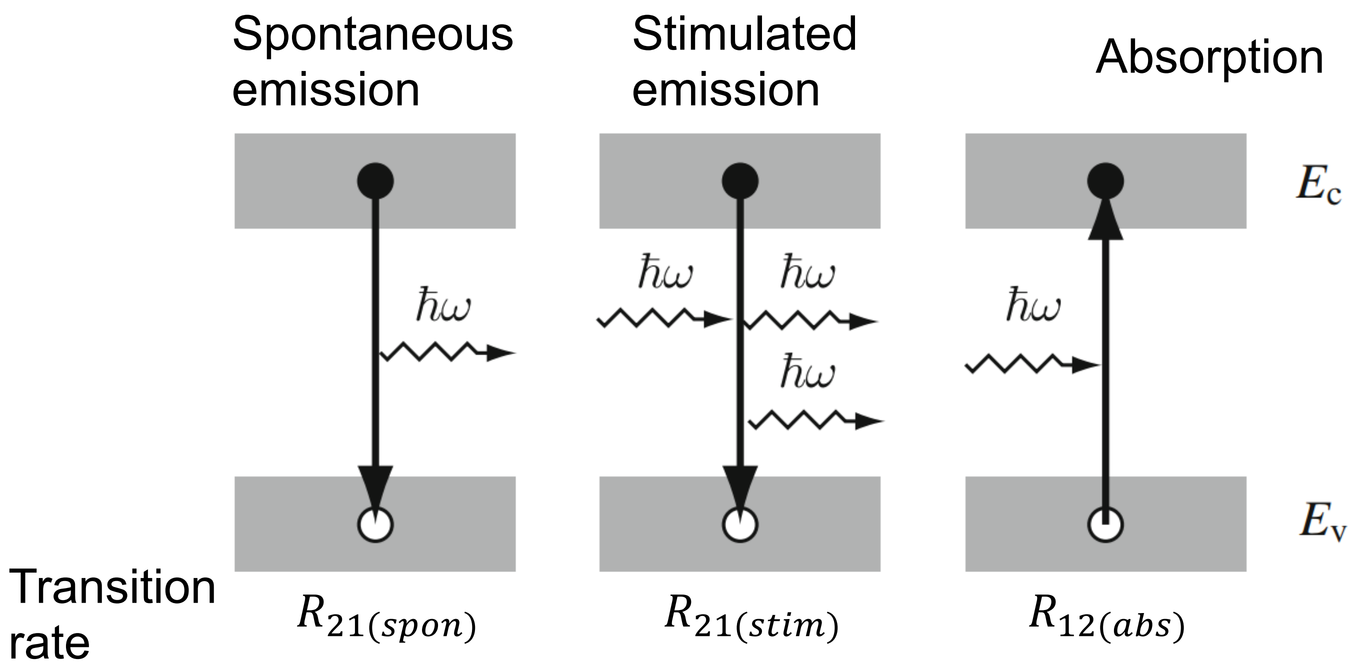
- Monochromatic
- Directional
- Coherent
- High intensity

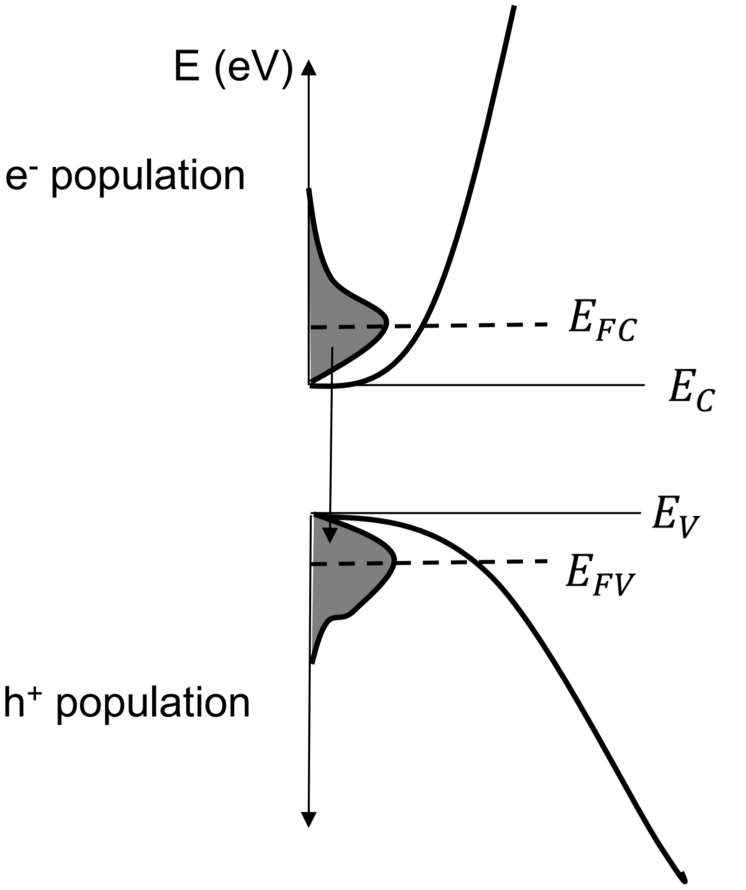
Wide applications of laser:

Manufacturing, medical, data storage, communication, display, spectroscopy, military and so on.

Perovskite materials can be used for semiconductor lasers.

Fundamentals of Semiconductor Laser





Condition of population inversion (enough carrier density):

$$E_{FC} - E_{FV} > E_C - E_V = E_g$$

$$R_{21(stim)} > R_{12(abs)}$$ → Optical gain > 0

E_{FC} : Quasi fermi level of electron

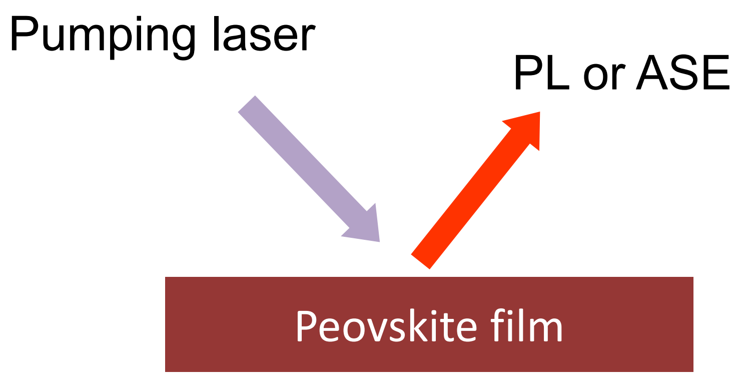
E_{FV} : Quasi fermi level of hole

T. Numai, (2015), *Fundamentals of semiconductor laser*, Springer

ASE of Perovskites

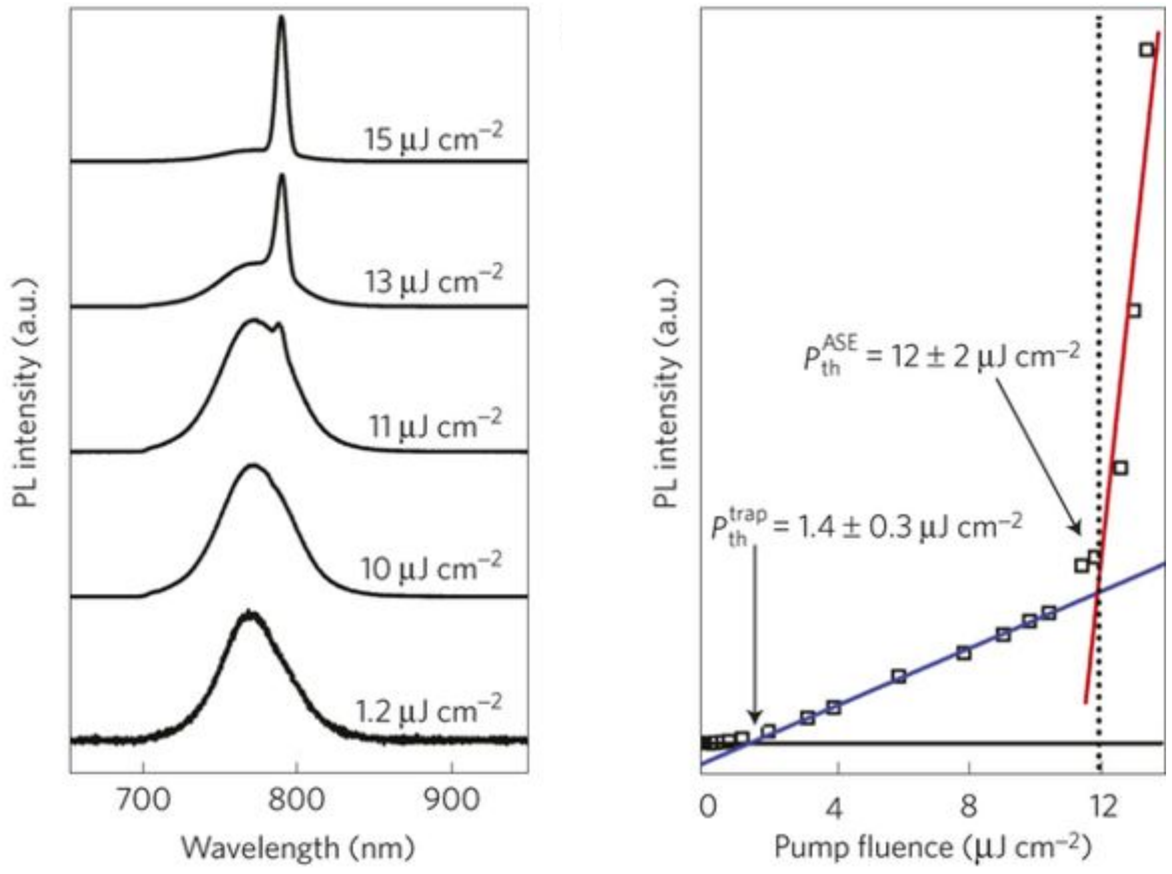
Amplified **S**pontaneous **E**mission (**ASE**)

No optical feedback



Pumping laser: 600 nm, 150 fs,1 kHz

Materials: $MAPbI_3$



Xing *et al. Nat. Mater.*, 2014, **13**, 476-480.

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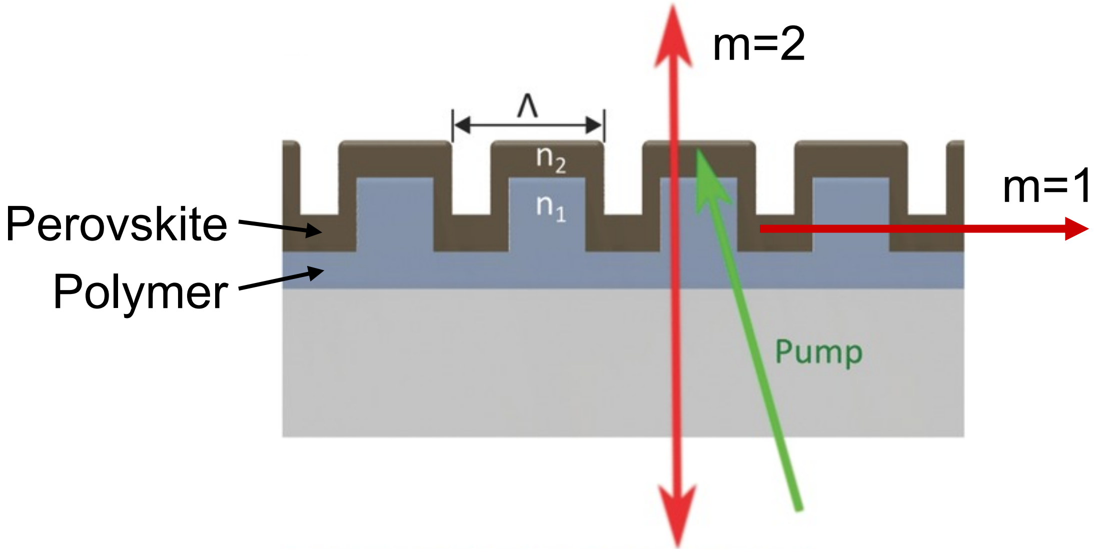
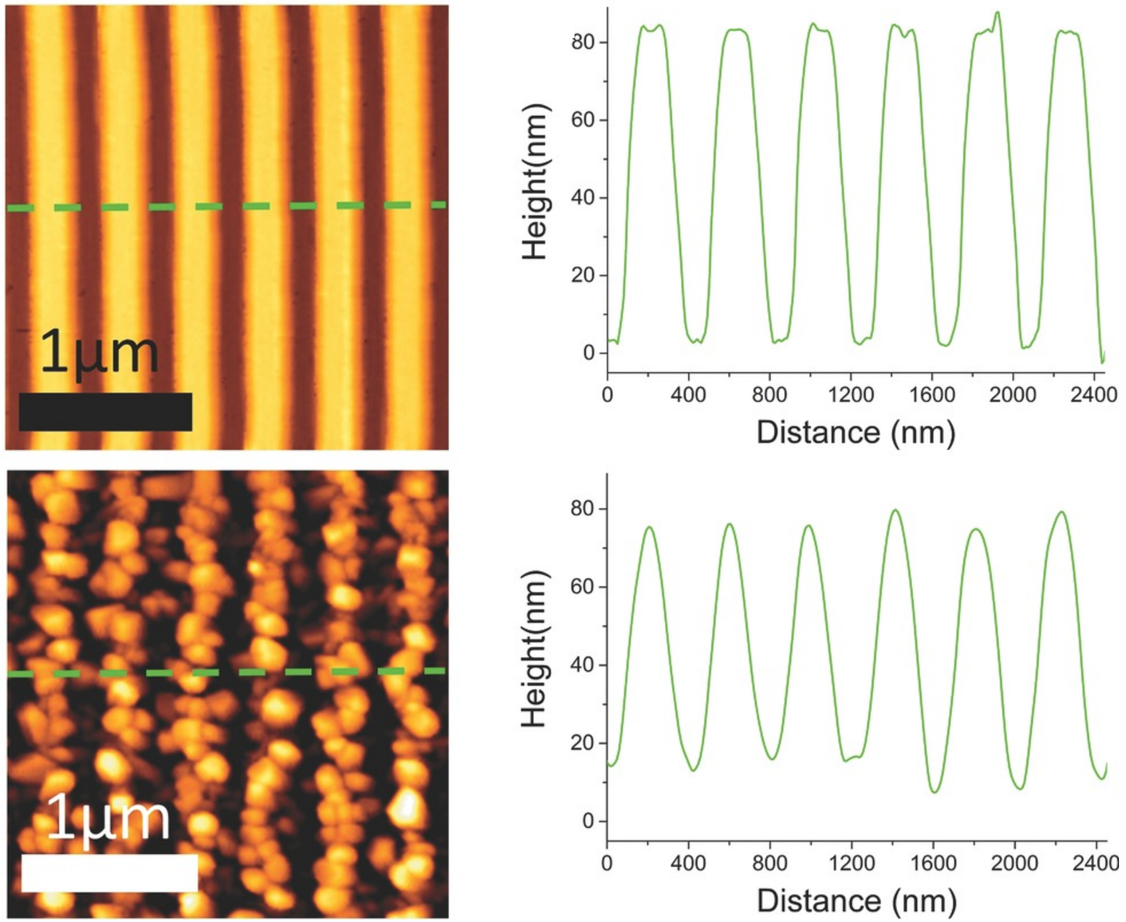
Distributed Feedback Laser by Perovskite



$$2n_{eff}\Lambda = m\lambda_{Bragg}$$

m=1: edge emission mode

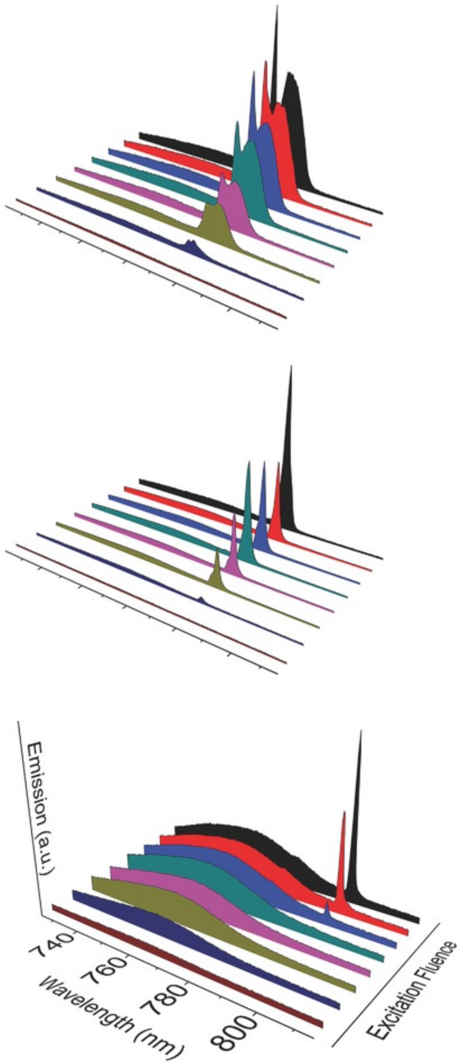
m=2: surface emission mode

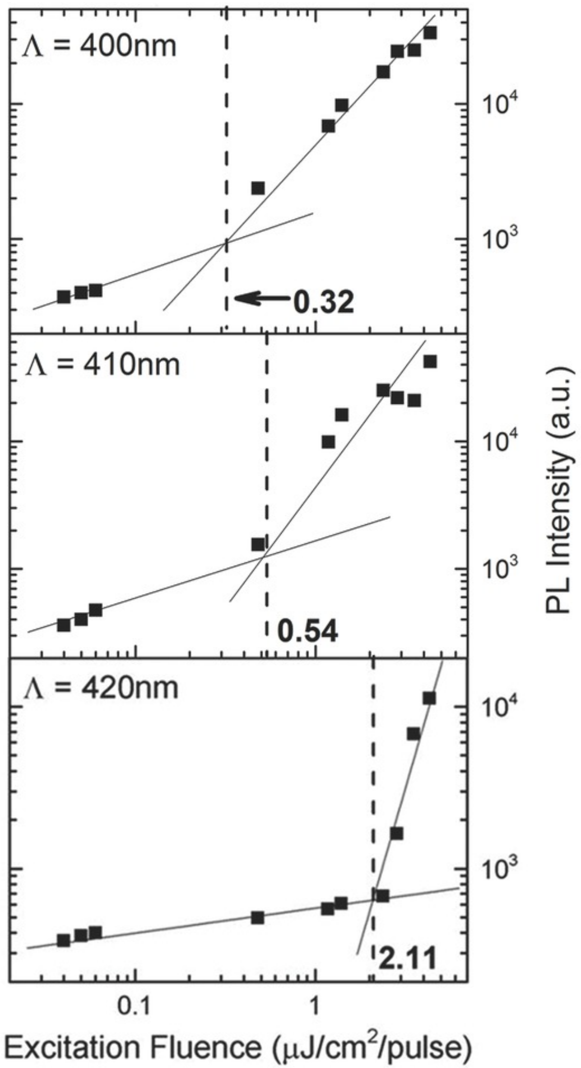


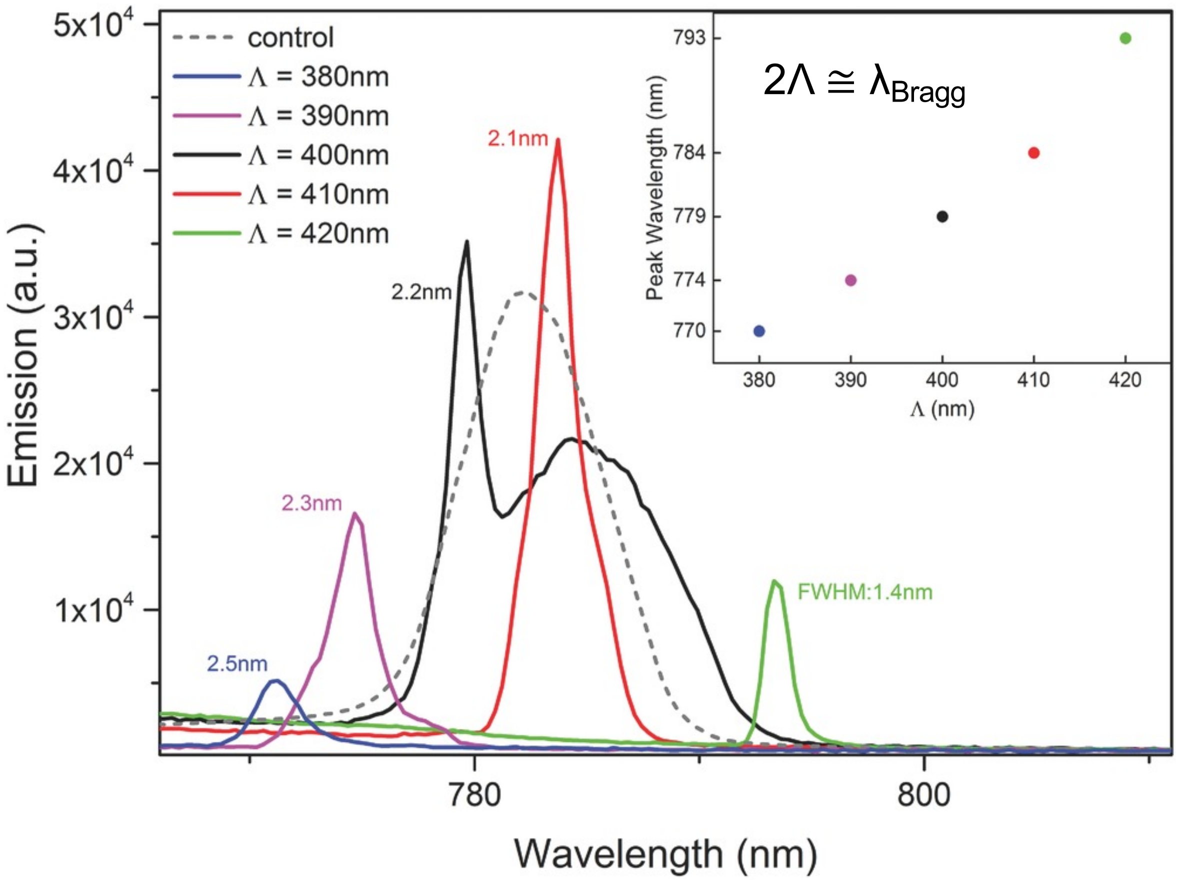
Saliba *et al. Adv. Mater.*, 2016, **28**, 923-929

Distributed Feedback Laser by Perovskite

Pumping laser: 532 nm, 1ns,1 kHz







$2n_{eff}\Lambda = m\lambda_{Bragg}$

n_{eff}=1.9~2.0

m=2

→ $2\Lambda \cong \lambda_{Bragg}$

Saliba *et al. Adv. Mater.*, 2016, **28**, 923-929

Optical Design of OLED and Perovskite LED

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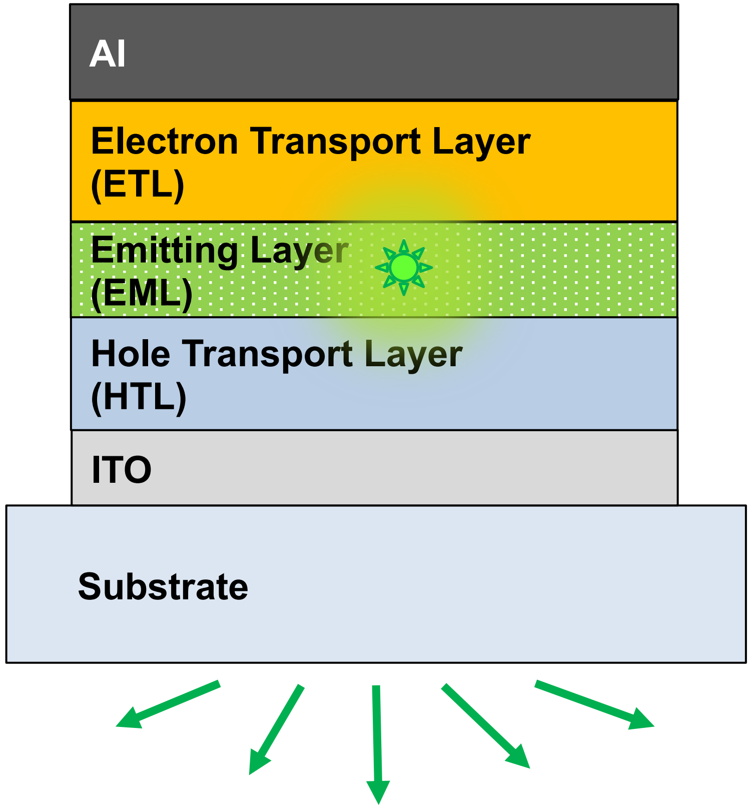
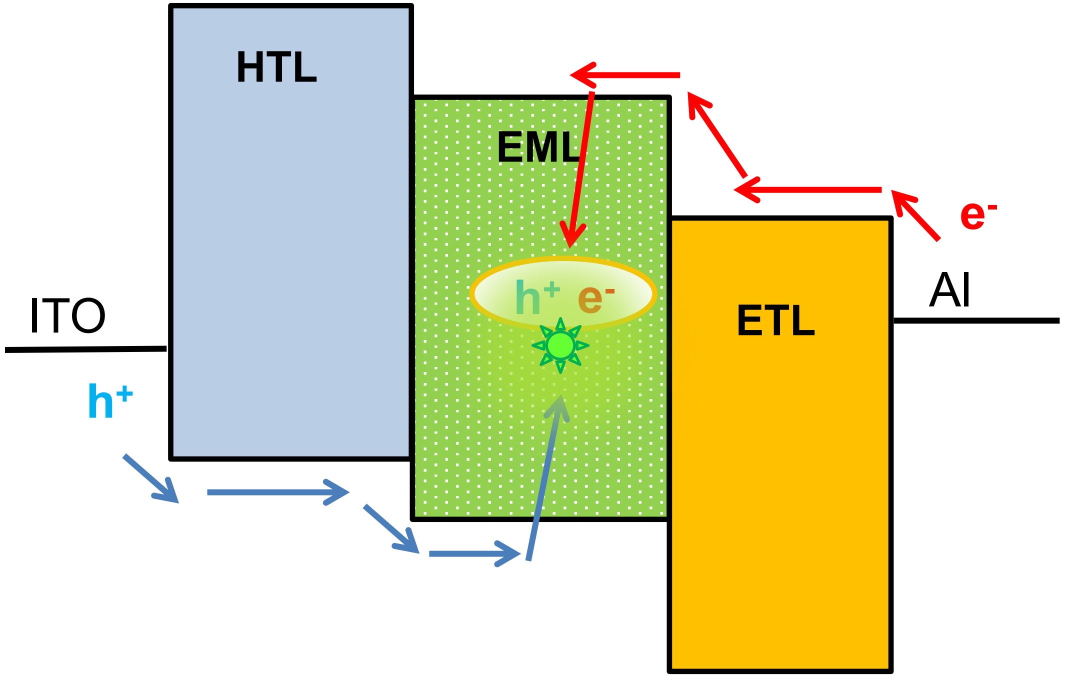
Typical OLED/PeLED Structure

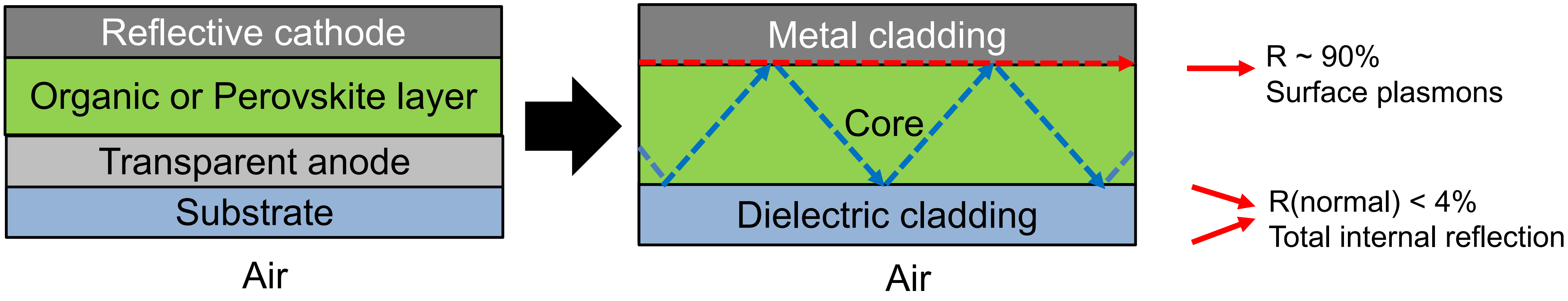




- Light is generated in the high refractive index thin film (< 200 nm)
- 20~30% of all the light goes to air mode

Optical Structure

Asymmetric metal-clad waveguide

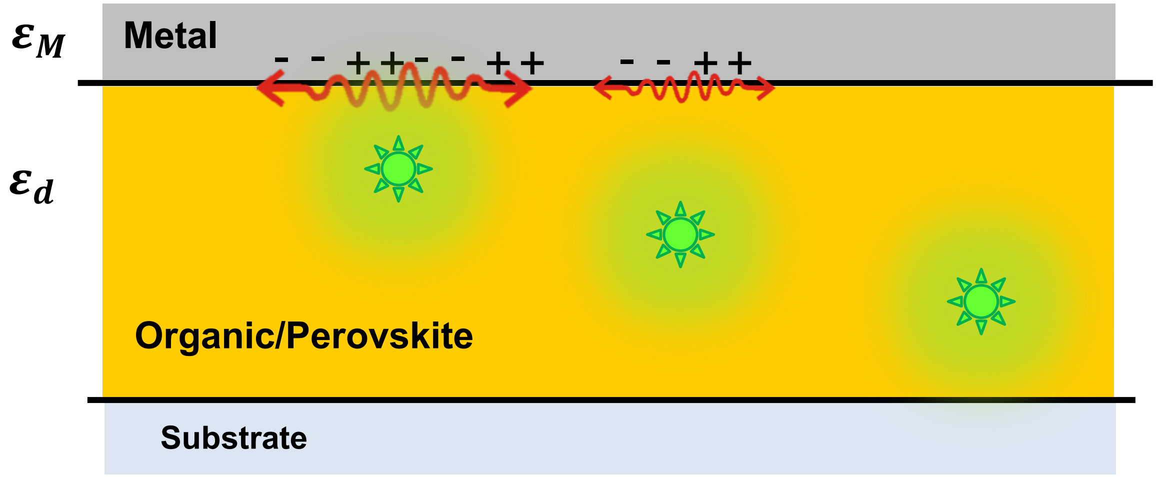


Material	Refractive Index
Perovskite	2.5
ITO	2.0
Organic	1.8
Glass	1.5
Air	1.0

OLED/PeLED can be regarded as **optical microcavities** which support waveguide modes and SPP modes

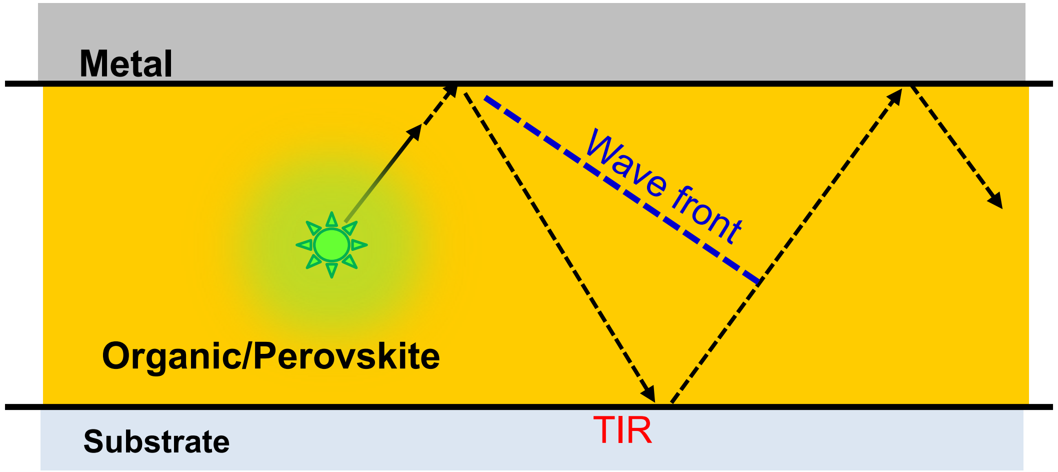
SPP and Waveguide Modes

Surface Plasmon Polariton (SPP) mode



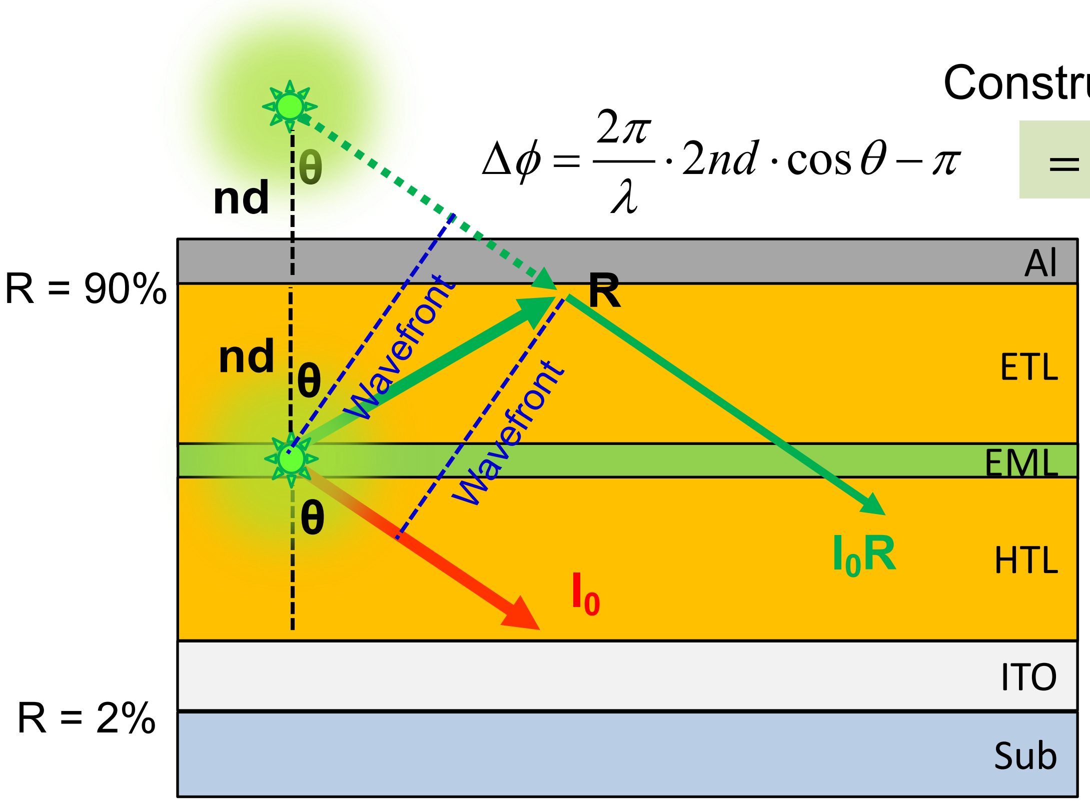
$$k_{SPP}(\omega) = \frac{\omega}{c}\sqrt{\frac{\varepsilon_d \varepsilon_M}{\varepsilon_M + \varepsilon_d}}$$

Waveguide Mode



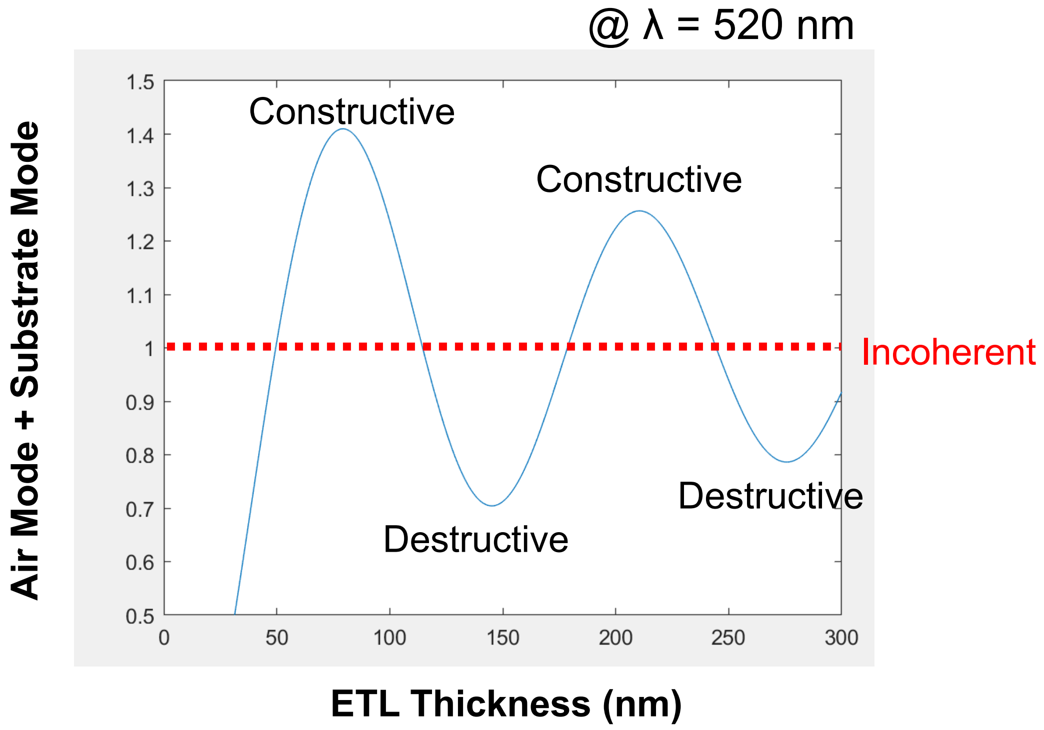
- Both SPP and waveguide modes have quantized mode dispersion relation

Microcavity Effect



Constructive Interference

$$\Delta\phi = \frac{2\pi}{\lambda}\cdot 2nd\cdot\cos\theta - \pi \quad = m\cdot 2\pi$$

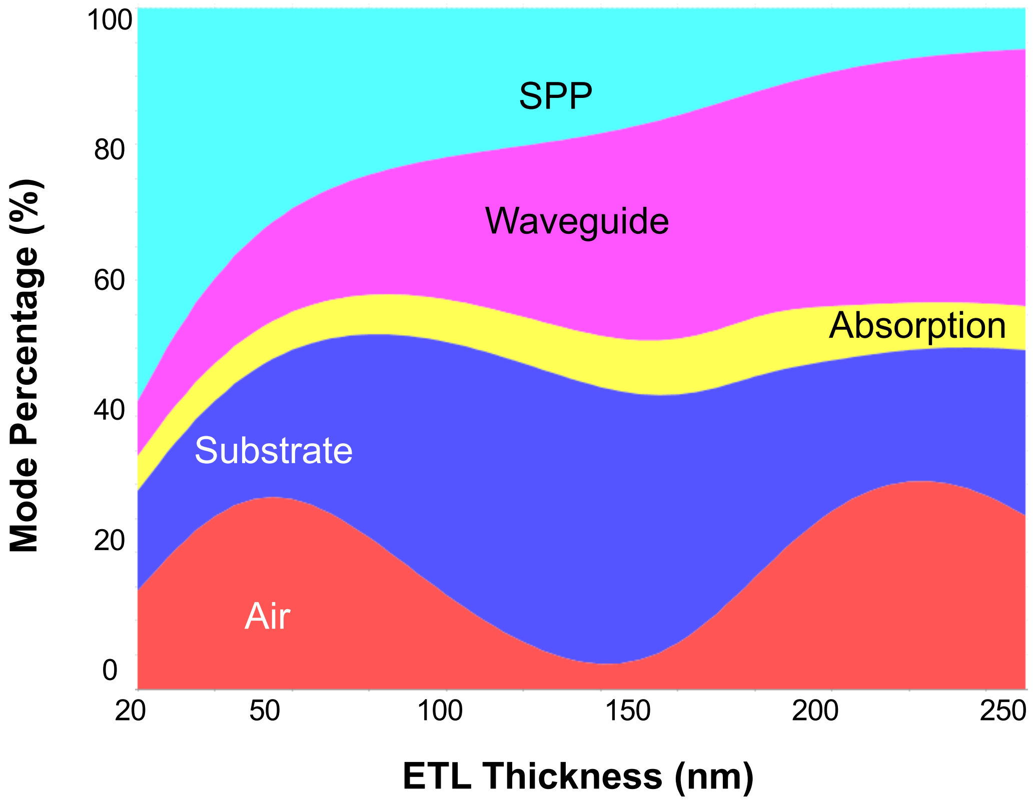


$$I = I_0 + I_0\cdot R + 2\sqrt{I_0\cdot I_0\cdot R}\cos\Delta\phi = I_0\left(1+R+2\sqrt{R}\cos\Delta\phi\right)$$

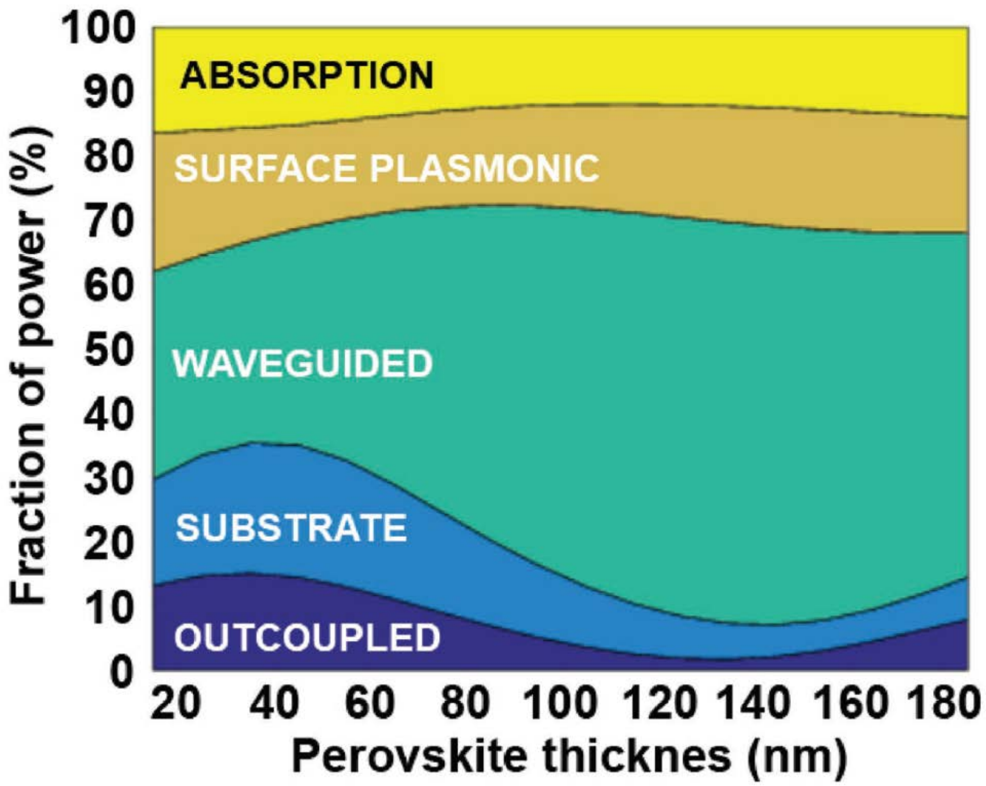
$$I_{\text{integrated}} = I_0\int_{-\frac{\pi}{2}}^{\frac{\pi}{2}}\left(1+R+2\sqrt{R}\cos\Delta\phi\right)d\theta$$

Optical Mode Distribution

OLED



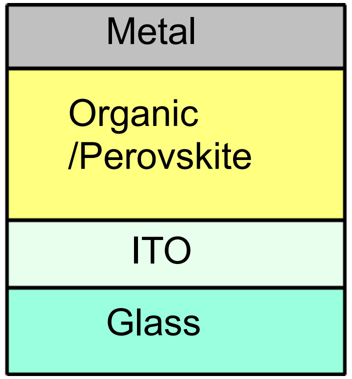
Perovskite LED (PeLED)



Adv. Mater. **2019**, *31*, 1805836

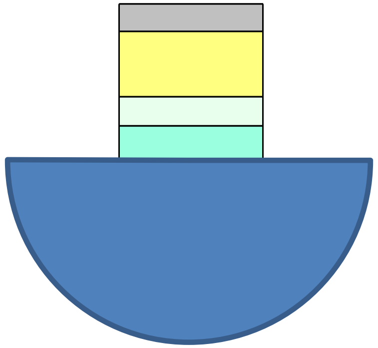
Light Extraction

Planar OLED/PeLED



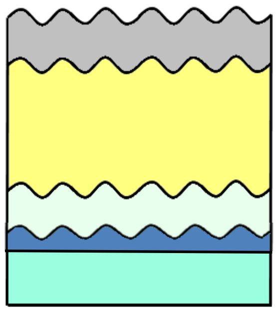
Suppress TIR

Half-ball lens

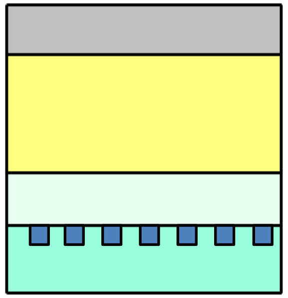


Diffraction

Corrugation

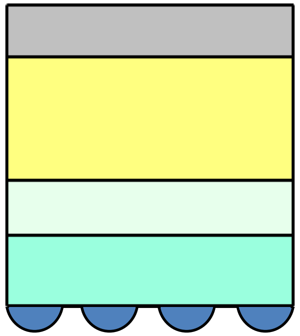


Sub-anode grids

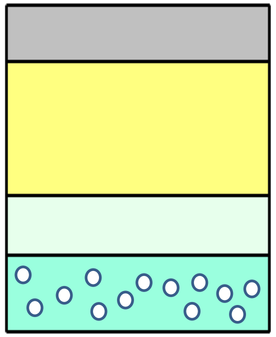


Random Scattering

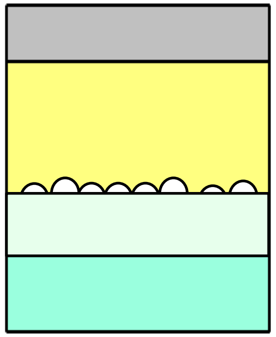
Microlens arrays



Porous substrate



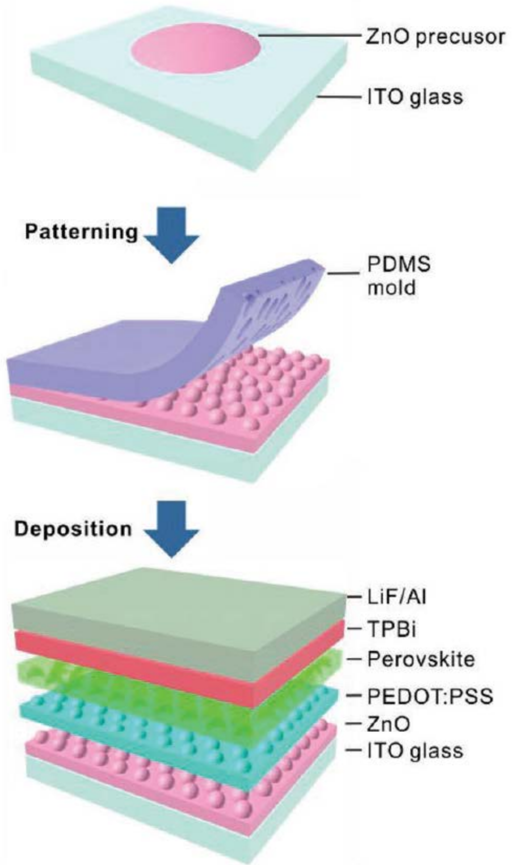
Roughened surface

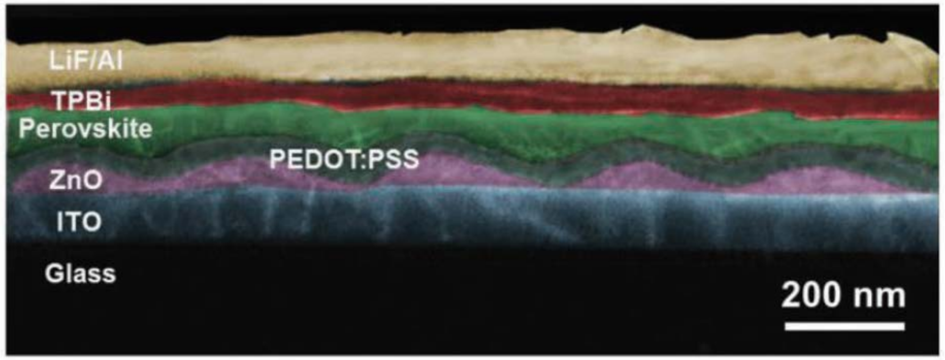


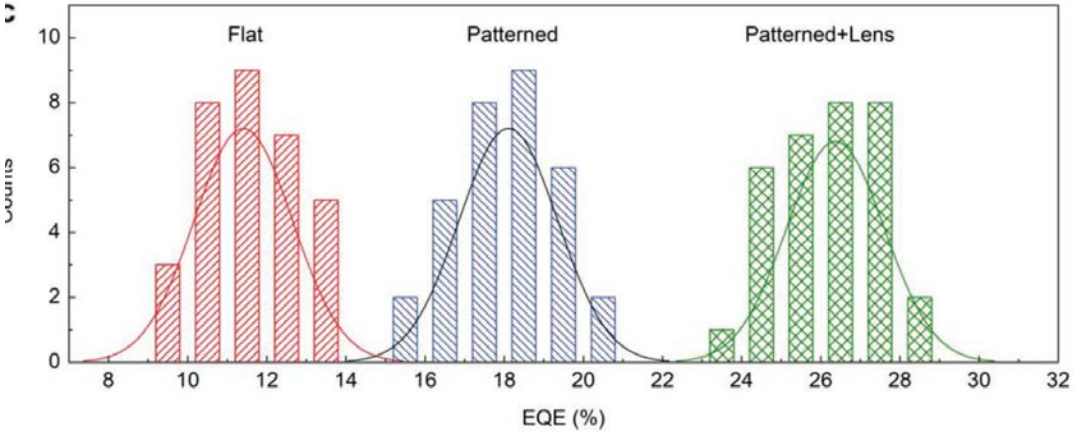
Soft-Imprinted ZnO

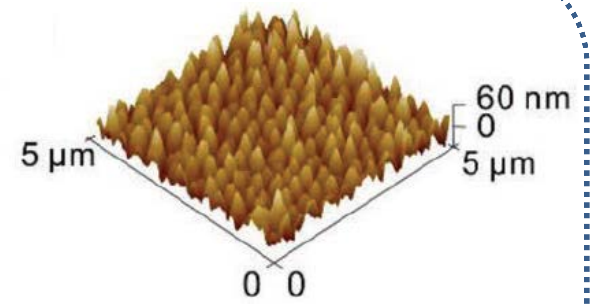
High-Efficiency Perovskite Light-Emitting Diodes with Synergetic Outcoupling Enhancement

Yang Shen, Li-Peng Cheng, Yan-Qing Li, Wei Li, Jing-De Chen, Shuit-Tong Lee,* and Jian-Xin Tang**









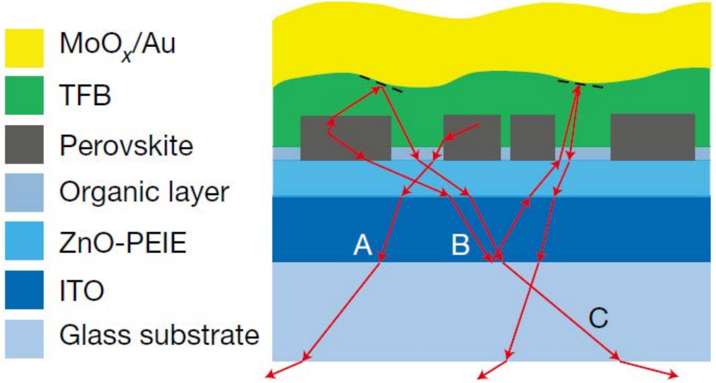
- Moth eye nanostructures
- periodicity ~400 nm

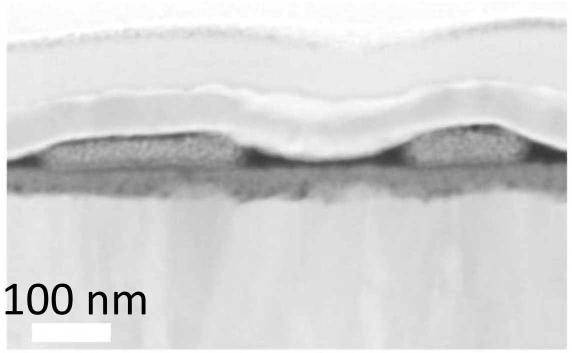
Adv. Mater. **2019**, *31*, 1901517

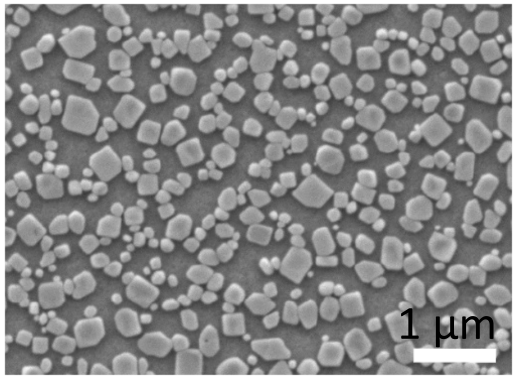
Spontaneously Formed Perovskite Platelets

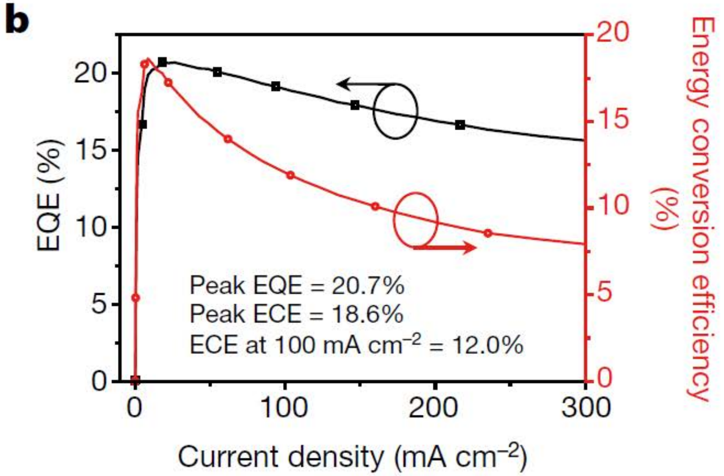
Perovskite light-emitting diodes based on spontaneously formed submicrometre-scale structures

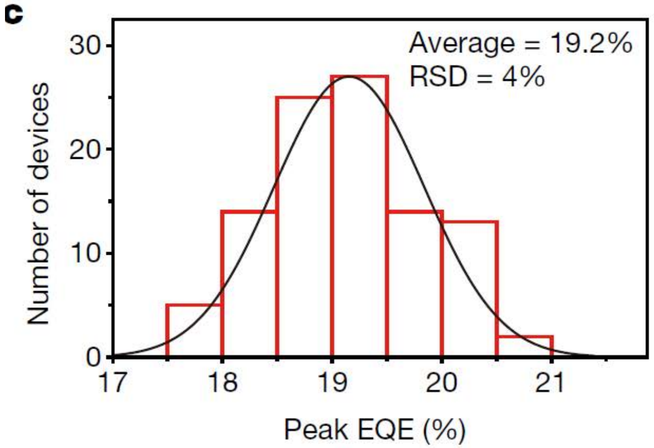
Yu Cao[1,7], Nana Wang[1,7], He Tian[2,7], Jingshu Guo[3,7], Yingqiang Wei[1], Hong Chen[1], Yanfeng Miao[1], Wei Zou[1], Kang Pan[1], Yarong He[1], Hui Cao[1], You Ke[1], Mengmeng Xu[1], Ying Wang[1], Ming Yang[1], Kai Du[2], Zewu Fu[1], Decheng Kong[1], Daoxin Dai[3], Yizheng Jin[4], Gongqiang Li[1], Hai Li[1], Qiming Peng[1], Jianpu Wang[1]* & Wei Huang[1,5,6]*

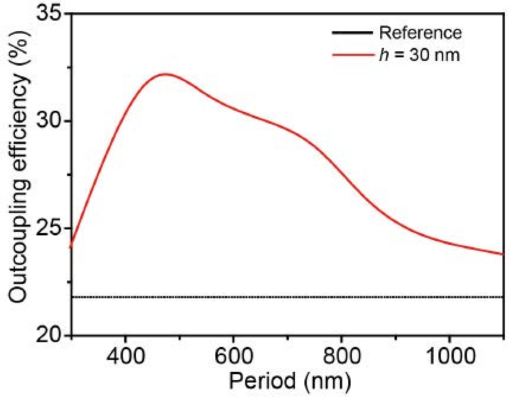








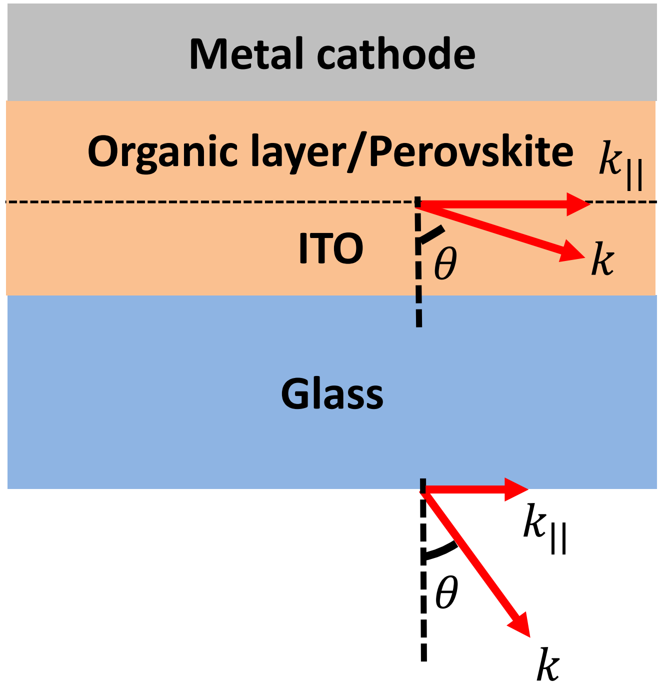




Nature 562.7726 (**2018**): 249.

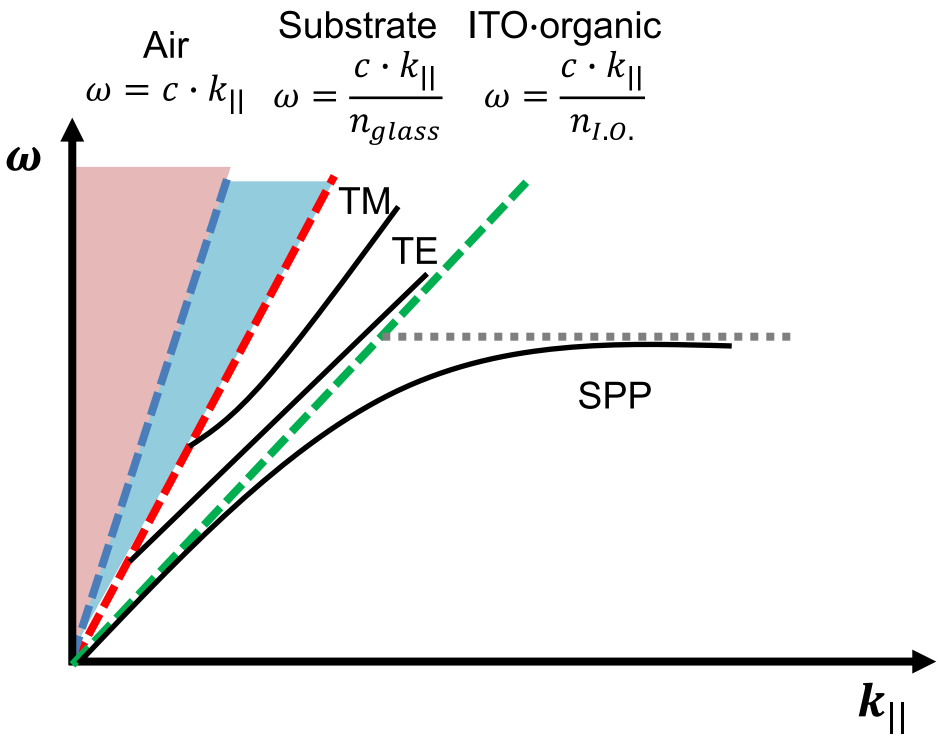
In-plane Wavevector and Dispersion Diagram

In-plane wavevector



$$k_{||} = nk_0 \sin\theta = \frac{\omega}{c} n \sin\theta$$

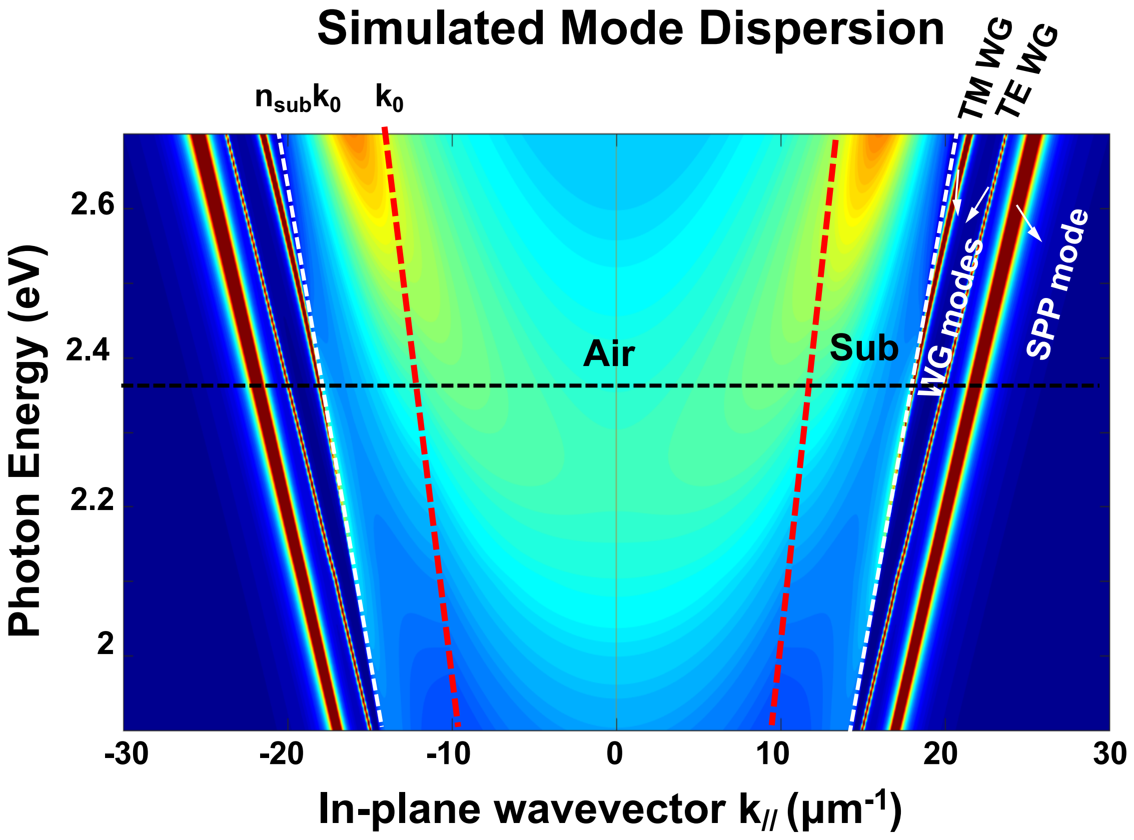
Dispersion diagram for an OLED

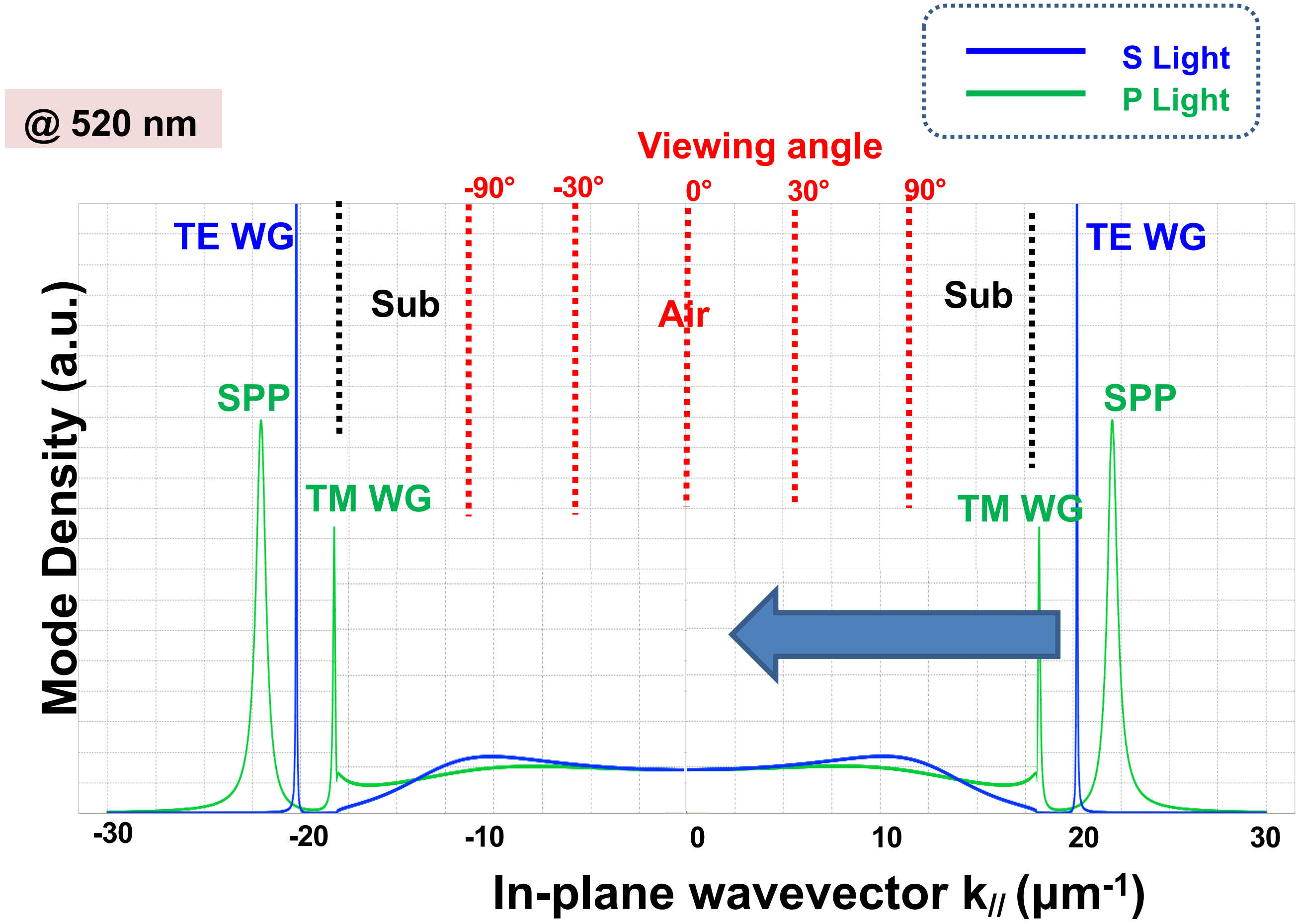


Advantage of the concept of in-plane wavevector

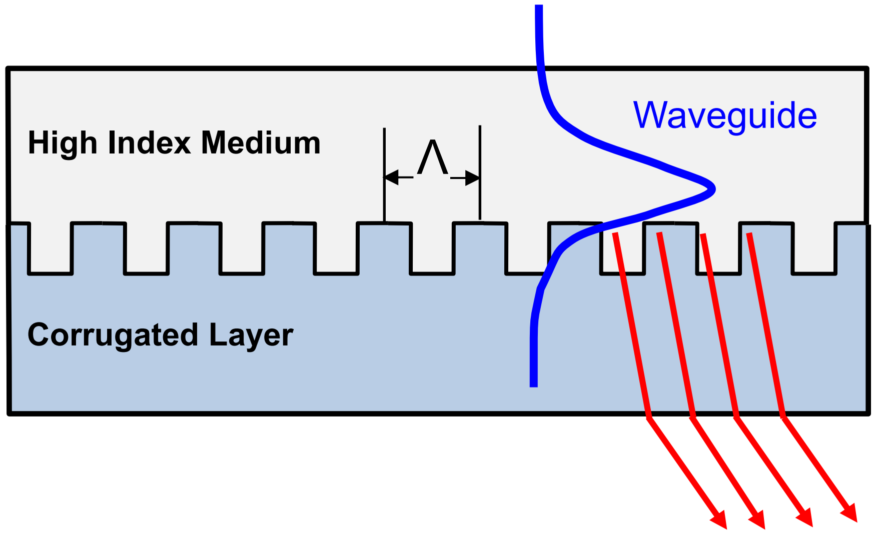
1. It describes light traveling under a certain angle
2. It is conserved at the interfaces
3. We could plot dispersion diagram for an OLED/PeLED

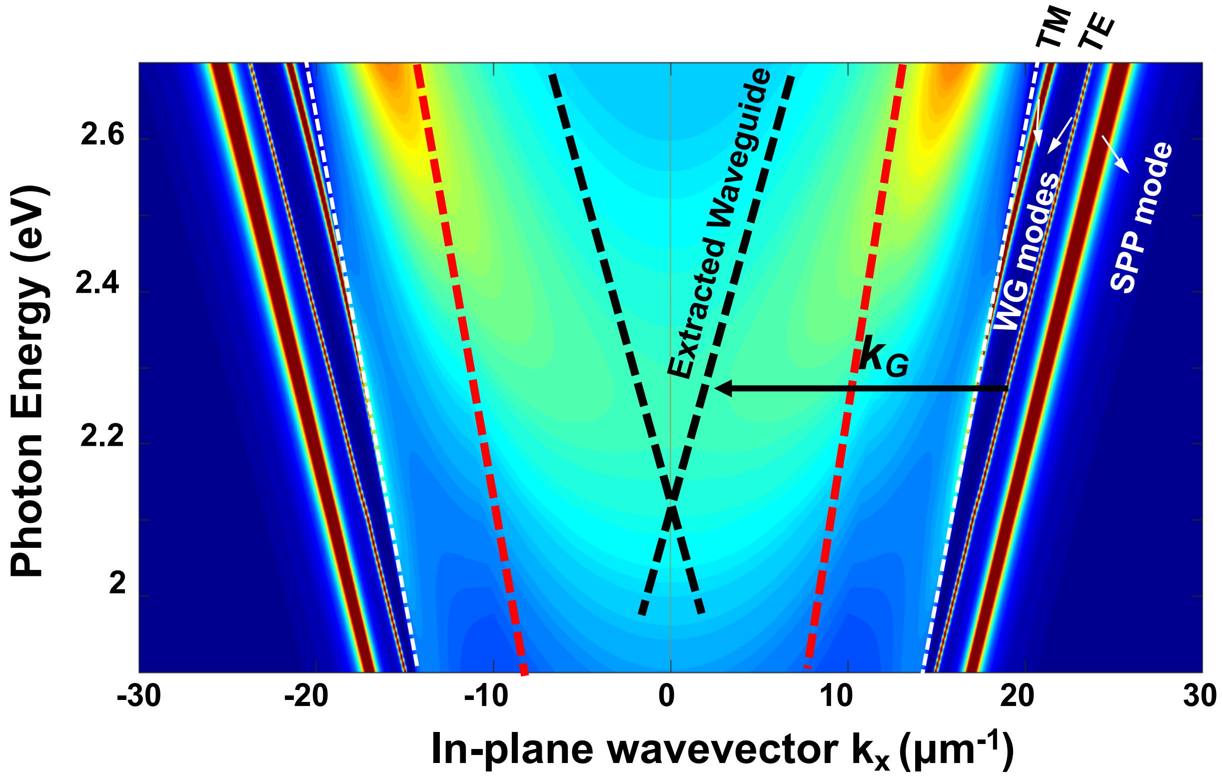
Simulated Mode Dispersion





Bragg Diffraction





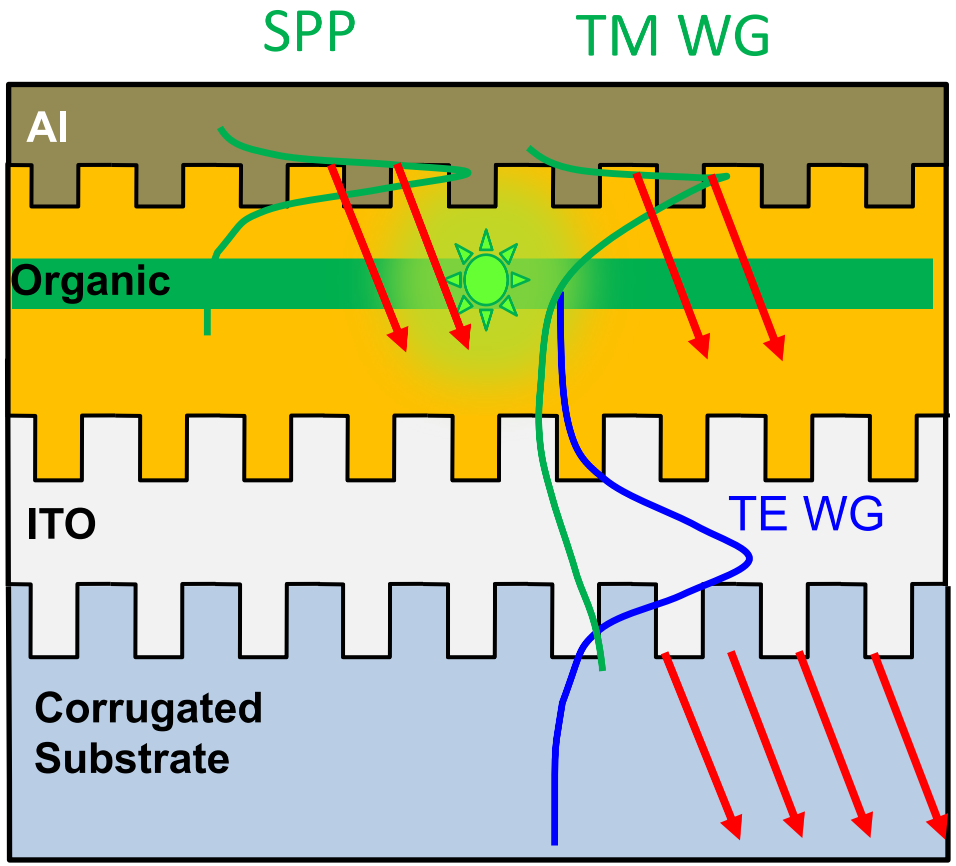
Bragg Diffraction

$$k'_{WG} = k_{WG} - k_G$$

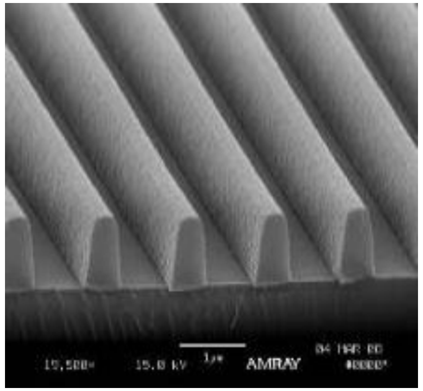
Grating Vector $k_G = 2\pi/\Lambda$

- Bragg diffraction is useful in PeLEDs due to the large waveguide mode portion and narrow spectrum

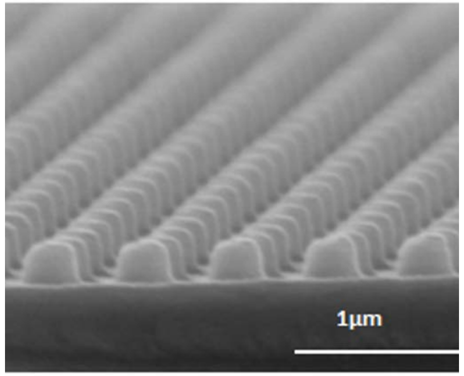
Light Extraction with Corrugated Substrates



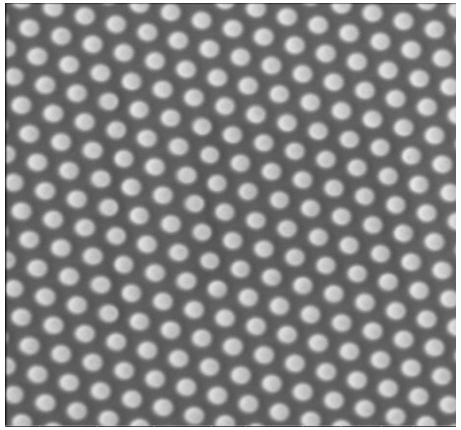
Linear grating



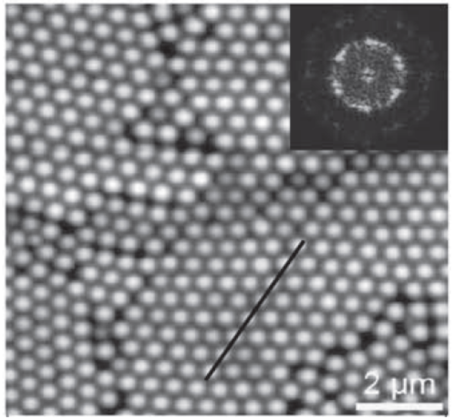
Square lattice (single crystal)



Hexagonal lattice (single crystal)



Hexagonal lattice (poly crystal)



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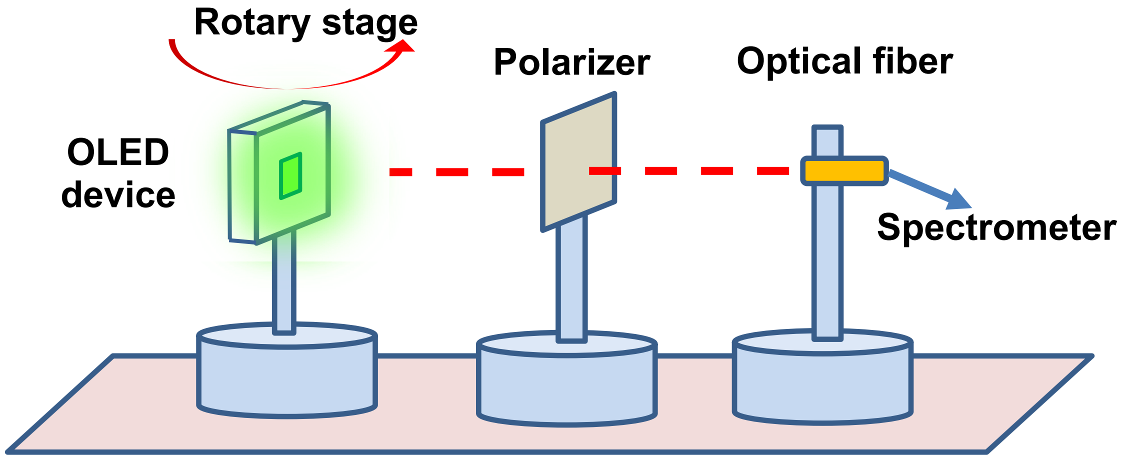
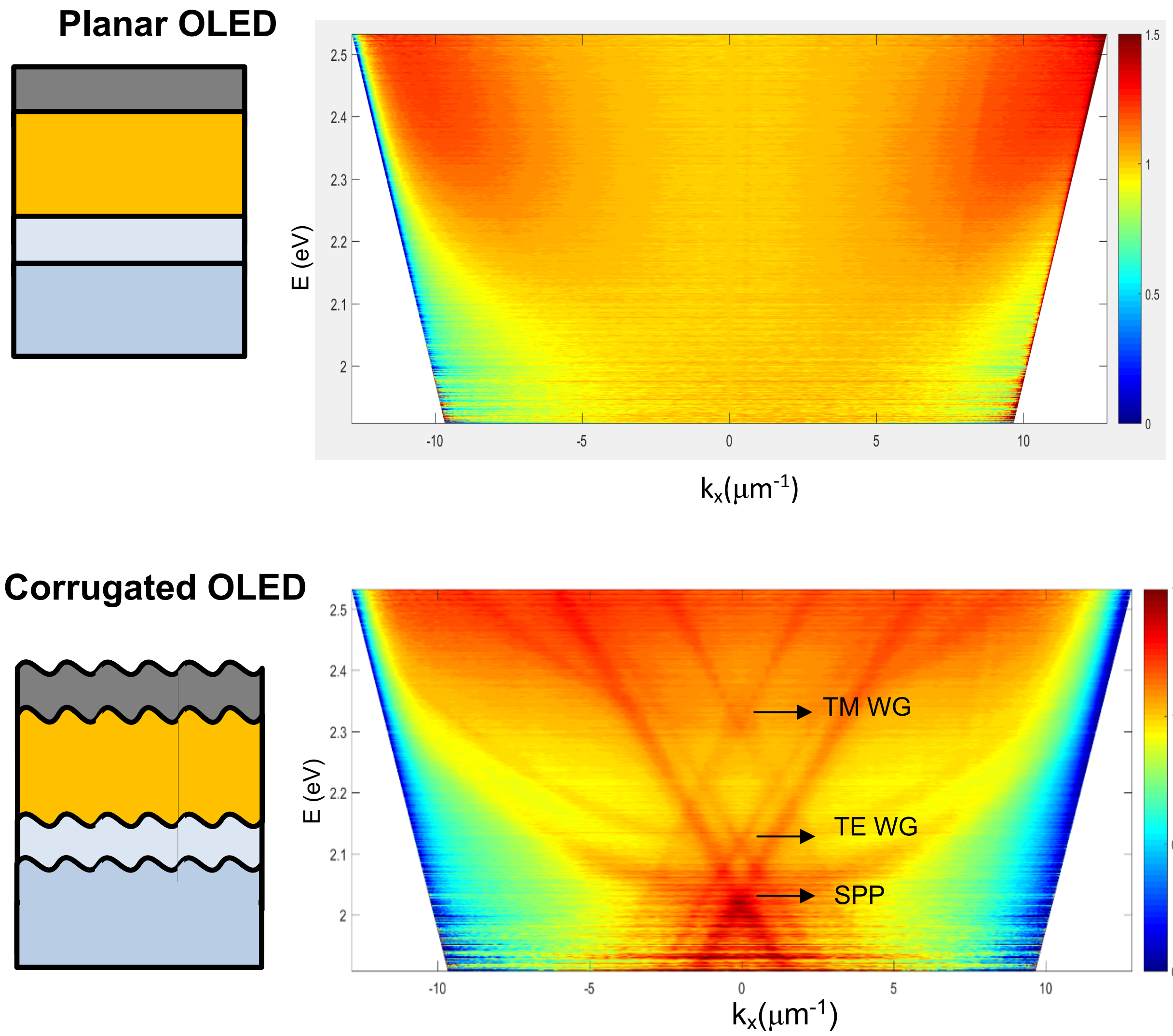
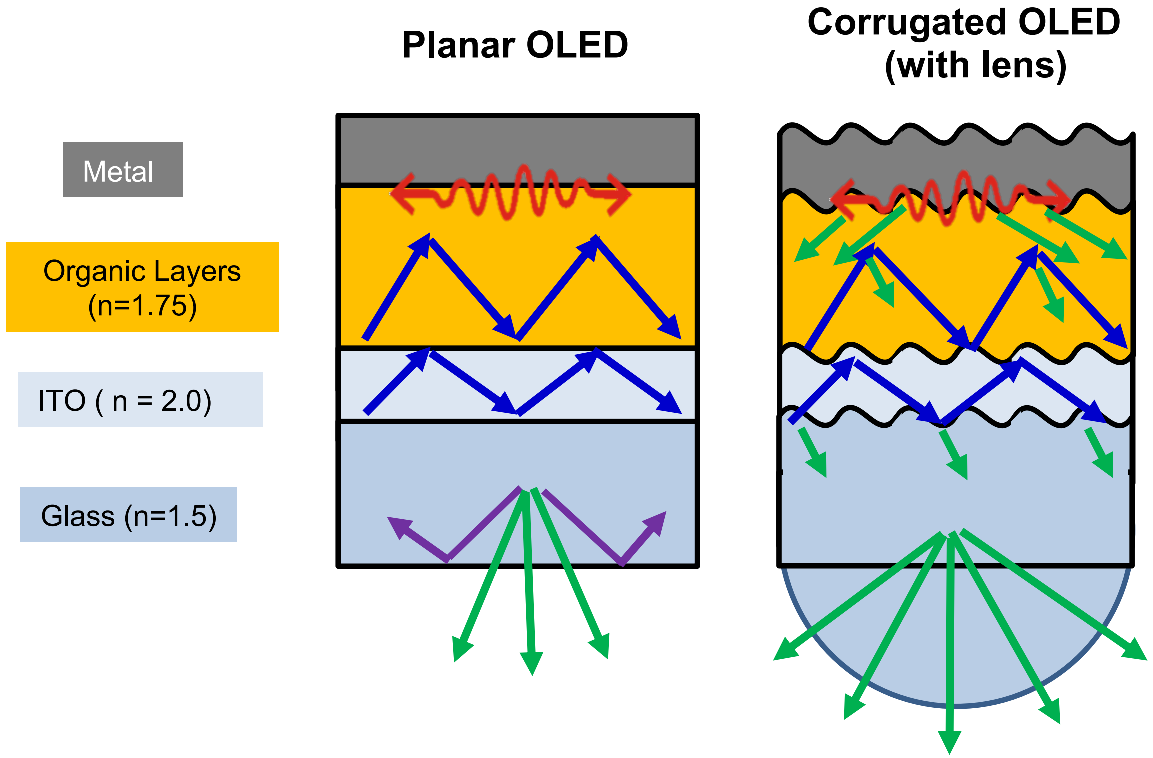
Mode Dispersion Comparison

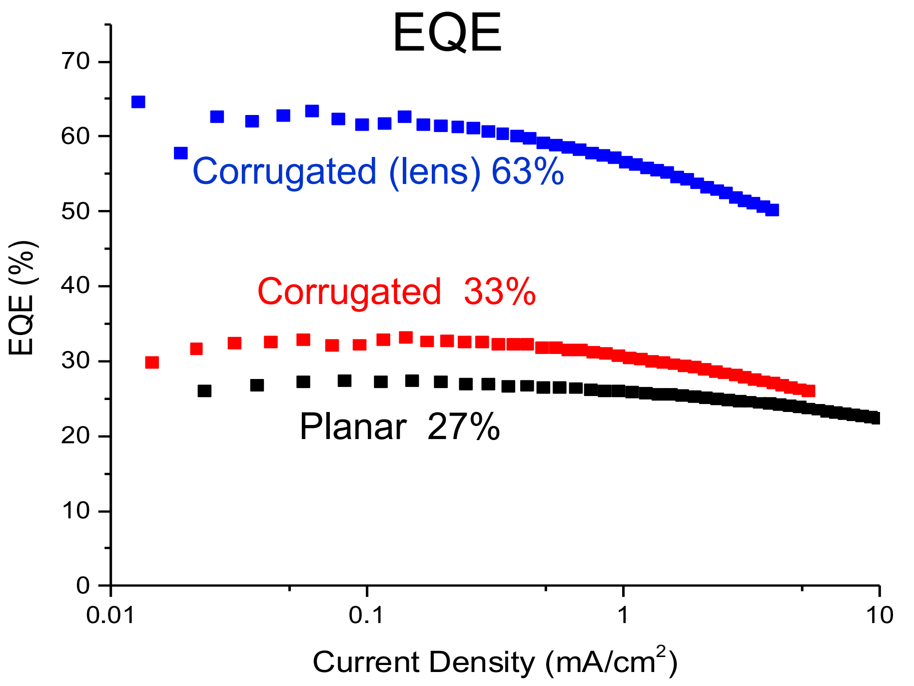




- Angular EL spectra (ARES) measurements reveal the origin of the extracted light
- Guides the design of devices

Corrugated OLED Performance



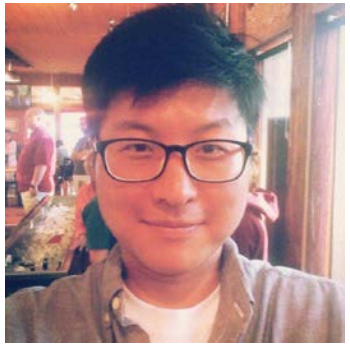


Summary

- OLED/PeLEDs are microcavity devices which support waveguide/substrate and SPP modes
- PeLEDs have strong waveguide loss due to the thick EML and high refractive index
- Current waveguide mode extraction in PeLEDs is mostly through random scattering, but Bragg diffraction with a periodic structure could be more advantageous
- Optical characterization through angle-resolved EL measurements will give important guidelines for optimization

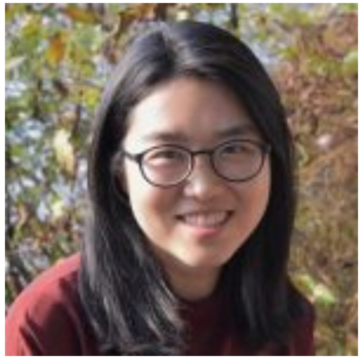
Acknowledgement

Dr. Franky So

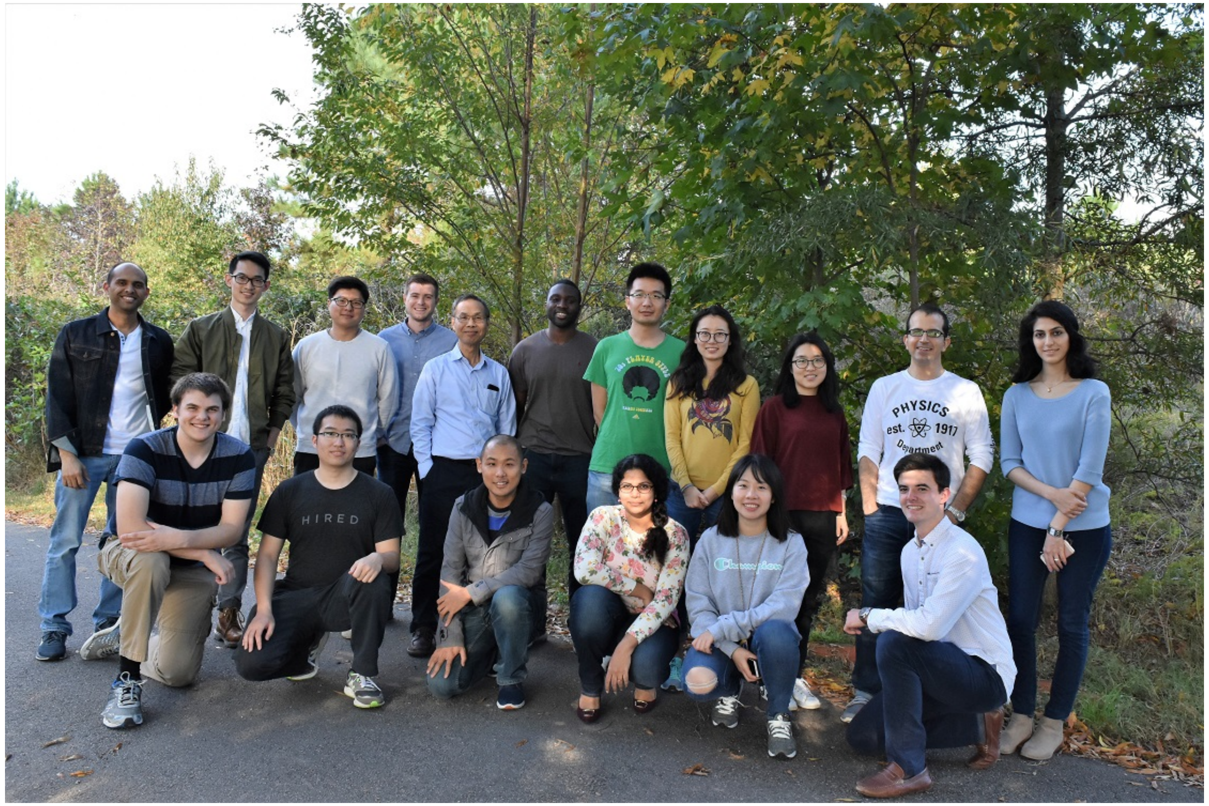


Dong-Hun Shin

Stephen Amoah



Lei Lei



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