

PHAS0058

Physics of Advanced Materials

Lecture 5: Perovskites

In this and next lecture...

- Introduction to Perovskite Semiconductors
- Fundamentals:
 - Structure and composition
 - Electronic and optical properties
 - Charge transport
- Applications and research:
 - Synthesis and fabrication
 - Device architectures
 - *Defects and passivation*
 - Future outlook

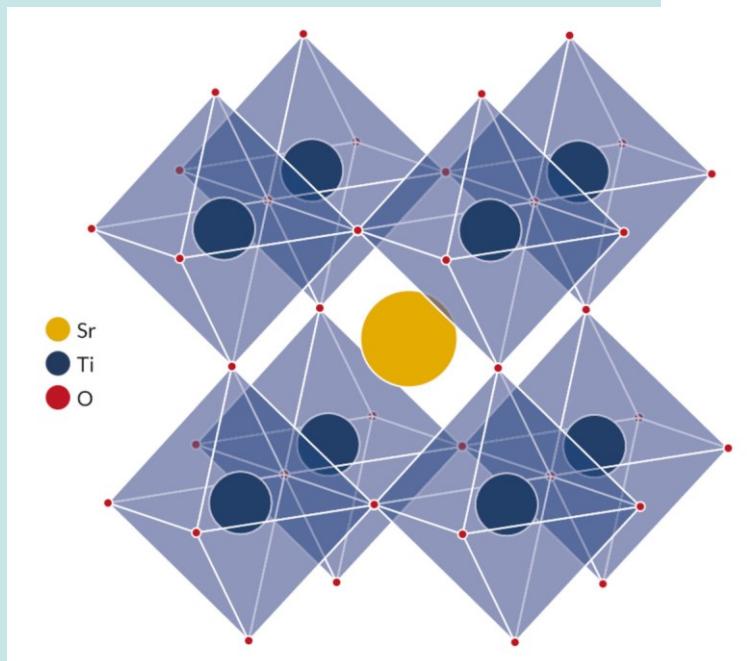
Introduction

What are perovskites and why are they interesting?

PEROVSKITES

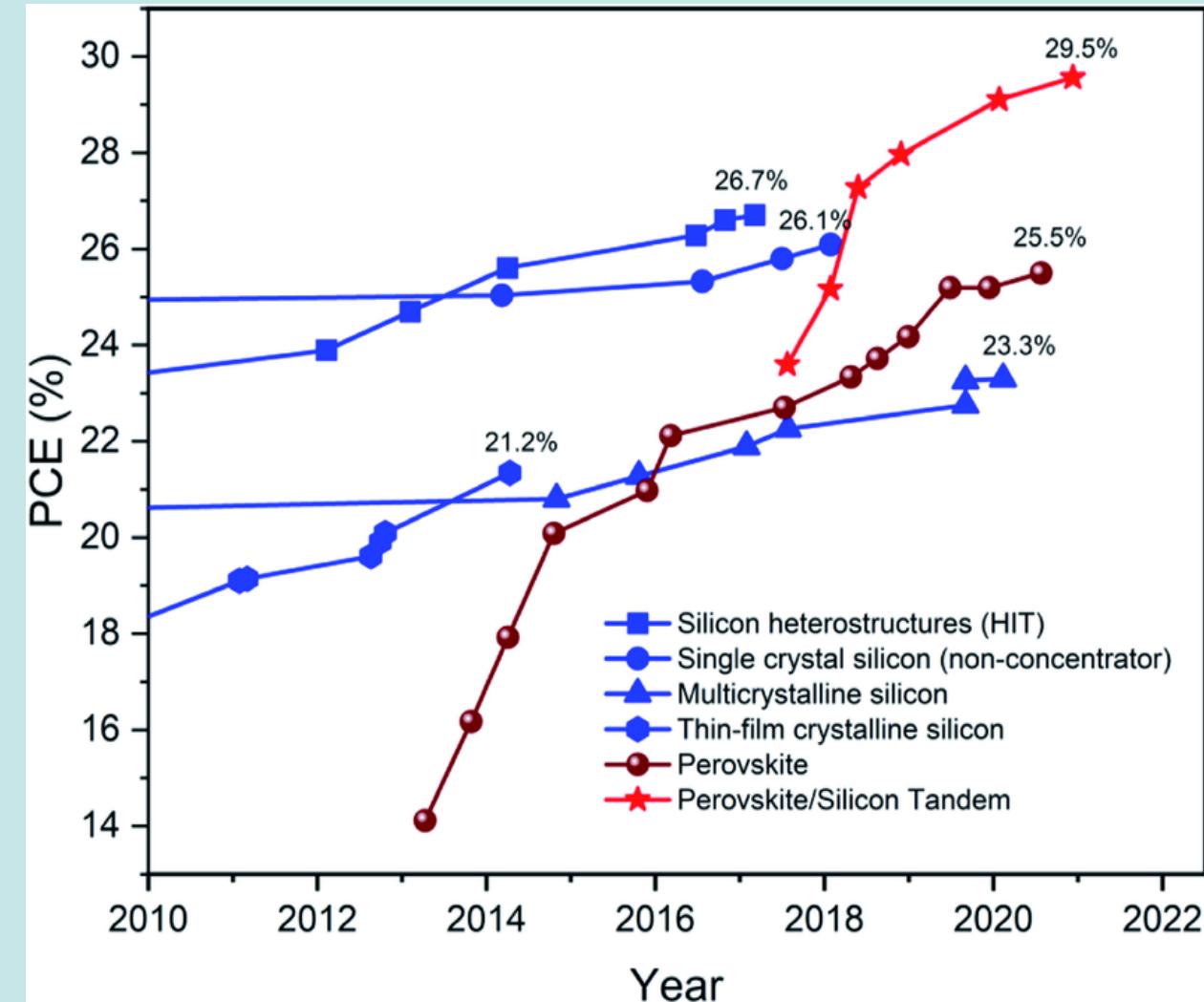
a class of materials with a specific crystal structure

(also: a specific CaTiO_3 mineral)



Why study perovskites?

- high absorption coefficient
- long charge-carrier diffusion length
- tunable bandgap
- applications mostly PV but great for other devices too
- low cost, flexible, efficient



Shrivastav, Nikhil & Madan, Jaya & Pandey, Rahul & Shalan, Ahmed. (2021). RSC Advances. 11. 37366-37374

History of perovskite research

1839

Natural perovskite crystals discovered

2012

The first all solid state perovskite was created

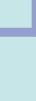


1990s

Discovery of the unique electronic properties of perovskites.

2020

Perovskite Solar Cells achieved efficiencies over 25%



1892

The first man-made perovskite structure was synthesized

2009

Perovskites first used in dye-sensitized solar cells

2017

First successful perovskite/silicon tandem solar cells



Commercial applications



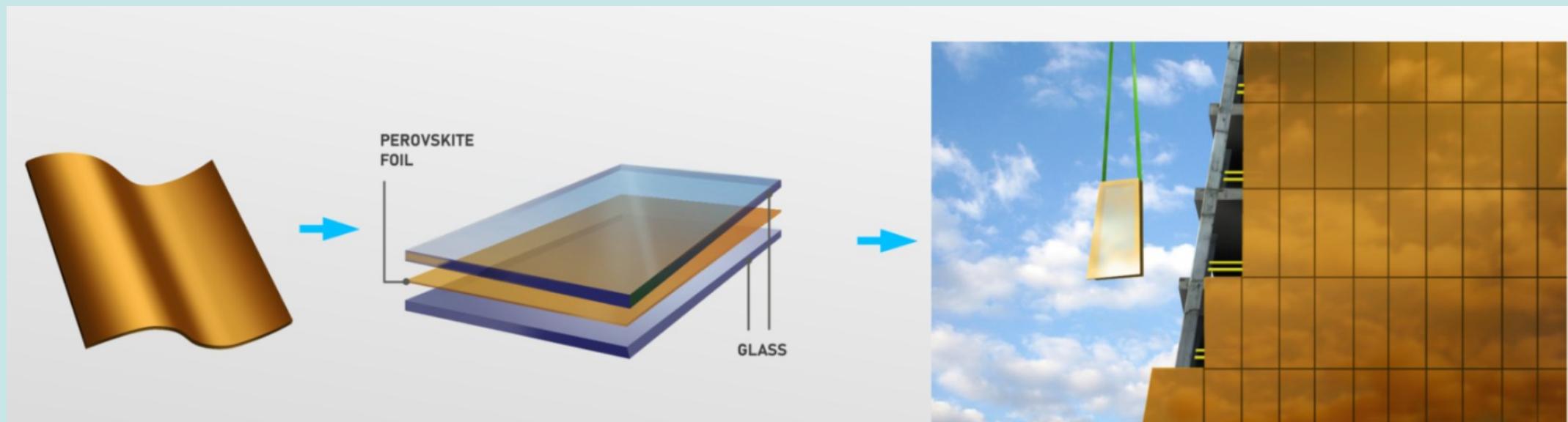
- perovskite-on-Si tandem solar cells
- residential use
- 29.5% efficiency
- founded by Prof. Henry Snaith (Oxford)



- inkjet printed perovskites
- building-integrated solutions (perovskite photovoltaic glass, blinds, etc)
- lightweight and flexible
- founded by Dr Olga Malinkiewicz

Emerging applications:

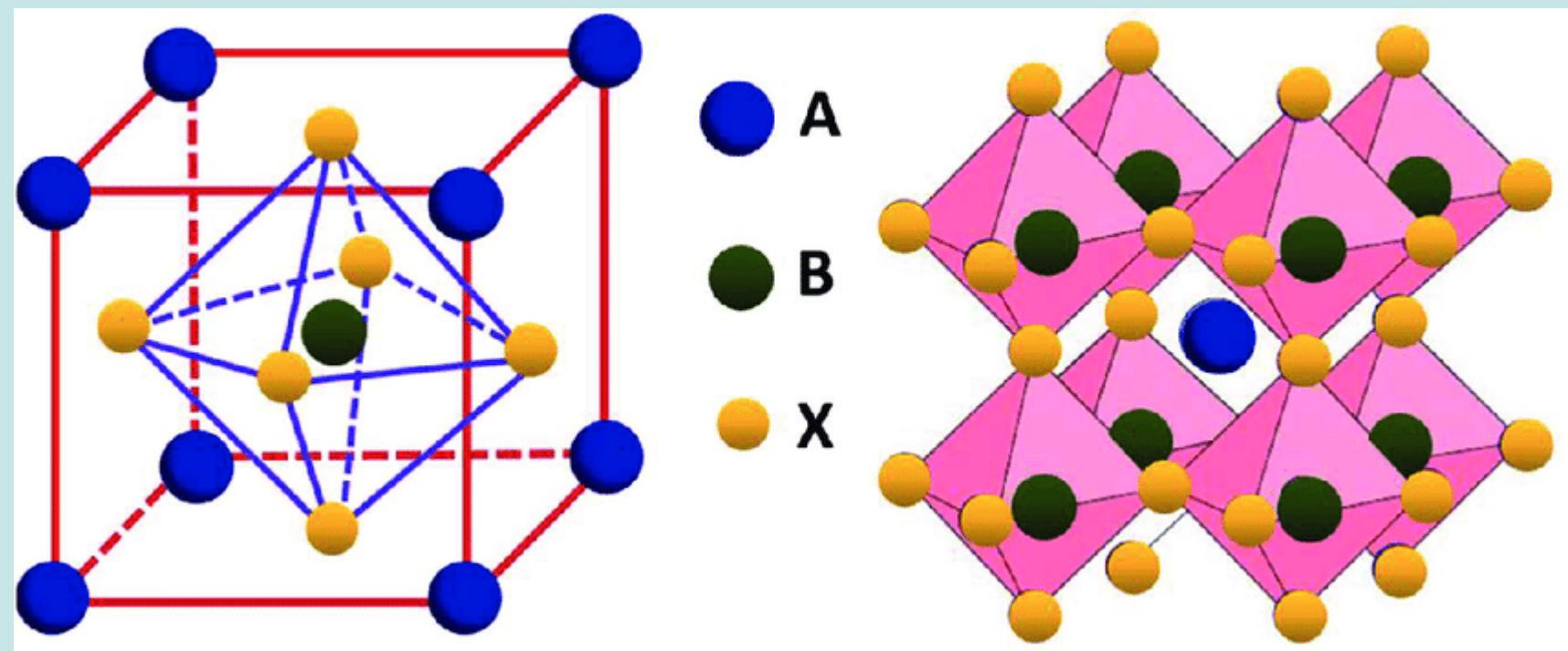
- LEDs and lasers
- photodetectors and imaging sensors
- transistors and memory devices
- scintillators and radiation detectors
- photocatalyst and water splitting
- wearable electronics



Composition and structure

How to build a perovskite?

Perovskite structure



A – large cation

(e.g. methylammonium [MA], formamidinium [FA], cesium [Cs])

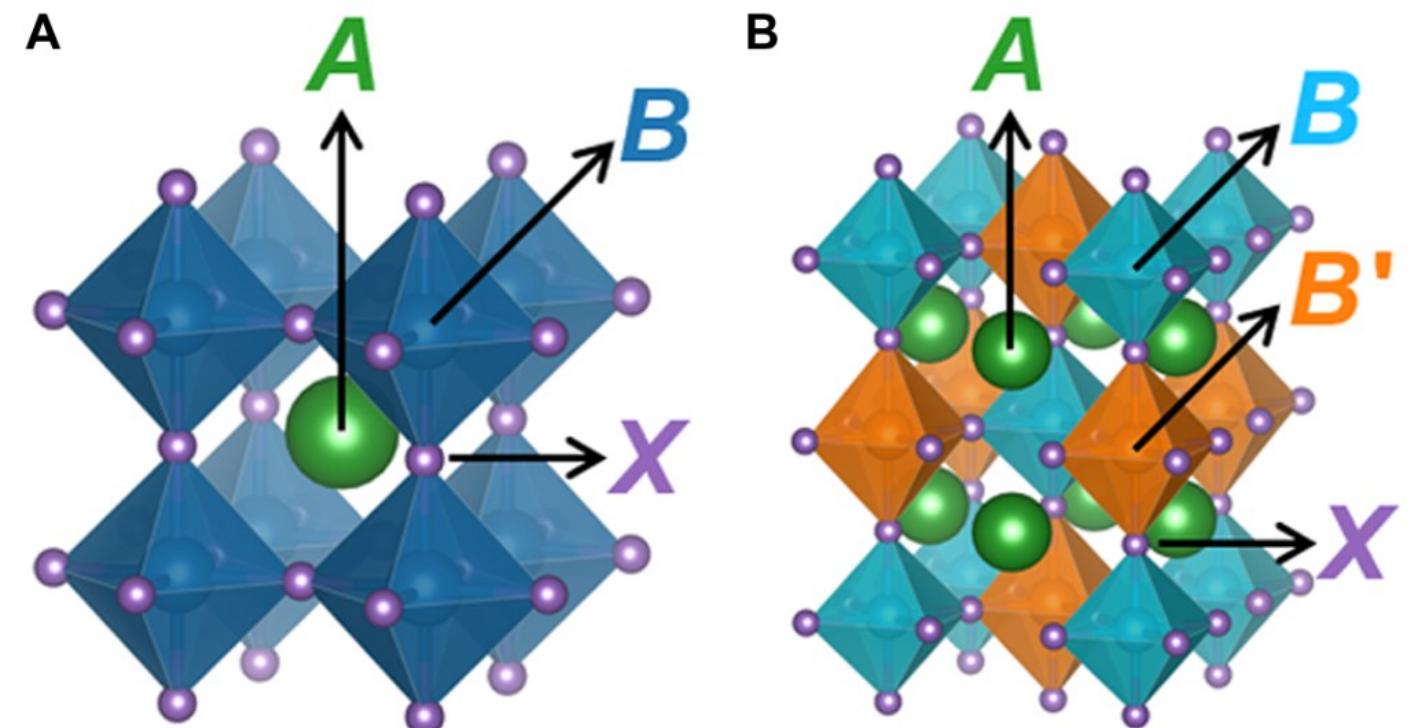
B – smaller metal cation

(e.g. lead [Pb], tin [Sn])

X – anion

(halide e.g. iodide [I], bromide [Br], chloride [Cl] or oxygen in perovskite oxides)

Perovskite composition



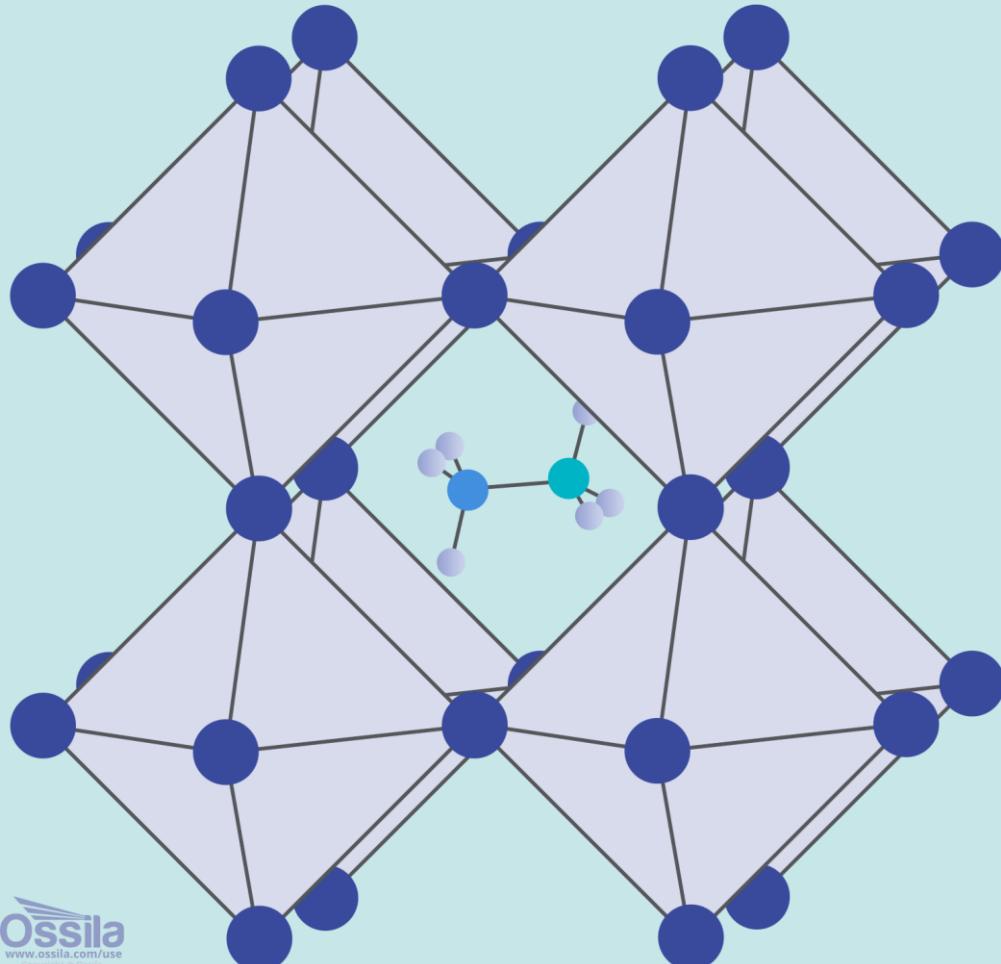
Bartel et al., Sci. Adv. 2019; 5 : eaav0693

Oxide vs. halide

	oxide perovskites	halide perovskites
formula	ABO_3 A,B metal cations	ABX_3 A – organic or inorganic cation, BX_3 – metal halide*
structure	cubic, tetragonal or orthorhombic	cubic
what affects structure	ionic sizes and tolerance factor	external conditions (temperature and pressure)
influence of ionic radii	transition between structures	structural instability
stability	good (heat and moisture) thanks to strong metal-oxygen bonds (ionic and covalent bonds)	varying, usually sensitive to light and moisture due to weaker metal-halogen bond
properties	ferroelectric, magnetic, superconductivity	high absorption, tunable band gap, long diffusion lengths

*A **halide** is a chemical compound that consists of a halogen atom (from Group 17 of the periodic table) bonded to another element. The halogens include **fluorine (F)**, **chlorine (Cl)**, **bromine (Br)**, **iodine (I)**, and **astatine (At)**.

Hybrid perovskites



MAPbI₃

(methylammonium lead iodide)

HYBRID = halide perovskite with organic
and inorganic components

- solution processed
- bandgap 1.55eV
- tolerance factor: 0.81
- carrier diffusion length: >100nm
- exciton binding energy: 10-24 meV

Common perovskites

Formula	name /type	properties
CaTiO_3	oxide	The “original” perovskite mineral; the structure type is named after it.
SrTiO_3	oxide	Ideal cubic perovskite at room temperature; used in high-permittivity dielectrics & substrate crystals.
BaTiO_3	oxide	Classic ferroelectric; widely used in capacitors, piezoelectrics, and electro-optic applications.
LaAlO_3	oxide	Slightly distorted (rhombohedral); a common substrate for growing other perovskite thin films.
LaFeO_3	oxide	A magnetic and semiconducting perovskite; studied for catalysis and spintronic applications.
MAPbI_3 ($\text{CH}_3\text{NH}_3\text{PbI}_3$)	hybrid halide	benchmark material in perovskite solar cells with high photovoltaic efficiency.
FAPbI_3 ($\text{HC}(\text{NH}_2)_2\text{PbI}_3$)	hybrid halide	tends to have better thermal stability than MAPbI_3 and used in next-gen PV cells.
CsPbI_3	inorganic halide	All-inorganic perovskite with good thermal stability; studied for LEDs and solar cells.
CsSnI_3	inorganic halide	Lead-free (tin-based) perovskite; promising but sensitive to oxidation ($\text{Sn}^{2+} \rightarrow \text{Sn}^{4+}$).
$(\text{BA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{n+1}$	Butylammonium (2D/hybrid)	Example of layered perovskite, offering enhanced stability vs. 3D perovskites.

Structural factors

Goldschmidt tolerance factor

- r_A : Ionic radius of the A-site cation
- r_B : Ionic radius of the B-site cation
- r_X : Ionic radius of the X-site anion

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

$t \approx 1$ – ideal (cubic structure, stable perovskite)

$t > 1.1$ – the A-site cation is too large -> non-perovskite structures (hexagonal or layered)

$t < 0.8$ – the A-site cation is too small -> distortions and tilting of the BX_6 octahedra

Structural factors – ctd.

Octahedral factor

$$\mu = \frac{r_B}{r_X}$$

- r_A : Ionic radius of the A-site cation
- r_B : Ionic radius of the B-site cation
- r_X : Ionic radius of the X-site anion

0.414 < μ < 0.732 ideal range

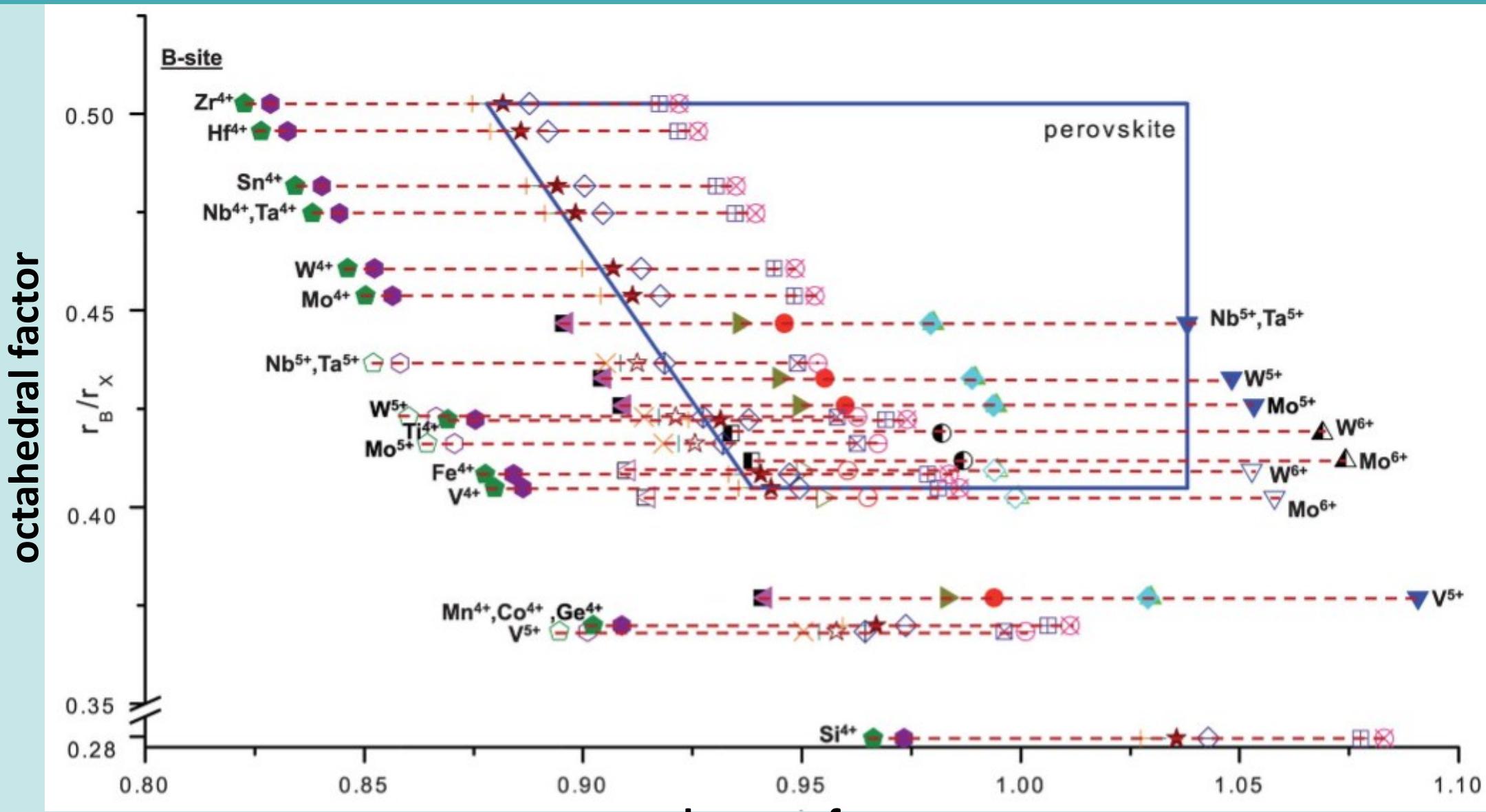
• Too Small (<0.414):

- The B-site cation is too small
- under-bonding and instability in the octahedral framework
- The structure may collapse or transition to a different phase.

• Too Large (>0.732):

- The B-site cation is too large
- causing over-bonding and distortion of the octahedral framework
- This can lead to lattice strain and deviations from the ideal perovskite structure.

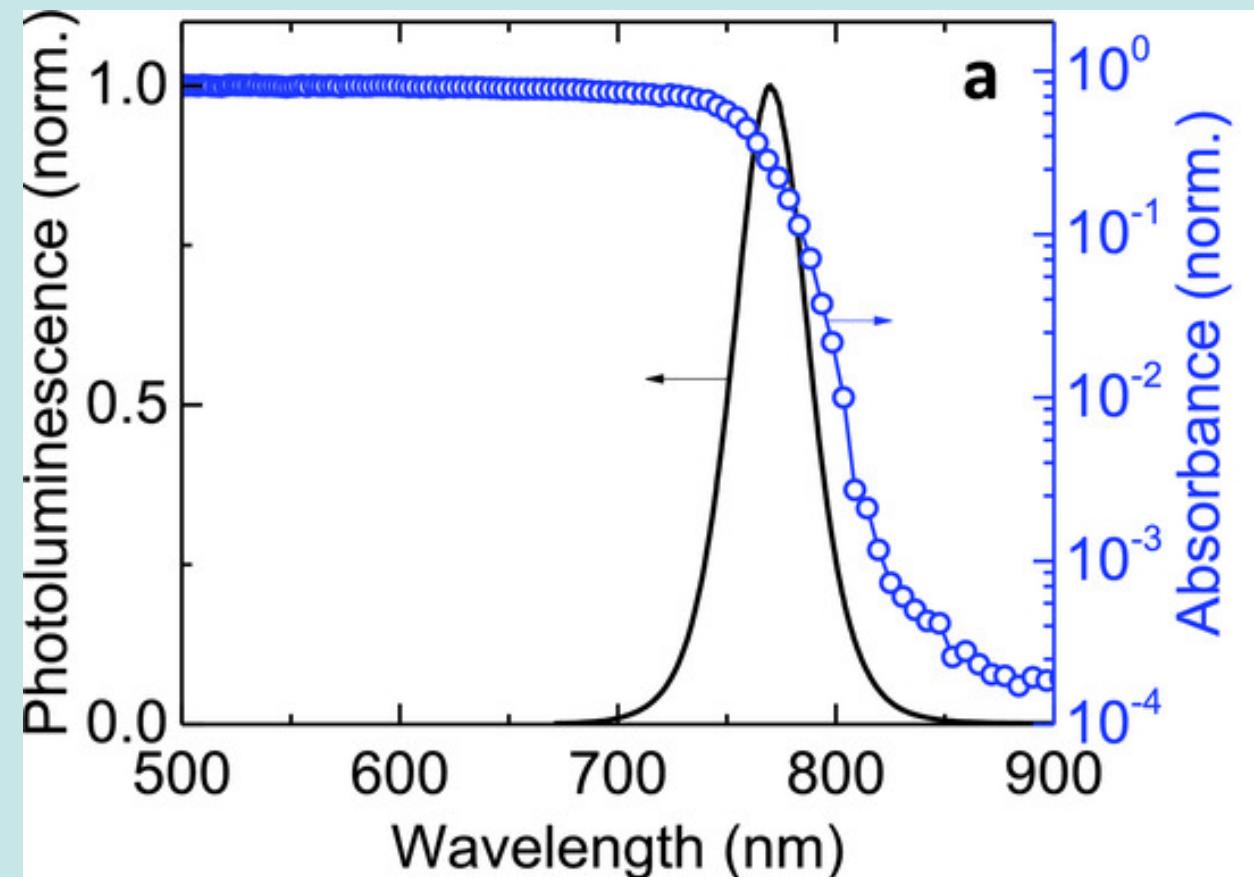
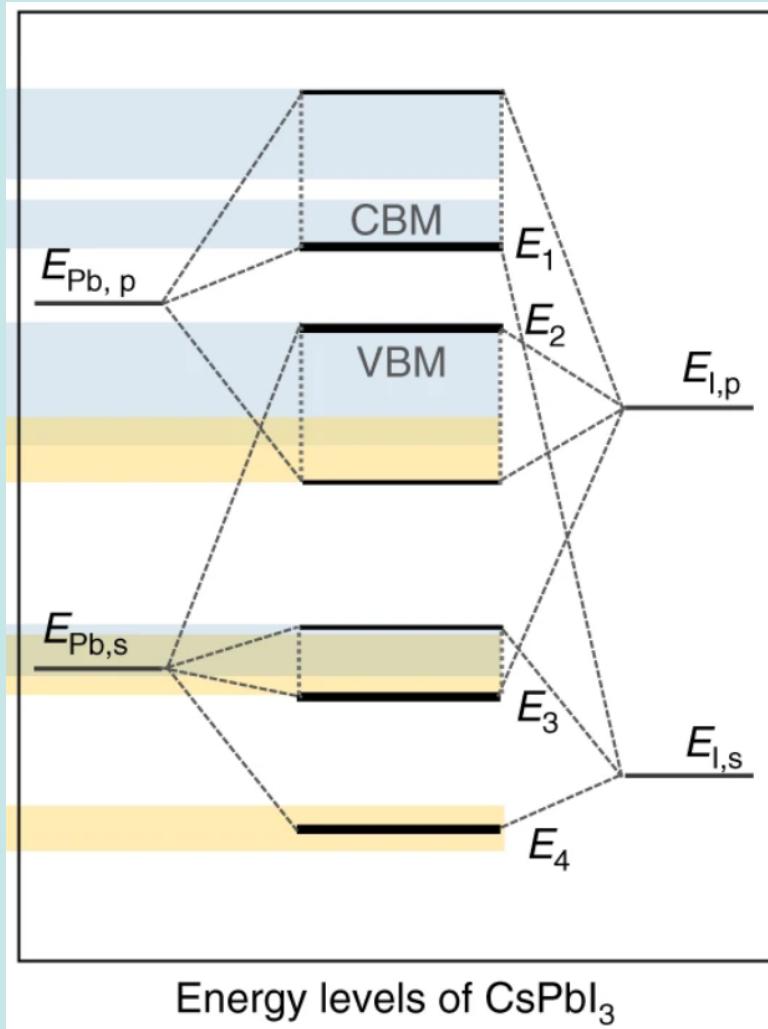
Structural factors – combined



Optoelectronic properties

Underlying mechanisms and performance

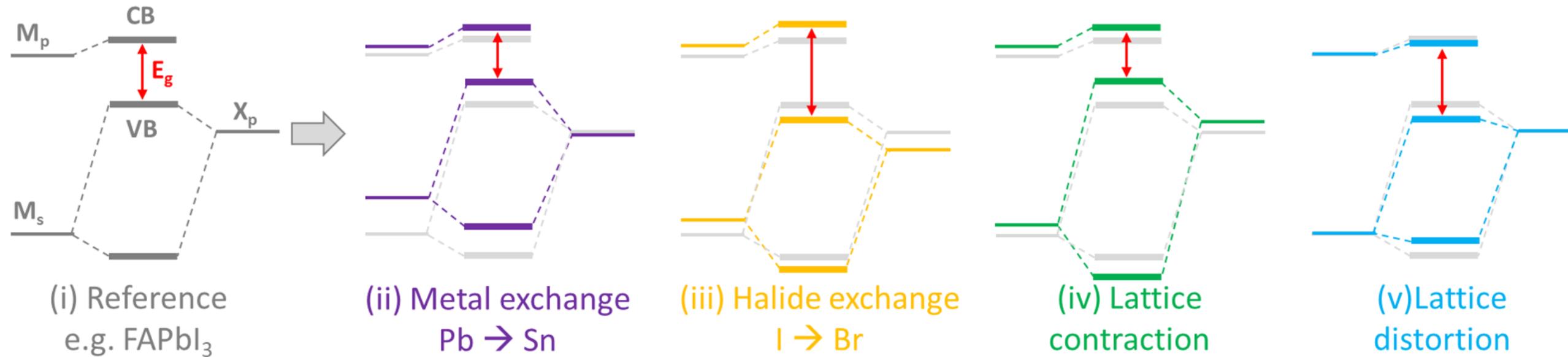
Electronic structure



S. D. Stranks, R. L. Z. Hoye, D. Di, R. H. Friend, F. Deschler, *Adv. Mater.* 2019, 31, 1803336

- VBM is primarily composed of the antibonding combination of lead (Pb) 6s and halide p orbitals.
- CBM consist mainly of Pb 6p orbitals.

Bandgap composition



1. composition (choice of B&X ions)

- top of VB = hybridized metal (s) and halide (p) states
- bottom of CB = metal (p) and halide (s) orbitals

2. lattice size (ionic radii)

- smaller lattice – confinement effects (VB and CB shifted up)
- increased hybridisation (VB shifts up)

3. lattice distortion (bond angles)

- cubic – smallest bandgap (highest orbital overlap)
- hybridisation reduces with lattice distortion (lowering of VB, CB not affected as more ionic)

Ion intermixing

1. Partial substitution of anion

- tune bandgap, tune charge transport (increase carrier lifetimes), improve stability (structural and chemical)
- e.g. $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ – bandgap increases with x
- e.g. $\text{MAPb}(\text{I}_{1-x}\text{Cl}_x)_3$ – diffusion length of e and h increases with Cl

2. B-site cation mixing

- tune bandgap, stabilise crystal structure at lower temp, increase luminescence
 - e.g. add Sn^{2+} reduces bandgap and increases carrier lifetimes
 - add Ge^{2+} to improve solubility ($\text{FA}_{0.83}\text{MA}_{0.17}\text{Ge}_x\text{Pb}_{1-x}(\text{I}_{0.9}\text{Br}_{0.1})_3$)

3. A-cation mixing

- little effect o the bandgap (only via crystal size and bond angles modification)
- changes phase and temperature stability

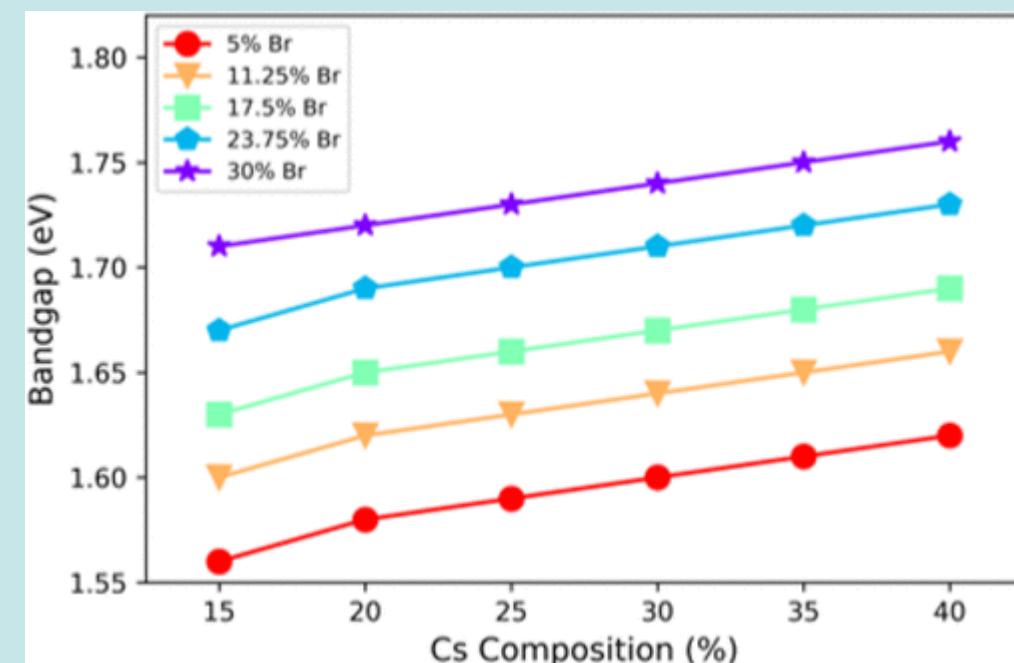
Bandgap tuning - examples

Methylammonium Lead Halides

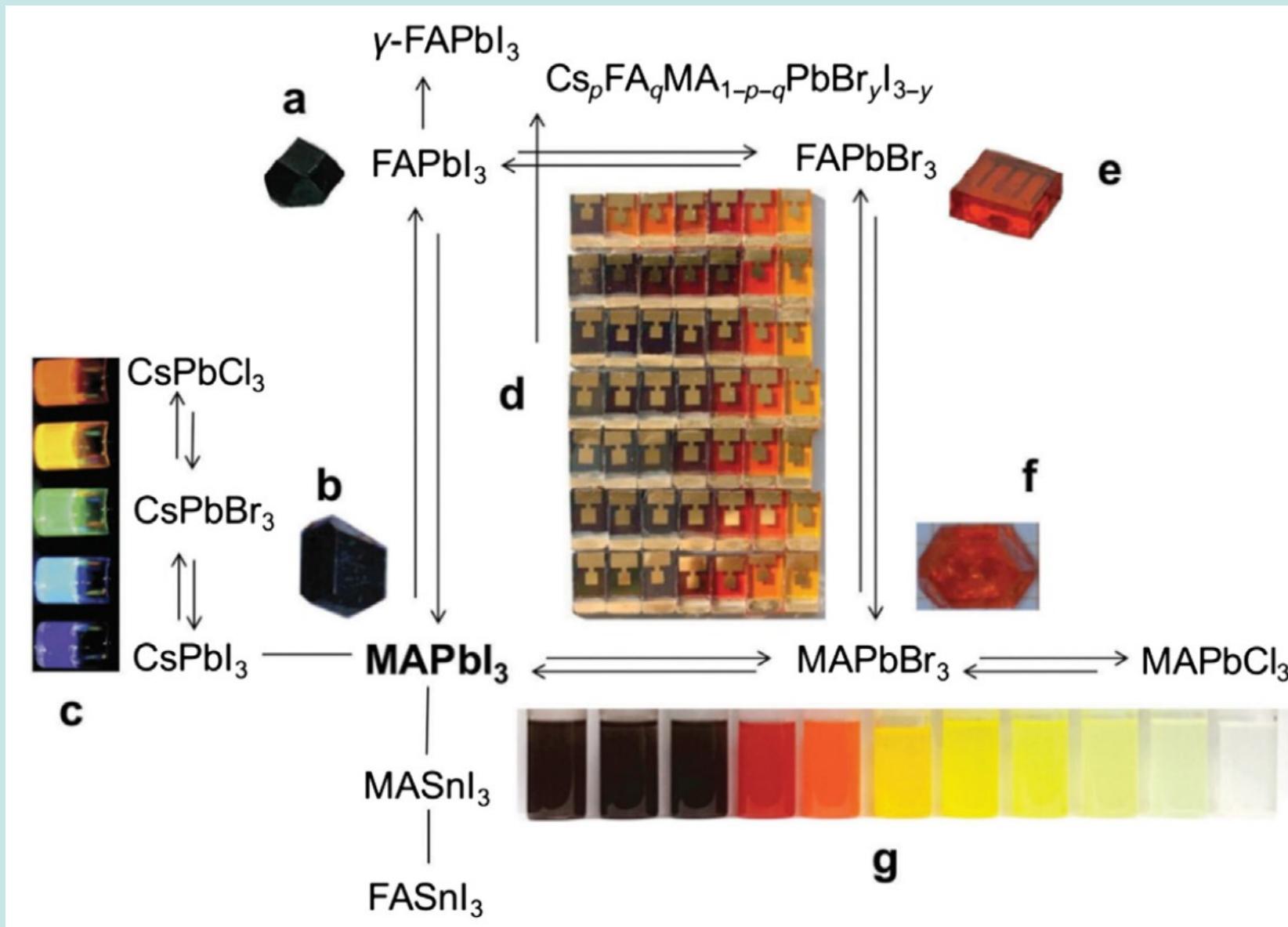
- **MAPbI₃**: Band gap ~1.55 eV (near-infrared).
- **MAPbBr₃**: Band gap ~2.30 eV (green light).
- **MAPbCl₃**: Band gap ~3.0 eV (ultraviolet).

Mixed-Cation, Mixed-Halide Perovskites

- **(FAPbI₃)_{1-x}(MAPbBr₃)_x:**
 - Allows fine-tuning of the band gap while improving thermal stability.
 - **Cs_xFA_{1-x}Pb(Br_yI_{1-y})₃** on the graph ->

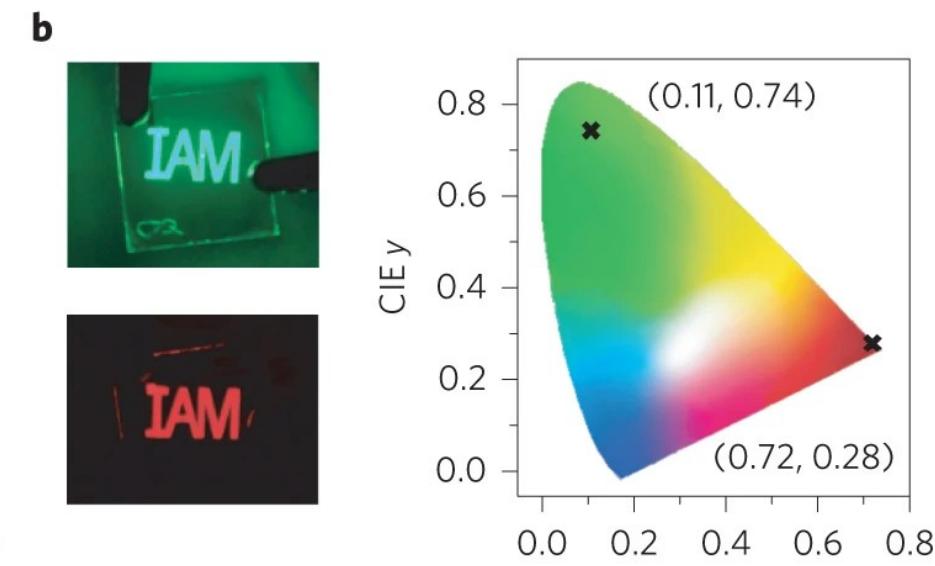
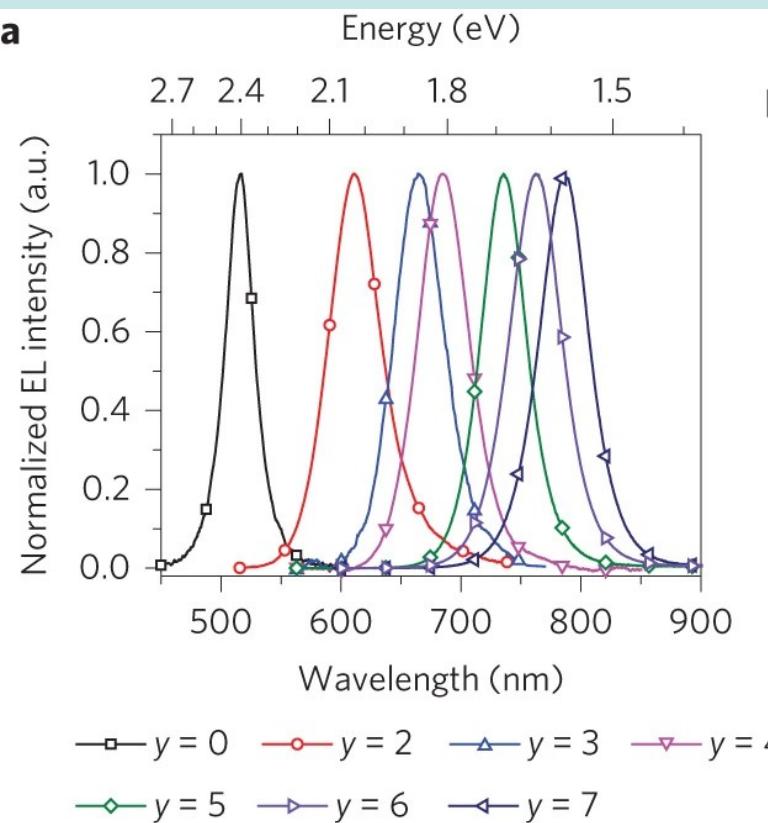


Bandgap tuning - examples



Bandgap tuning - examples

- a.** EL spectra of MQW LEDs based on the $\text{NFPI}_y\text{B}_{7-y}$ films, $y = 0, 2, 3, 4, 5, 6$ and 7 , respectively, which are processed using various combinations of precursor solutions of NMAI, FAI and PbI_2 .
- b.** Photographs of green and red MQW LEDs with the logo of the IAM, and the corresponding CIE coordinates.
- c.** Stability data for a NFPI_7 EL device tested at a constant current density of 10 mA cm^{-2} .



Carrier dynamics

Charge generation, transport and recombination

Charge carriers in perovskites

perovskites behave like crystalline semiconductors:

- e and h carry charge
- low exciton binding energy – easy dissociation
- valence and conduction band dynamics

HOWEVER

ions can move within the material:

- hysteresis in JV curves (PVs)
- instabilities building over time can affect charge extraction
- screening effect (Coulombic)
- phonon coupling
- ...

Charge generation

- direct bandgap -> high absorption coefficients (exceeding 10^5 cm^{-1})
- low exciton binding energy 10-25meV (comparable to thermal energy at room temperature, $\sim 26\text{meV}$)
 - exciton dissociation into free carriers without assistance
- high dielectric constant (reduced Coulombic interactions) -> free carriers formed rather than excitons
- photon recycling -> emitted photons can be reabsorbed and re-emitted

Diffusion length

$$L = \sqrt{D\tau}$$

L – carrier diffusion length
D – carrier diffusion coefficient
 τ – carrier lifetime
 μ – carrier mobility
 k_B – Boltzmann's constant
T – temperature
q – elementary charge

Einstein relation

$$D = \frac{\mu k_B T}{q}$$

Carrier lifetime

Carrier lifetime due to defect-assisted recombination:

$$\tau = \frac{1}{\sigma v_{th} N_d}$$

σ – capture cross-section of the defect
(typically 10^{-15} cm^2)
 v_{th} – thermal velocity of the carriers
(10^7 cm/s at RT)
 N_d – defect density

- In high-quality perovskites, micro- or even milliseconds.
- Defects can lower it to tens of nanoseconds.

Defects in perovskites

Types of Defects:

- **Vacancies:**

- Missing ions (e.g., halide vacancies).

- **Interstitials:**

- Extra ions occupying interstitial sites.

- **Anti-Site Defects:**

- Ions occupying incorrect lattice positions.

- **Dynamic Lattice:** The organic cations (e.g., methylammonium) in hybrid perovskites are rotationally mobile, leading to dynamic disorder.
- **Self-Healing Properties:** The mobility of ions allows the lattice to reorganize around defects, effectively "healing" them or mitigating their impact on electronic properties

Due to defect tolerance, carrier mobilities and lifetimes remain high even with defects.

Phonon coupling

The Frohlich model of large polarons

$$\alpha = \frac{e^2}{\hbar\omega_0} \left(\frac{1}{\bar{\epsilon}} \right) \sqrt{\frac{m\omega_0}{2\hbar}}$$

α – Frohlich constant (intrinsic carrier-LO phonon coupling strength)

ϵ – dielectric contrast (strength of the interaction)

m – effective mass of the carrier

$\hbar\omega_0$ - phonon energy

- couples the Coulomb field of a carrier with the macroscopic electric field of LO phonons
 - electric polarization caused by collective longitudinal optical vibrational modes (LO phonons) of the BX sublattice
 - charge carriers couple to the electric polarization field
- gives the upper limit of charge mobilities
- first approximation only

Charge transport - summary

- **high dielectric constant** reduces Coulomb scattering and improves mobility
- **high defect tolerance** (most defects are shallow)
- **photon recycling** extends apparent diffusion lengths and carrier lifetimes
- **symmetric** mobilities (balanced e and h transport) typically around 60-100 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ (better than OSCs, worse than silicon)
- **high crystallinity** improves mobility as grain boundaries contain defects
- mobility decreases with temperature due to increased **phonon scattering**
- **polarons** form
- **ion migration** (under E field) leads to current-voltage hysteresis and material degradation

Measurement Techniques for Charge Transport

a. Time-Resolved Photoluminescence (TRPL)

- Carrier Lifetimes:** Provides information on recombination dynamics and trap states.

b. Time-of-Flight (TOF) Measurements

- Mobility Determination:** Measures the transit time of carriers across the perovskite layer.

c. Hall Effect Measurements

- Carrier Concentration and Mobility:** Offers direct measurement of carrier mobility and type (electron or hole).

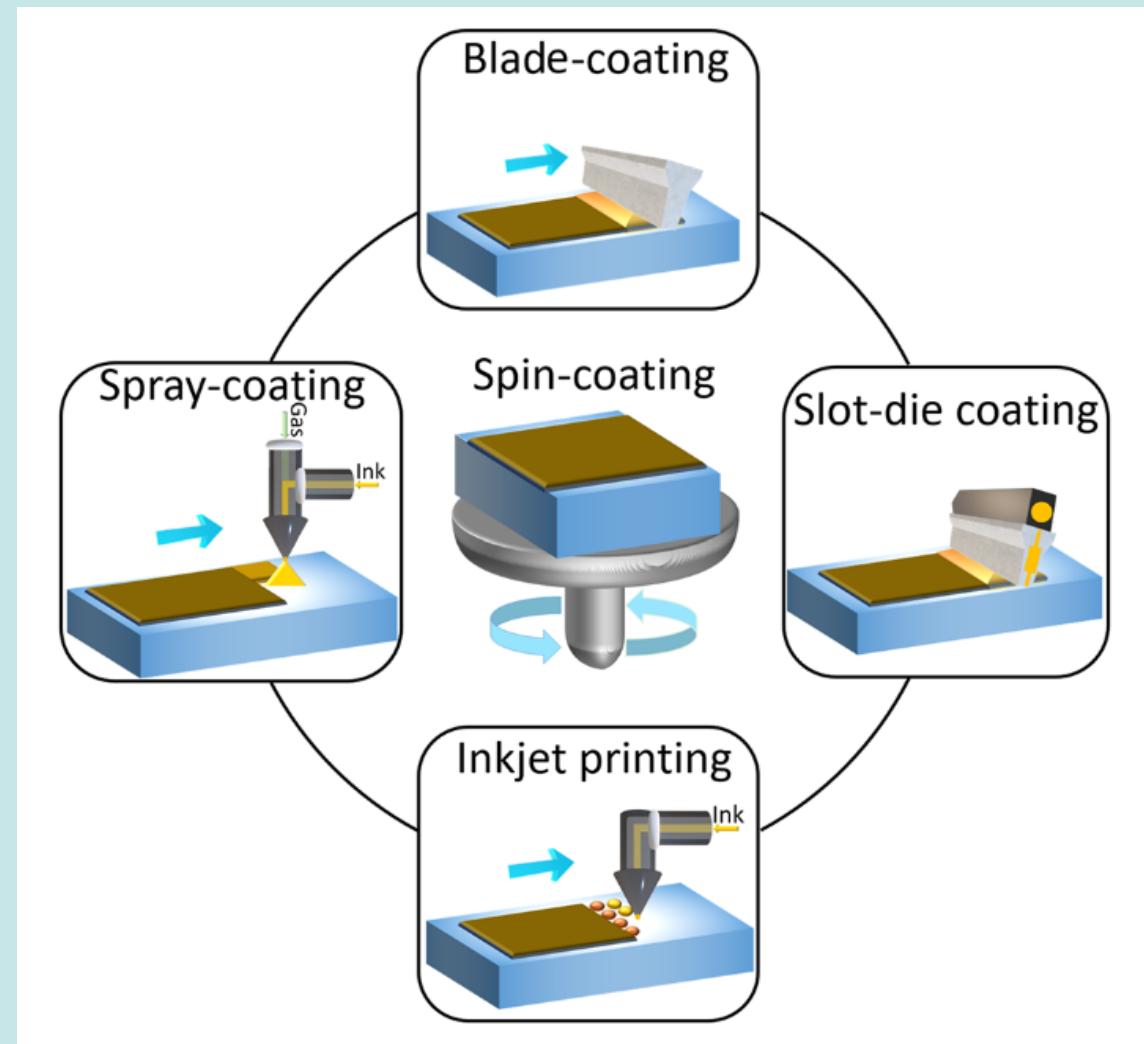
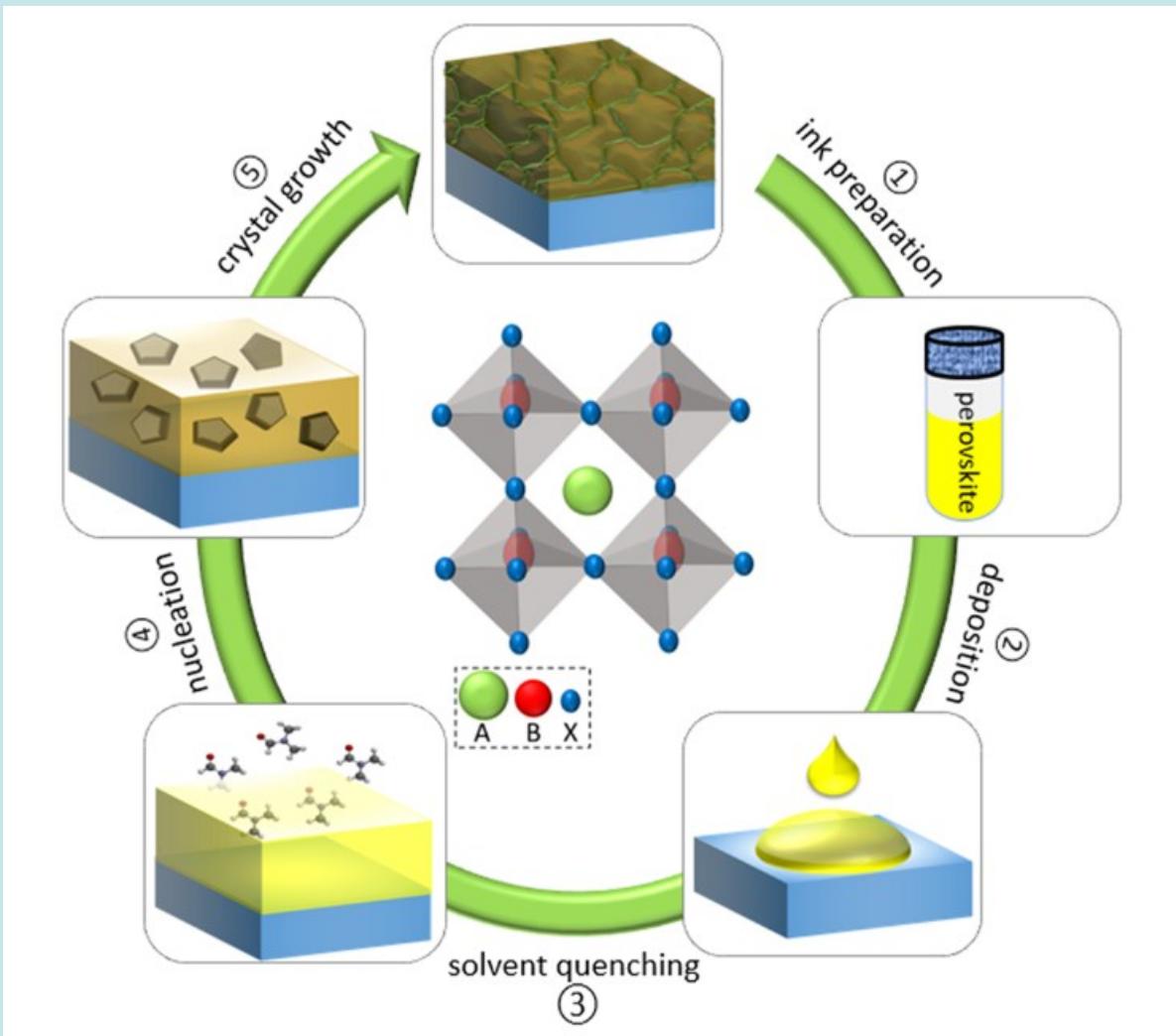
d. Transient Absorption Spectroscopy

- Ultrafast Dynamics:** Probes carrier relaxation and recombination on femtosecond to nanosecond timescales.

Fabrication techniques

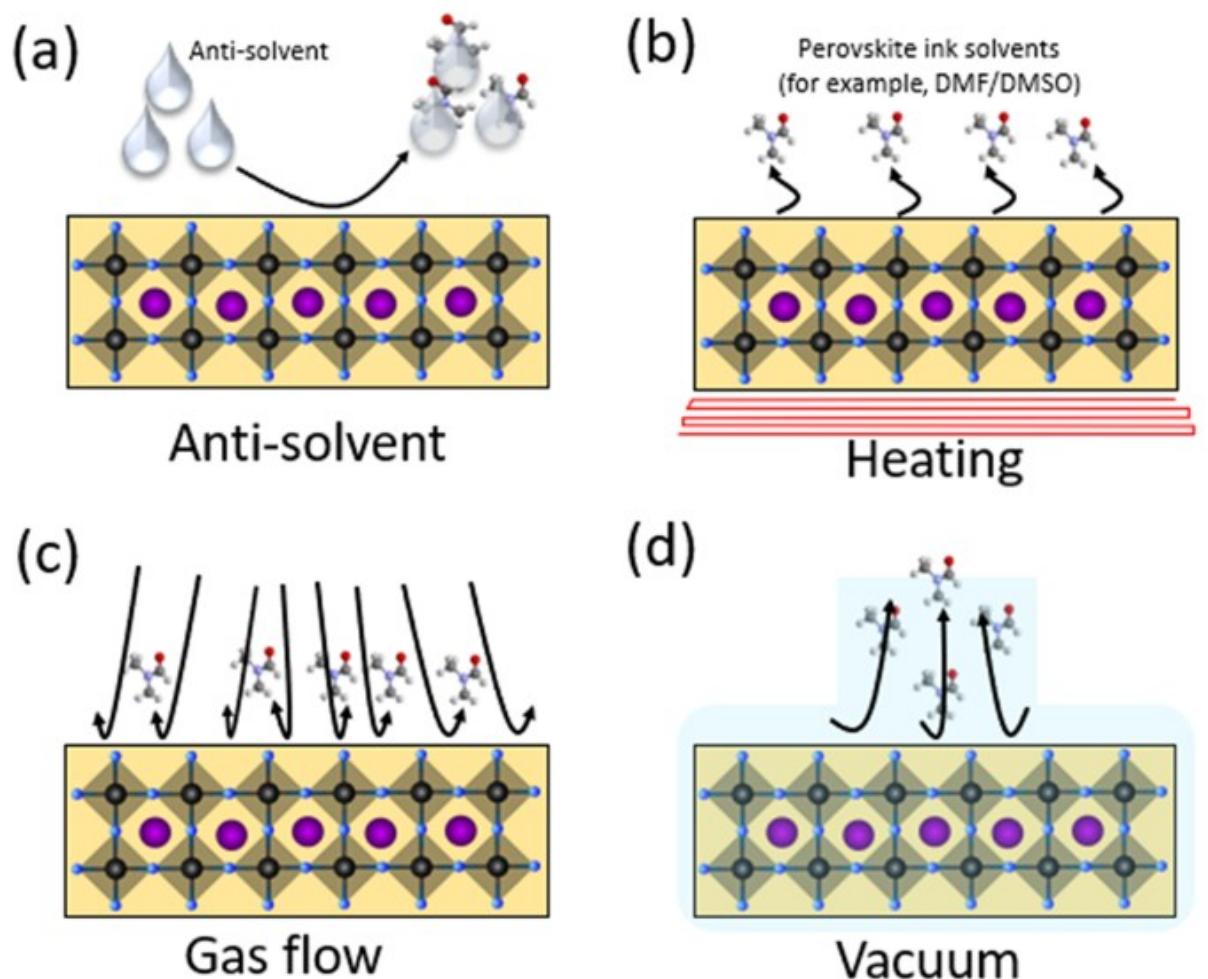
How to make a perovskite?

Perovskite deposition – from solution



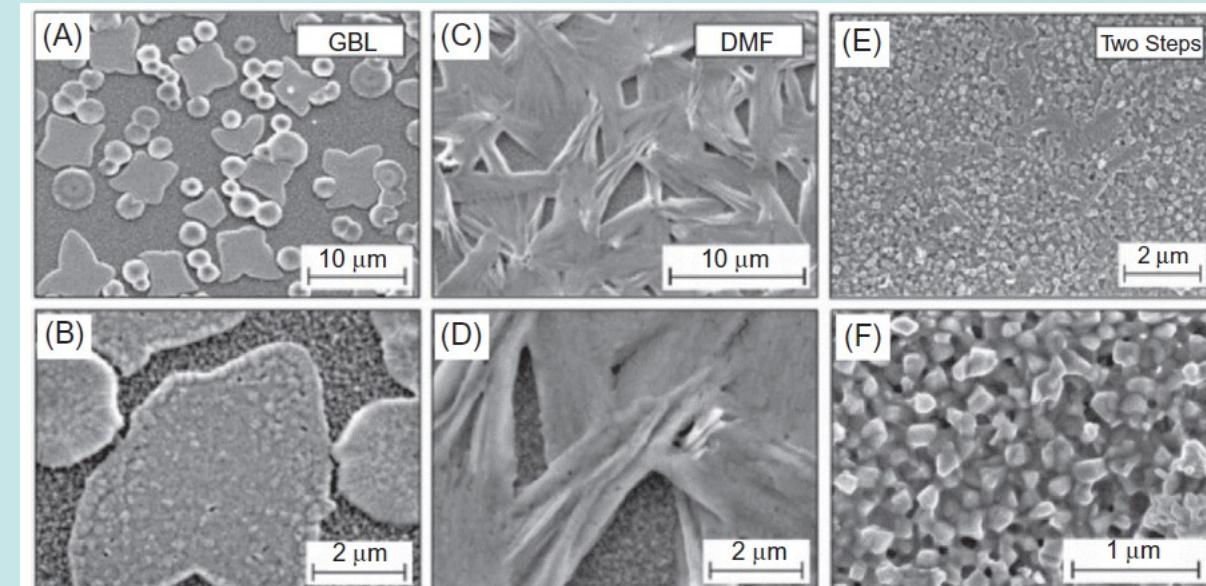
Perovskite deposition – from solution ctd.

Solvent extraction methods:



Two-step solution deposition

- improves surface coverage
- STEP 1: deposit a PbI_2 seed layer
- STEP 2: react with MAI in isopropanol solution (dipping or spin-coating)



Nature 499 (2013) 316-319

Perovskite deposition – from vapour

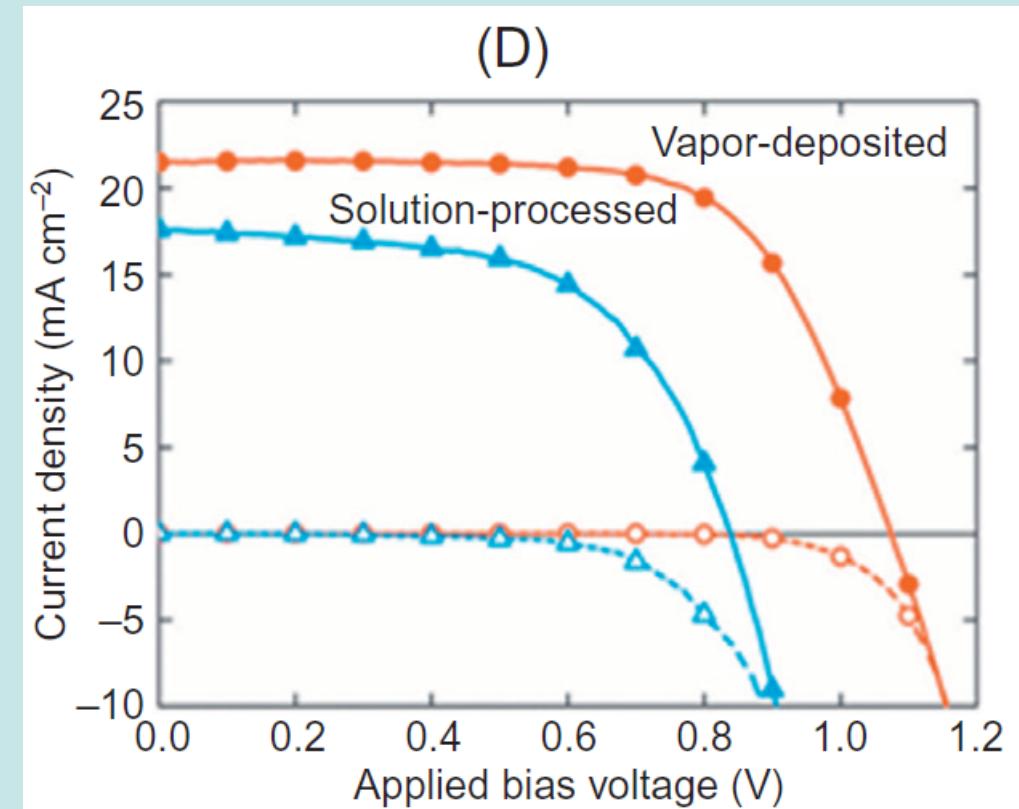
- **multi-source thermal evaporation (e.g.**

PbCl₂ and MAI)

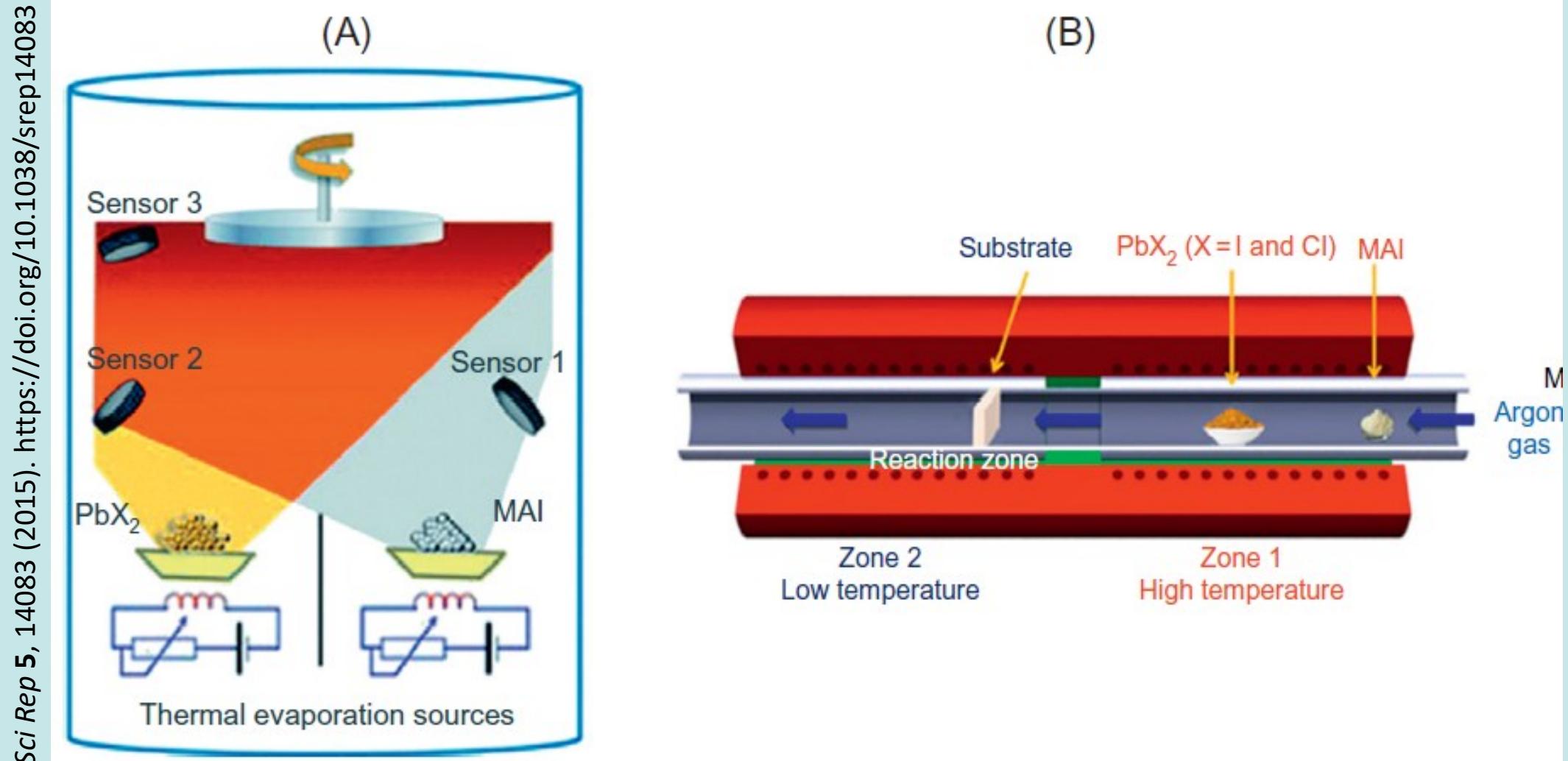
- in ultra high vacuum (10^{-6} mbar)
- ideally on a rotating substrate
- usually followed by annealing
- reaching over 20% efficiency in PV

- **CVD growth (Chemical Vapour Deposition)**

- (from lead halides and methylamine gas)
- epitaxial or polycrystalline
- highly reproducible



Perovskite deposition – from vapour



Thermal evaporation

CVD

Passivation techniques

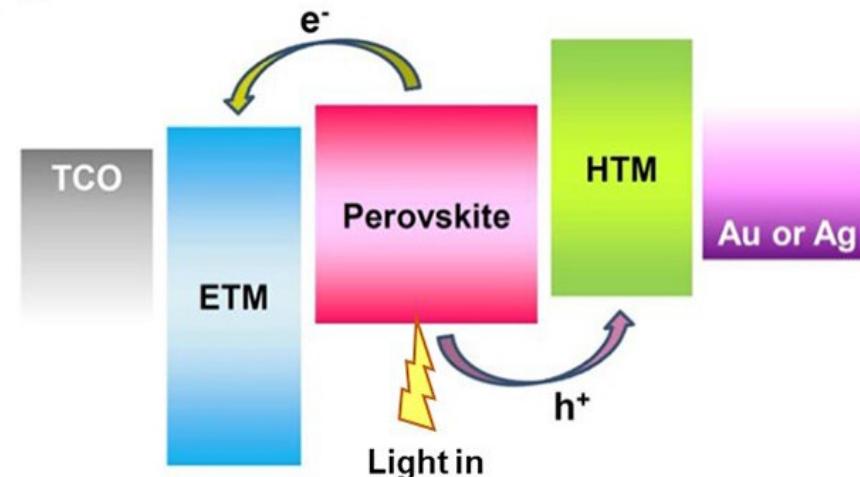
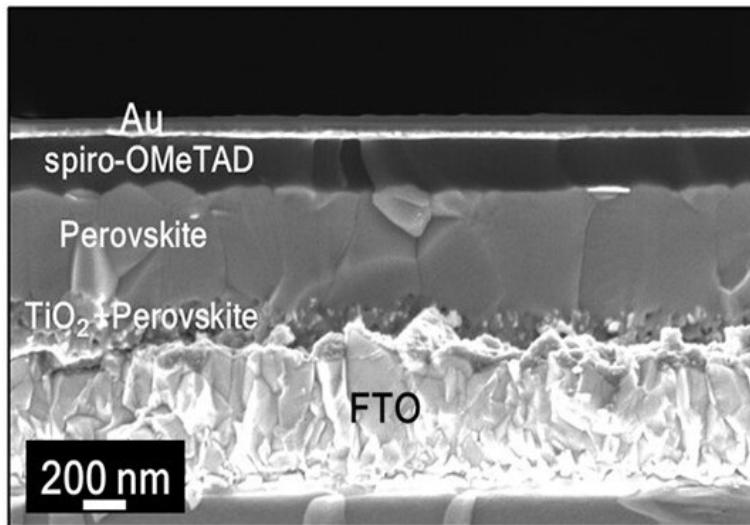
aim: reduce the detrimental effects of defects and trap states

- passivation agents during or after film formation
 - e.g. introducing small organic molecules like alkylammonium halides
 - can effectively passivate surface defects by binding to under-coordinated ions at the grain boundaries
- adding Lewis base molecules (e.g. thiocyanate or fullerene derivatives)
 - can interact with lead ions to reduce trap states within the bulk of the perovskite.
- interface engineering
 - using thin layers of polymers or metal oxides can serve as passivation layers
 - also protecting the perovskite from environmental factors
 - also reducing interfacial recombination.

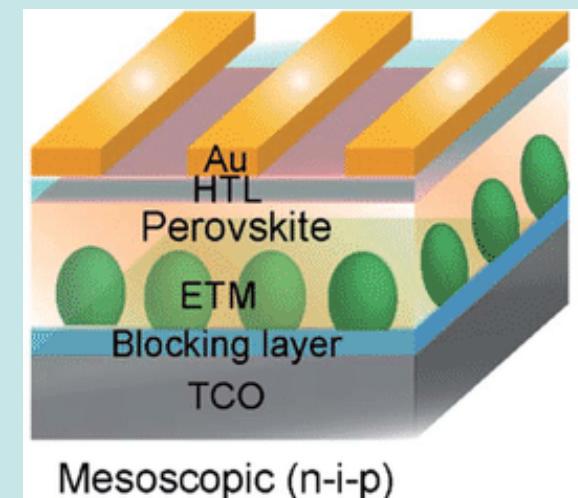
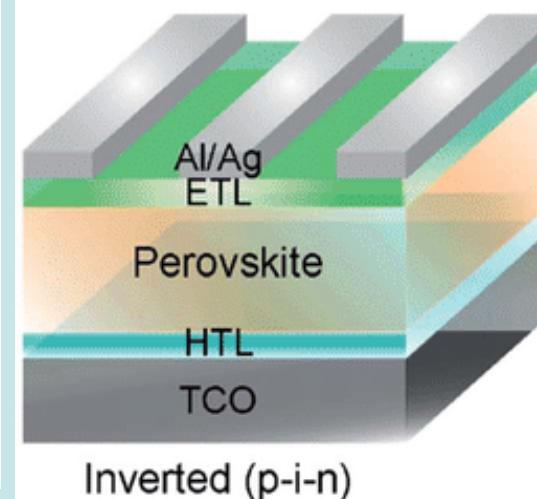
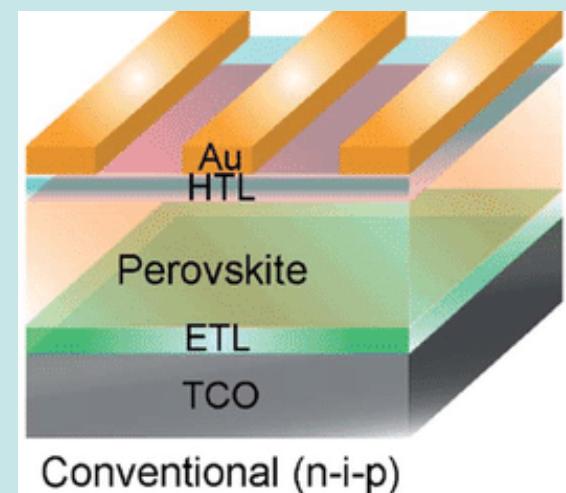
Perovskite devices

PVs, tandem PVs, LEDs...

Perovskite Solar Cells

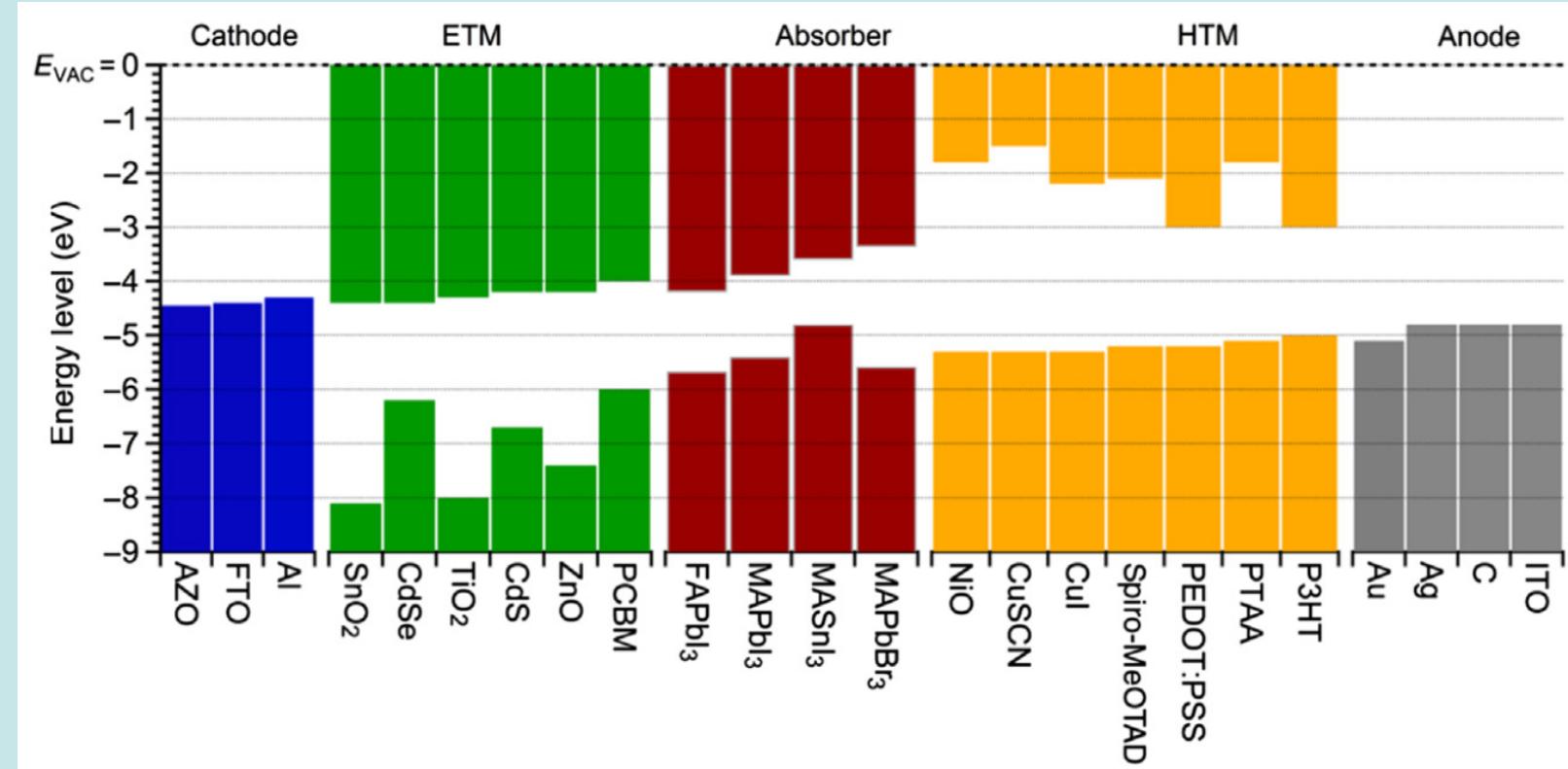


Baumeler, T. et al. *ACS Materials Letters* 2023 5 (9), 2408-2421



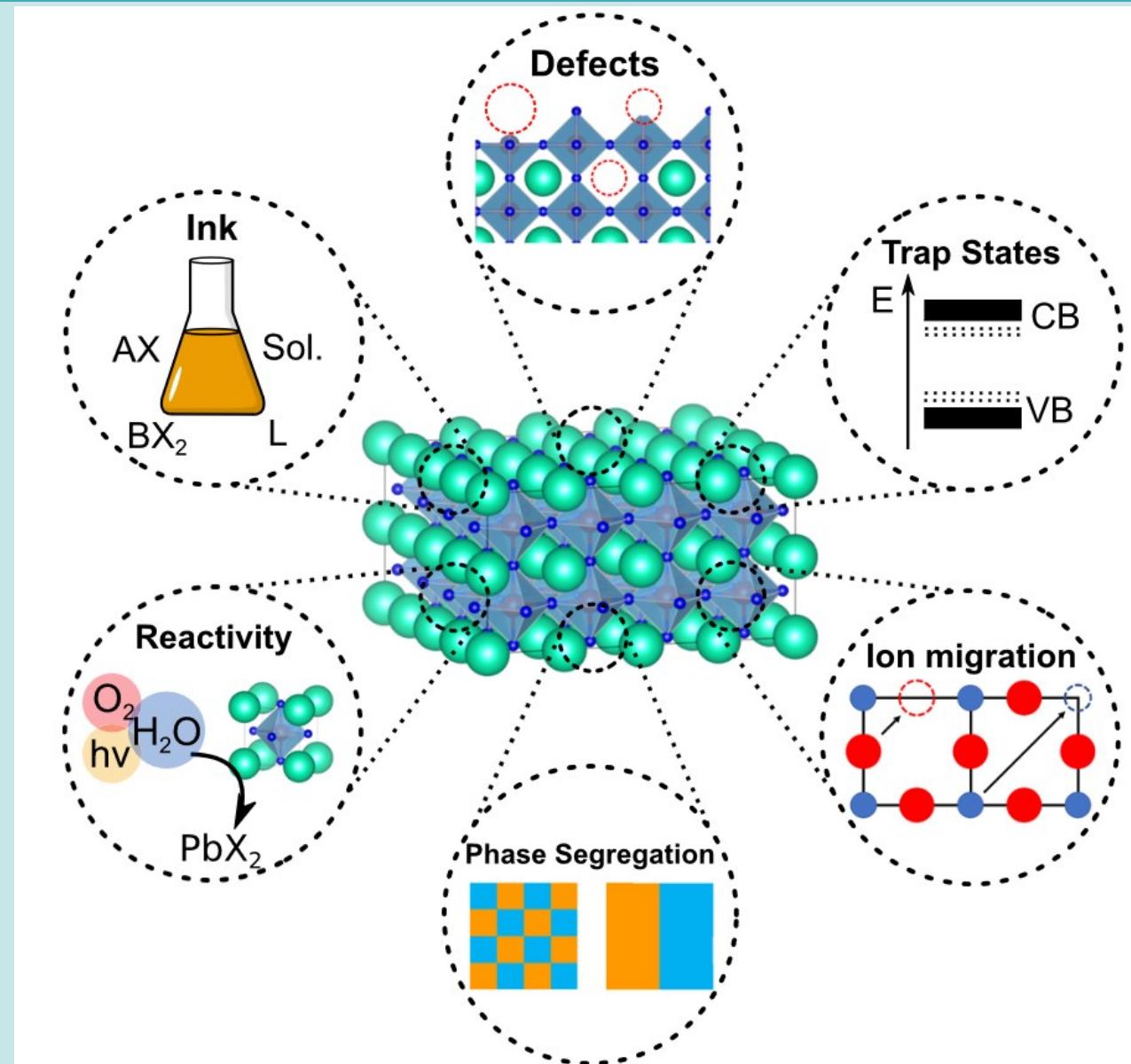
Perovskite Solar Cells - advantages

- high efficiency:
 - high carrier mobilities
 - effective exciton break-up
 - long lifetimes of carriers
- tunability!
- stable under ambient conditions
- solution processability at low temperatures (requires surface passivation to reduce defects)
- straightforward chemical synthesis

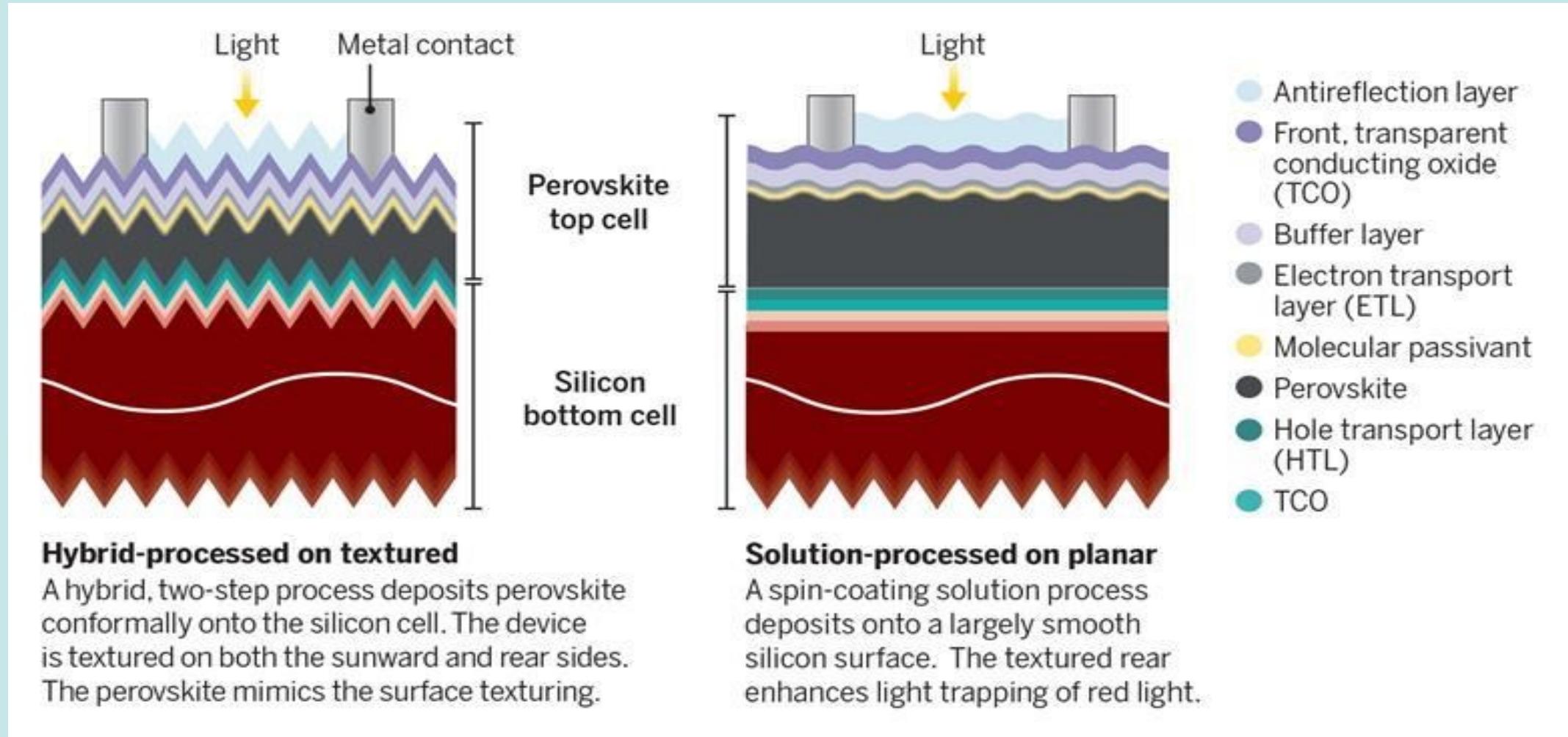


Perovskite Solar Cells - challenges

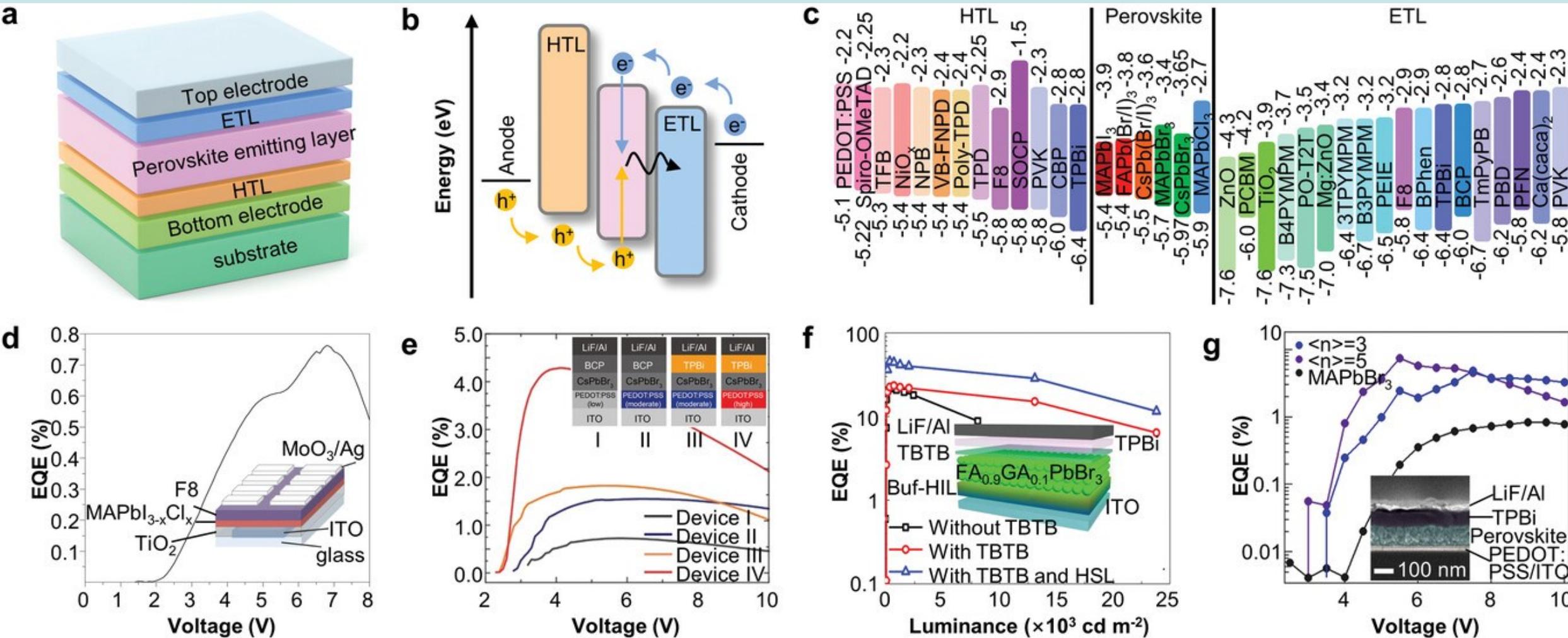
- ionic migration and phase segregation under illumination, reverse bias (different ions migrate with different mobility)
- phase segregation
- local heating (hybrid)
- need for controlled synthesis of precursor inks
 - understanding of nucleation and growth of crystals
 - stabilisation of inks to prevent uncontrolled growth and precipitation
- hysteresis



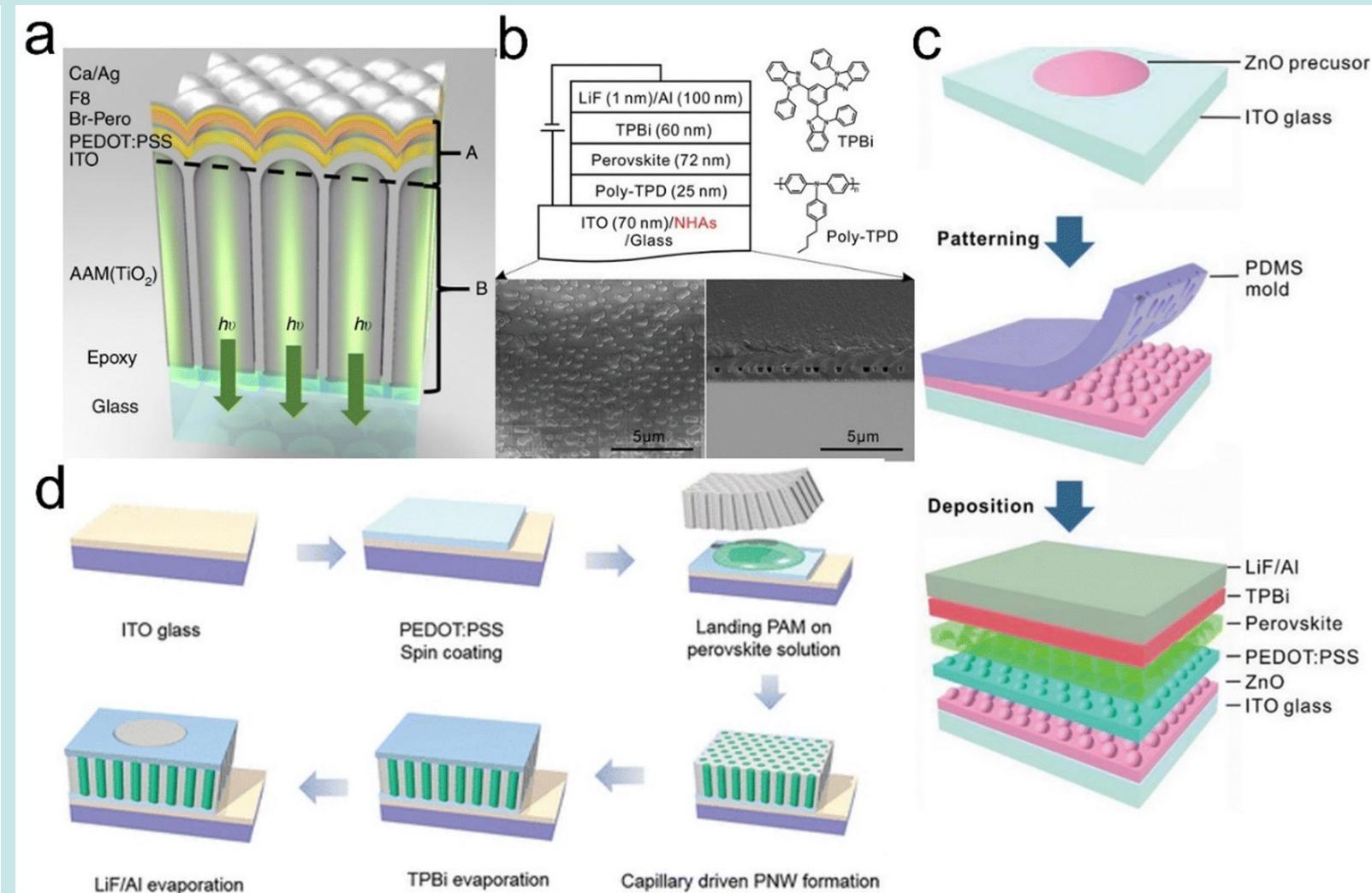
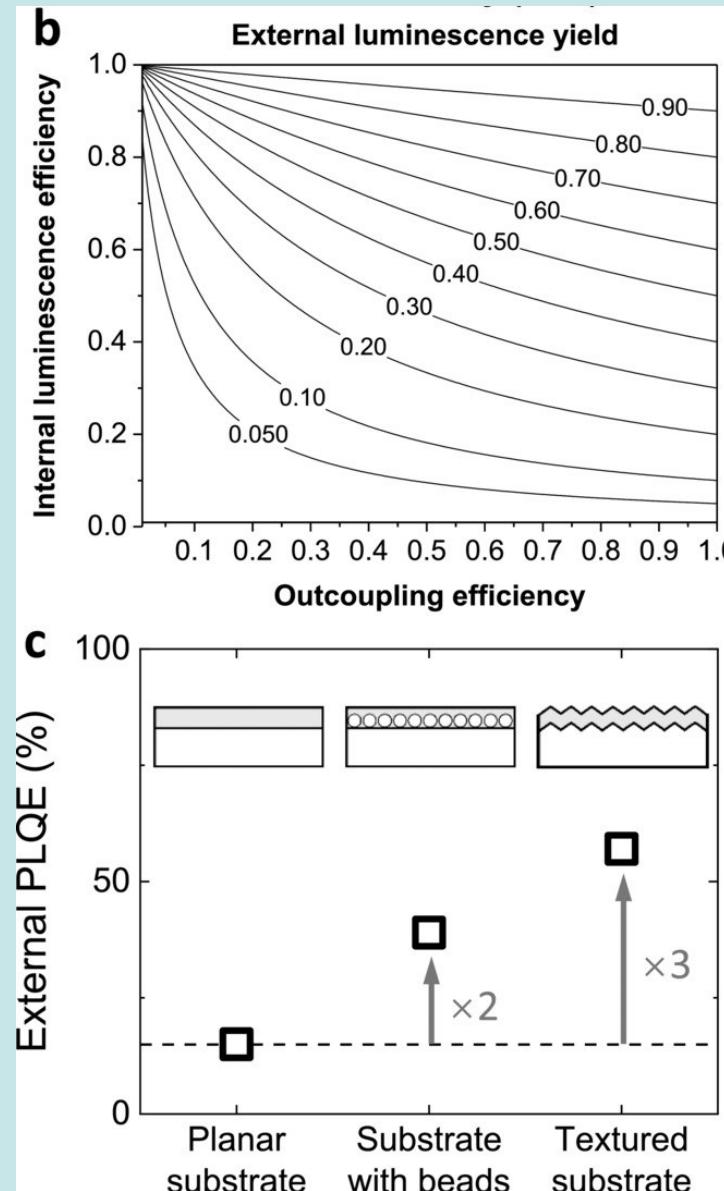
Tandem perovskite PVs



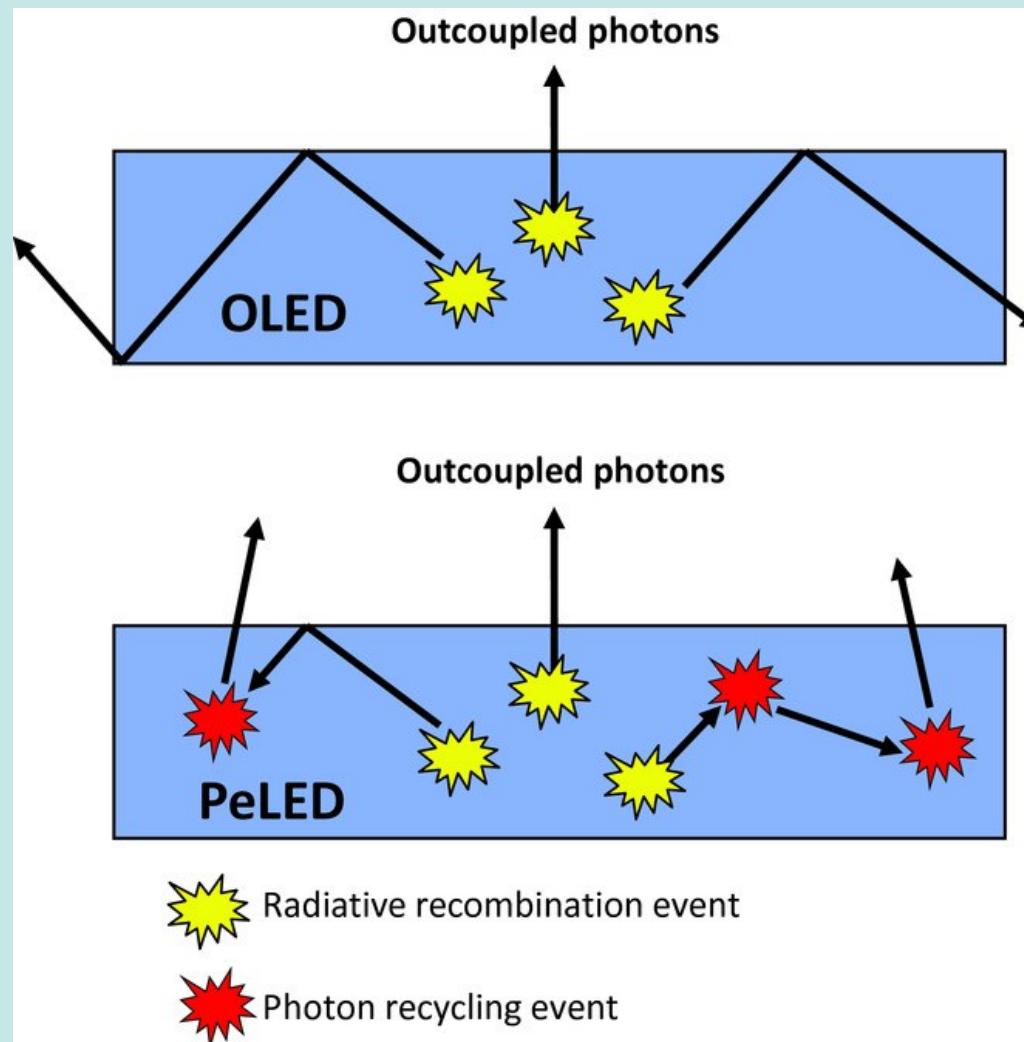
Perovskite LEDs



Light outcoupling



PeOLEDs and photon recycling



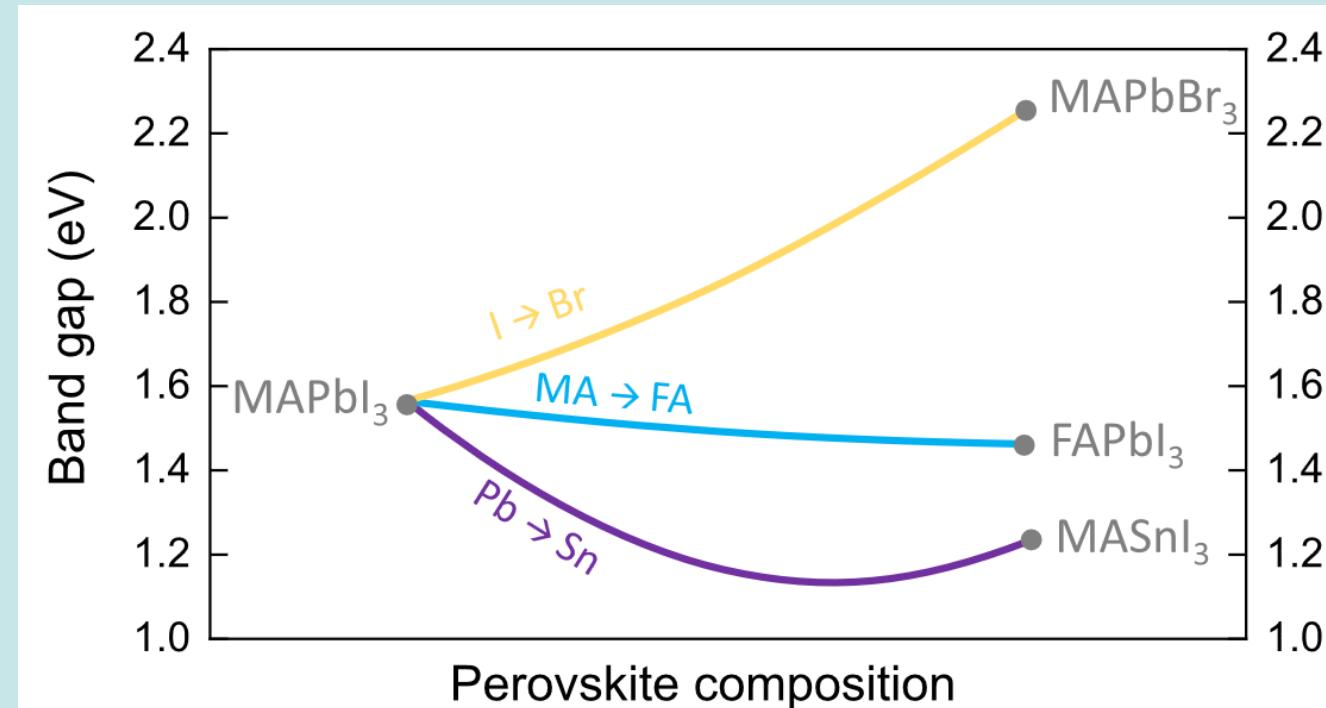
Photon recycling - a fraction of the photons that are generated in the active layer is reabsorbed before leaving the device, which then creates “recycled” photon emission.

- can increase the effective diffusion length
- requires alignment of absorption and emission profiles
- can be increased by improving outcoupling
- possible increase of 2% in PCE

Future outlook

What are the most interesting research questions in perovskites?

Unanswered questions



APL Mater. 9, 109202 (2021); doi: 10.1063/5.0047616

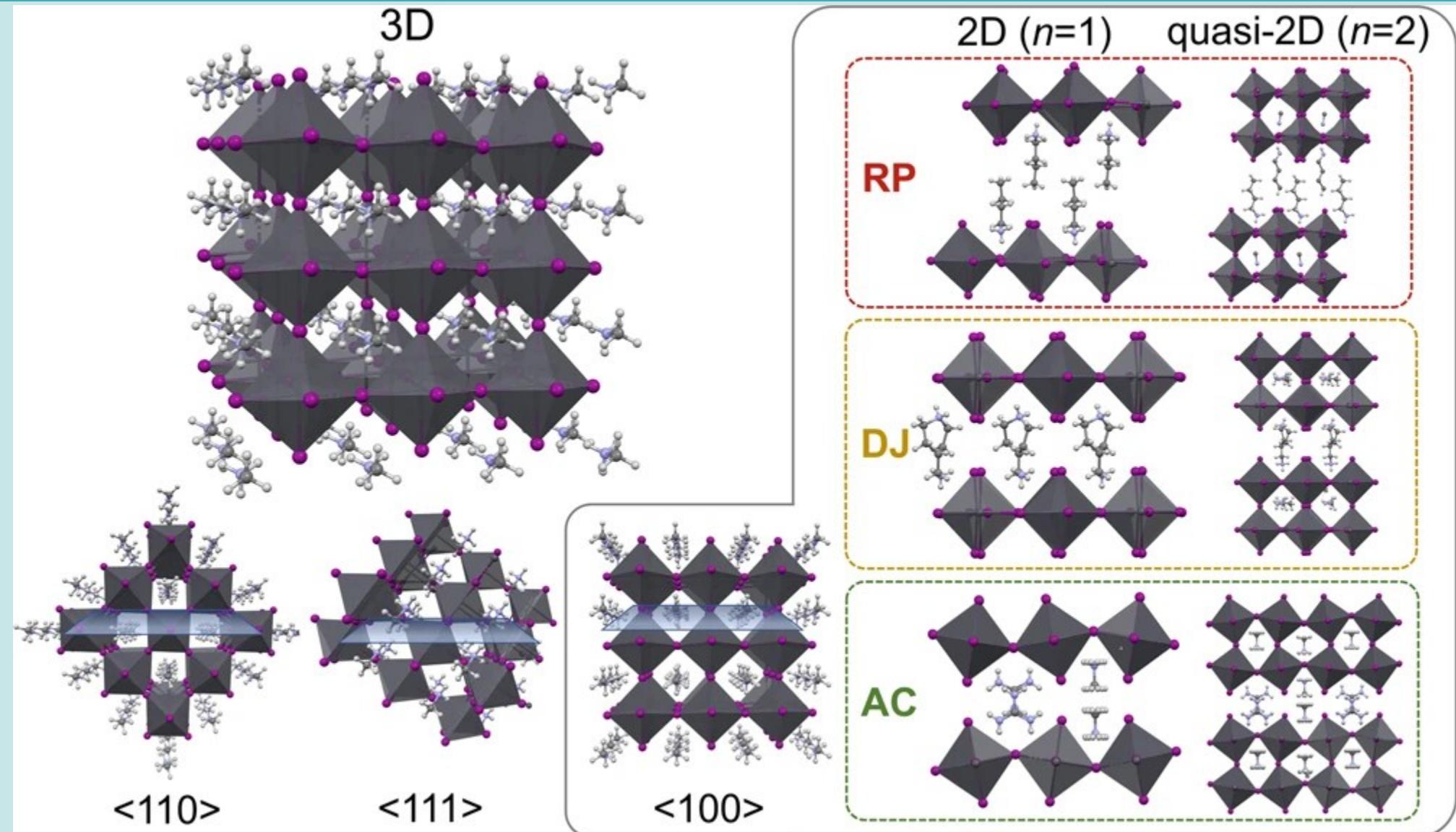
1. Bowing behaviour (non-linear change in bandgap with content ratio)
2. Distinguishing bandgap changes from defect state formation when tuning
3. Observing and controlling ion distribution in mixed perovskites

Future directions

1. Toxicity: making lead-free perovskites
 1. tin-based perovskites (e.g. $MASnI_3$) – challenge: oxidation of Sn^{2+} to Sn^{4+}
 2. bismuth and antimony-based materials
2. Understanding the behaviour of the soft crystal lattice under external electric field.
 1. DFT
 - predict electronic structure and band gaps
 - impact of defect states on electronic properties
 2. Molecular Dynamics
 - ion migration and dynamic disorder
3. Spintronics
 - Rashba effect (spin-orbit coupling)
4. Scalability – from lab scale to industrial scale
5. Long term stability

3D and 2D perovskites

Organic spacer cations can separate the n layers of corner-sharing lead halide octahedra ($n = 1$ for 2D, $n > 1$ for quasi-2D) along (100), (110), and (111) directions. For the most common case of (100) direction, RP, DJ, and ACI denote Ruddlesden-Popper, Dion-Jacobson, and alternating cations in interlayer space perovskites, respectively.



2D perovskites

Unique properties:

- quantum confinement (stronger exciton binding energy and localized states, higher PL efficiency)
- anisotropic transport
- tunable bandgap (by varying number of inorganic layers)
- moisture resistance (hydrophobic organic spacer layers)
- thermal stability

Challenges:

- lower power conversion efficiencies in PVs (wider bandgaps and more localized states)
- anisotropic charge transport (careful design required)

1D perovskites

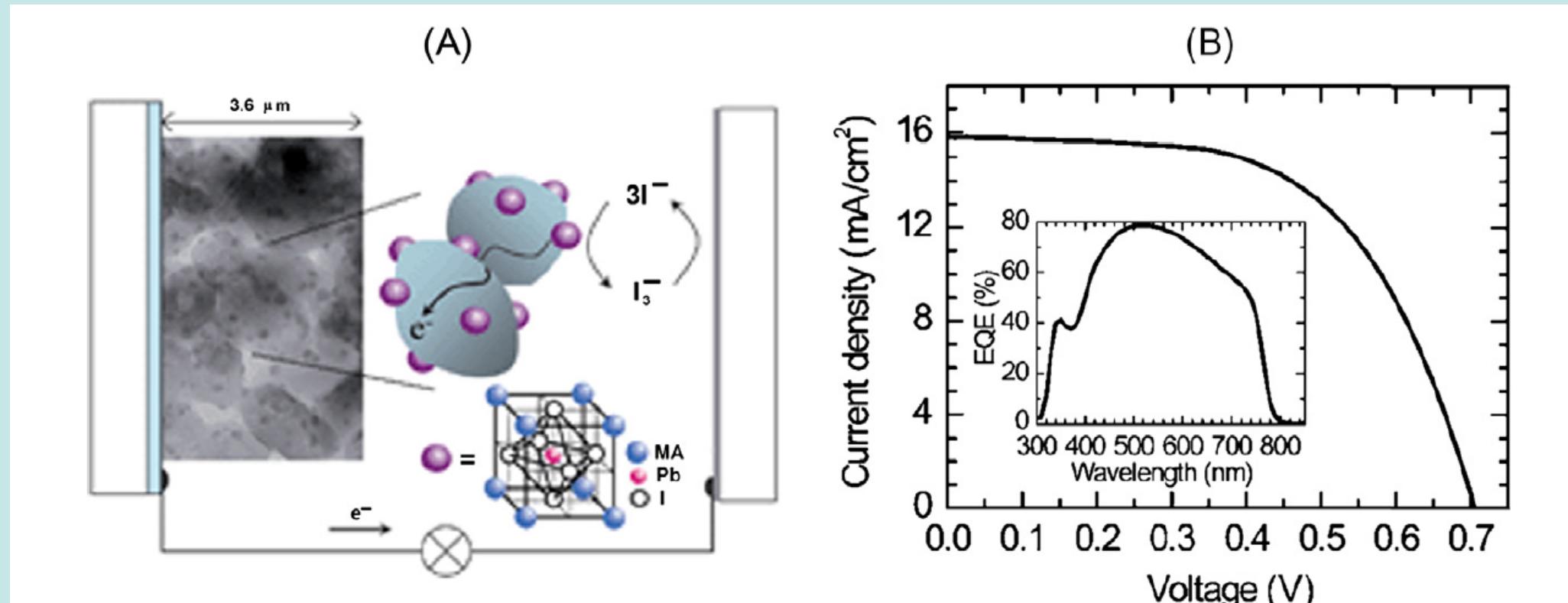


Figure 3.6 (A) Schematic of a dye-sensitized solar cells (DSSC) with the perovskite quantum dots (QDs). (B) Current density–voltage (J – V) and external quantum efficiency (EQE) curves of the device. *Reprinted with permission from J.-H. Im, C.-R. Lee, Nanoscale, 3 (2011) 4088-4093*

Summary

- perovskite is a crystal structure
- perovskites have tunable bandgaps and charge characteristics
- perovskite PVs are already surpassing Si-based device efficiencies
- tandem solar cells achieving 30% efficiencies outside of the lab

Next topic:

Nanomaterials