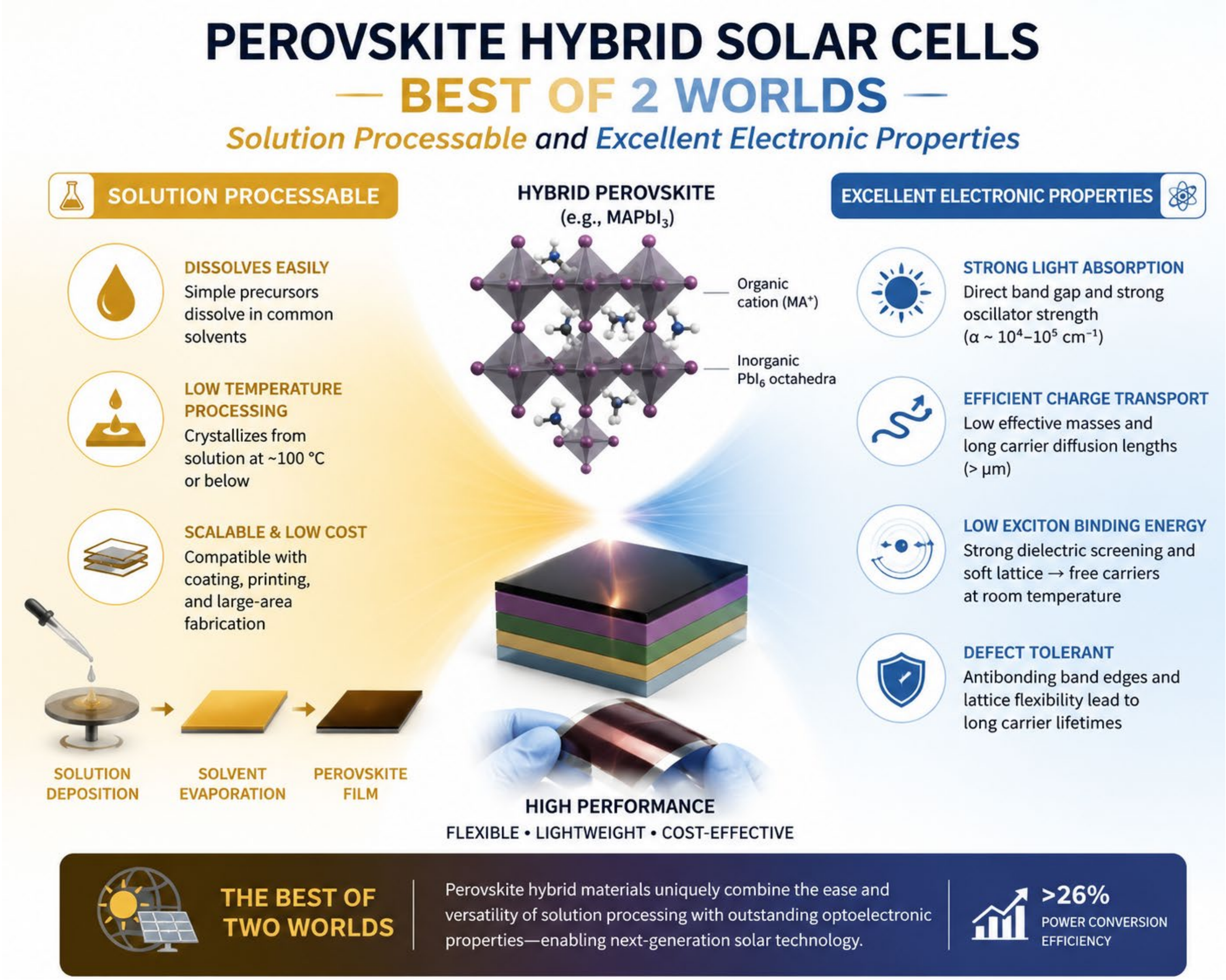
2.3A Hybrid solar cells - Perovskites

Learning goals

- ☐ What are Perovskite solar cells?
- ☐ Why are they so good?
- ☐ Processing
- ☐ Strategies for efficiency improvement
- ☐ Architectures? How are they made?
- ☐ Stability of Perovskite Solar cells
- ☐ Lead content is an issue
- ☐ Tandem solar cells
- ☐ Industrialization



PEROVSKITE HYBRID SOLAR CELLS

— BEST OF 2 WORLDS —

Solution Processable and Excellent Electronic Properties

SOLUTION PROCESSABLE

DISSOLVES EASILY
Simple precursors dissolve in common solvents

LOW TEMPERATURE PROCESSING
Crystallizes from solution at ~100 °C or below

SCALABLE & LOW COST
Compatible with coating, printing, and large-area fabrication

SOLUTION DEPOSITION → SOLVENT EVAPORATION → PEROVSKITE FILM

HYBRID PEROVSKITE
(e.g., $MAPbI_3$)

HIGH PERFORMANCE
FLEXIBLE • LIGHTWEIGHT • COST-EFFECTIVE

EXCELLENT ELECTRONIC PROPERTIES

STRONG LIGHT ABSORPTION
Direct band gap and strong oscillator strength ($\alpha \sim 10^4$–10^5 cm^{-1})

EFFICIENT CHARGE TRANSPORT
Low effective masses and long carrier diffusion lengths (> μm)

LOW EXCITON BINDING ENERGY
Strong dielectric screening and soft lattice → free carriers at room temperature

DEFECT TOLERANT
Antibonding band edges and lattice flexibility lead to long carrier lifetimes

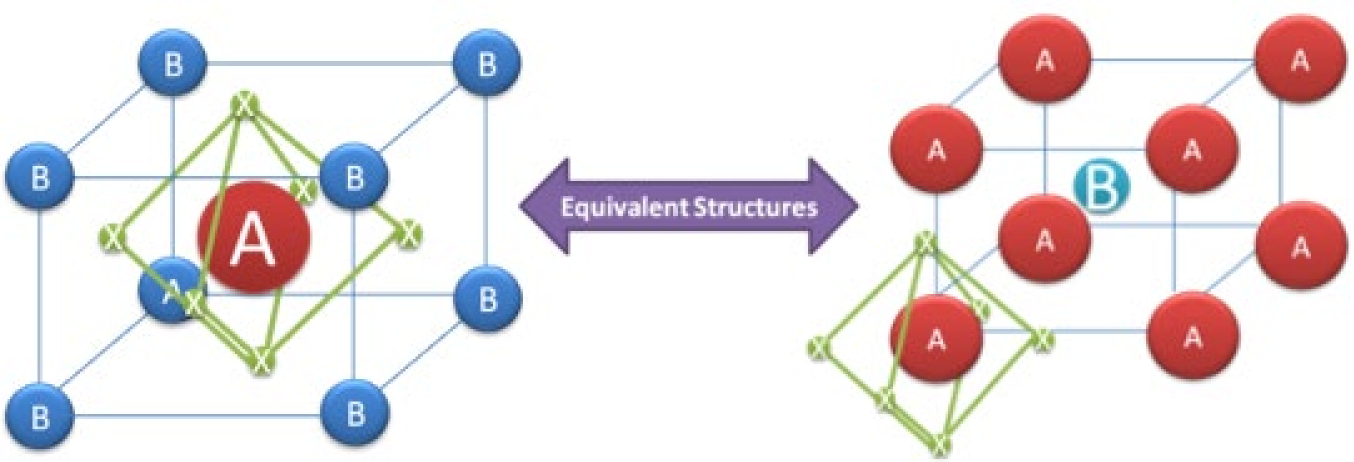
THE BEST OF TWO WORLDS

Perovskite hybrid materials uniquely combine the ease and versatility of solution processing with outstanding optoelectronic properties—enabling next-generation solar technology.

>26%
POWER CONVERSION EFFICIENCY

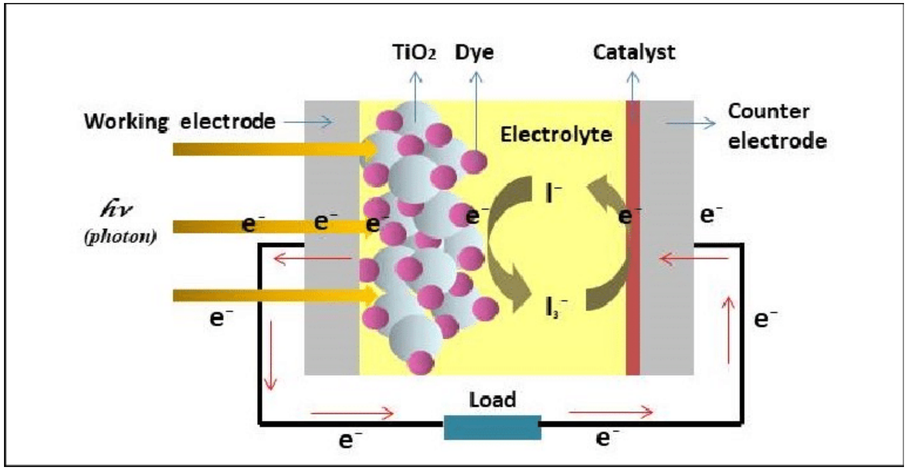
Perovskite

- ☐ The original ***perovskite*** (the mineral) is composed of calcium, titanium and oxygen in the form $CaTiO_3$.
- ☐ Today: any crystal structure of the form ABX_3



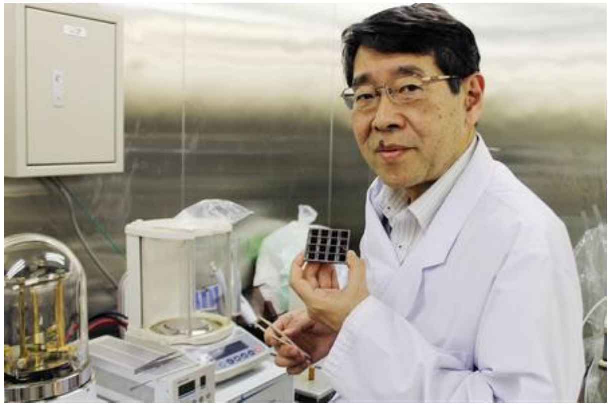
- ☐ Typically:
  - ☐ A = An organic monovalent cation – methylammonium ($CH_3NH_3^+$) or formamidinium ($NH_2CHNH_2^+$)
  - ☐ B = A inorganic divalent cation – usually lead(II) (Pb_2^+)
  - ☐ X_3= A slightly smaller halogen anion – usually chloride (Cl^-) or iodide (I^-)

Where it all started



Dye sensitized solar cells

- This principle works with dyes adsorbed onto TiO_2
- It also works with quantum dots as sensitizers, e.g. CdS or Perovskite



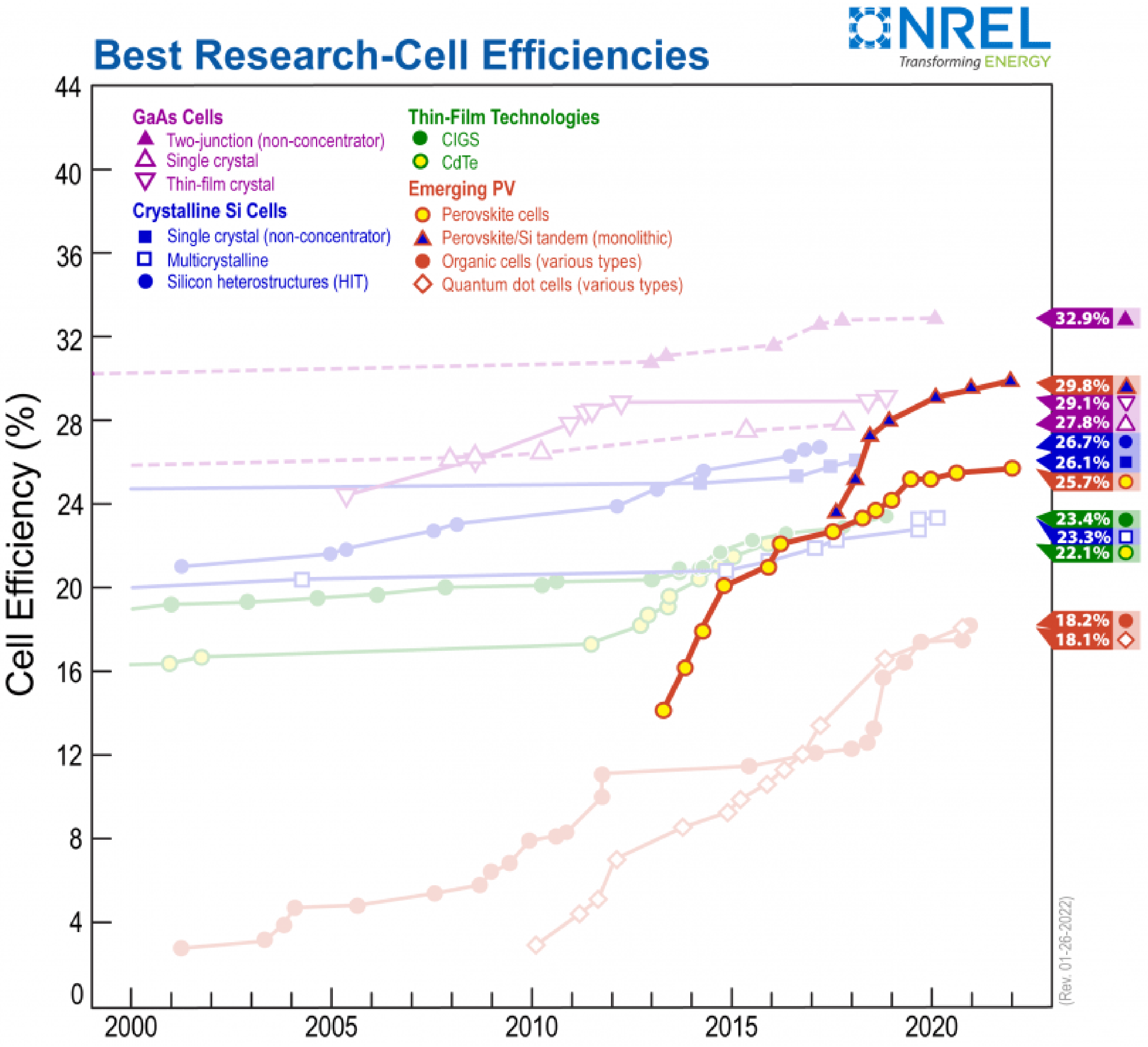
T. Miyasaka, J. Am. Chem. Soc., 2009, 131, 6050–6051

$MAPbI_3$ were first used as sensitizers in liquid electrolyte mesoporous cells

2009	Park (Korea)	4% to 6%
2012	M. Grätzel, S. I. Seok and H. Snaith	10-11% (solid-state perovskite)
2016	M. Grätzel group	21.1%

Elumalai et.al Energies (2016)

H. D. Pham et al., Energy Environ. Sci., 12, 1177 (2019)


Best Research-Cell Efficiencies
NREL
Transforming ENERGY
Cell Efficiency (%)
44
40
36
32
28
24
20
16
12
8
4
0
2000
2005
2010
2015
2020
GaAs Cells
▲ Two-junction (non-concentrator)
△ Single crystal
▽ Thin-film crystal
Crystalline Si Cells
■ Single crystal (non-concentrator)
□ Multicrystalline
● Silicon heterostructures (HIT)
Thin-Film Technologies
● CIGS
● CdTe
Emerging PV
● Perovskite cells
▲ Perovskite/Si tandem (monolithic)
● Organic cells (various types)
◇ Quantum dot cells (various types)
32.9% ▲
29.8% ▲
29.1% ▽
27.8% △
26.7% ●
26.1% ■
25.7% ●
23.4% ●
23.3% □
22.1% ●
18.2% ●
18.1% ◇
(Rev. 01-26-2022)

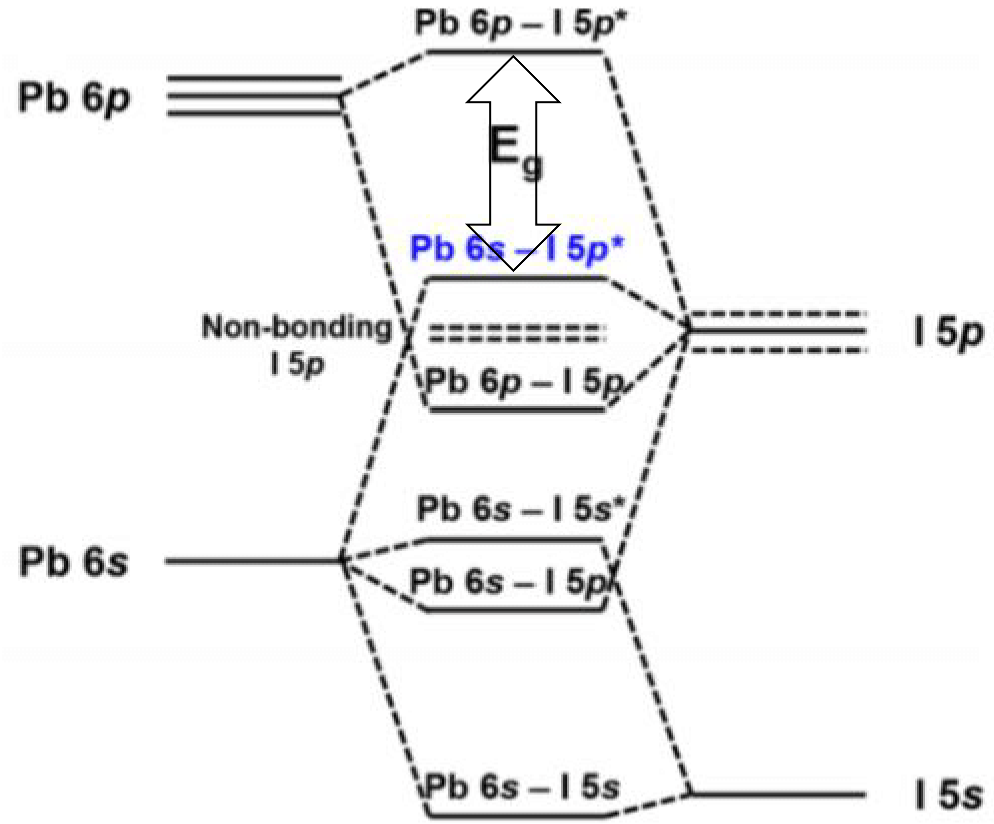
Properties

- ☐ High **absorption coefficient** (direct bandgap semiconductor)
- ☐ Low **exciton binding energy** (thermal generation of charge carriers)
- ☐ Long **carrier diffusion length**
- ☐ **Tunable bandgap** (**tandem cells**)

- ☐ **Good crystallinity**, large grains (few defects, reduced grain boundary scattering)
- ☐ High **defect tolerance**

- ☐ For many of these propoerties, the **hybrid character** can be made repsonsible

But looking at the Orbitals….



Bandgap:

Originates mainly from the inorganic corner-sharing PbX_6 octahedral network

Molecular orbitals of the organics lie energetically far away from the gap.

VB: Antibonding hybridization of the B-site metal's s orbitals and the X-site halide's p orbitals (Pb 6s and I 5p).

CB: Antibonding Pb 6p hybridized with I 5p orbitals.

How does that lead to a

- high **absorption coefficient?**
  - **Direct bandgap** semiconductor, no phonon assistance is required, momentum conservation is naturally satisfied.
  - **Antibonding states** are typically:more extended spatially, less localized around individual atoms, more delocalized across the lattice => their wavefunctions overlap strongly
  - **Transition dipole moment**: the Pb–I bonds are highly polarizable

How does that lead to a

- ☐ Low **exciton binding energies?**
  - ☐ **Enormous dielectric screening:** screening is unusually strong because the lattice is: ionic, soft, highly polarizable. Also strong contribution of the organic molecules.
  - ☐ **Small effective mass:** Pb–I orbital hybridization creates dispersive bands,electrons and holes are relatively light.

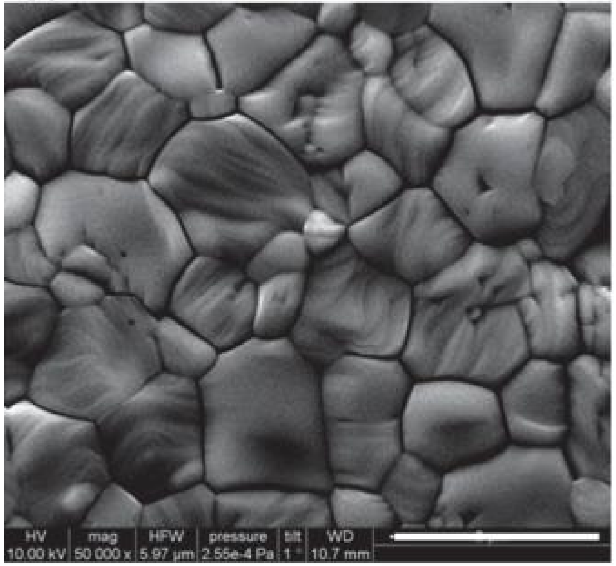
    Typical values: $m^* \sim 0.1 – 0.3 m_e$

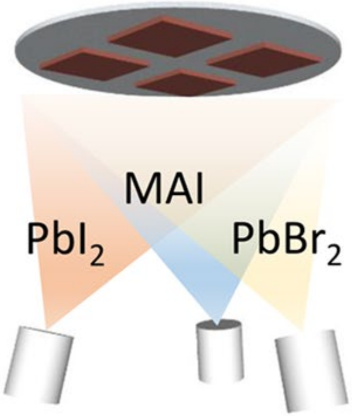
    Also reason for **good charge carrier mobility**

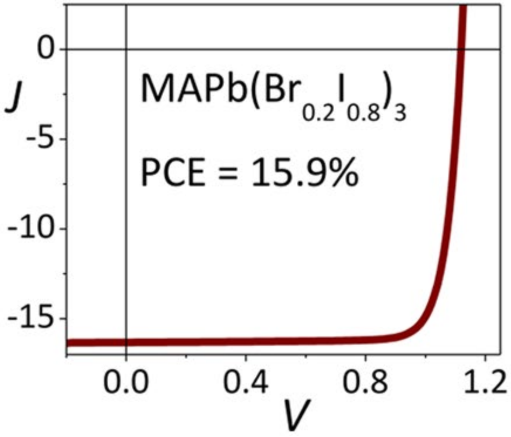
Good crystallinity and large grains

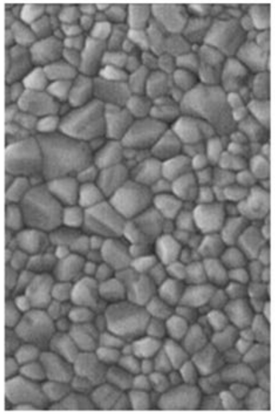
Solution-processed

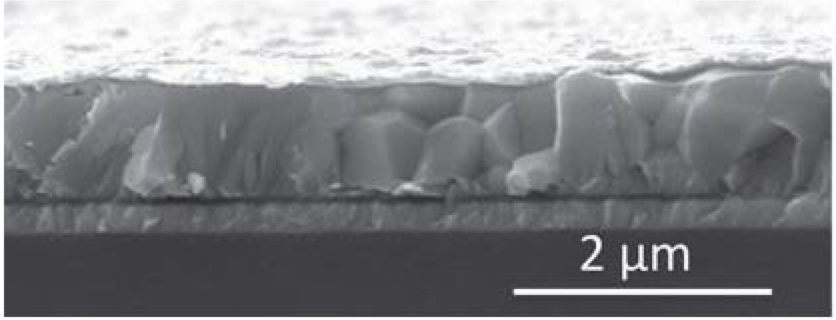
Vaccum-processed











- Good crystallinity gives rise to low defects concentration within perovskite
- Large grain size significantly reduces grain boundary scattering of carriers

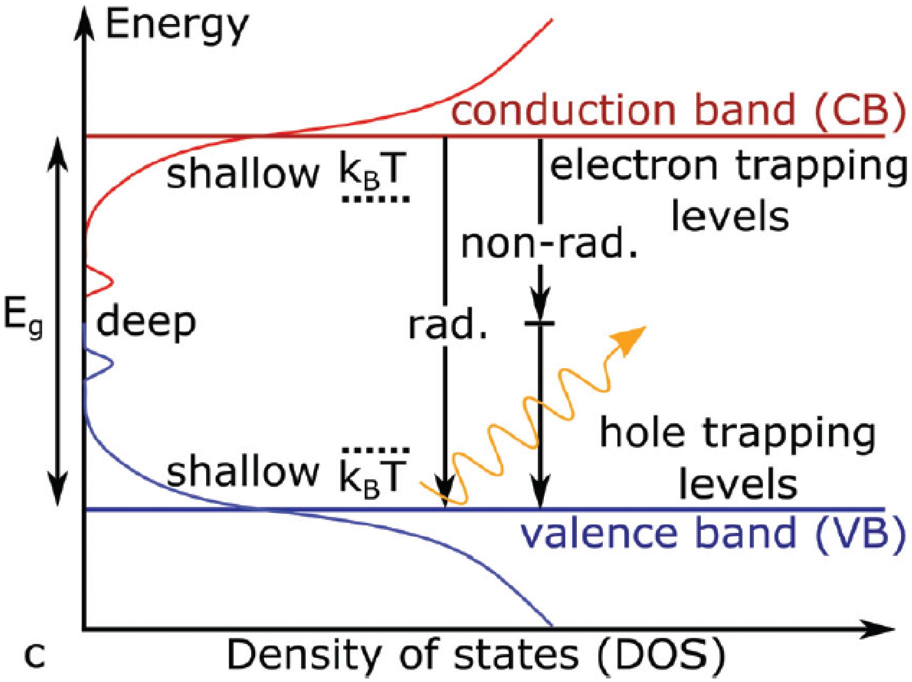
Snaith et al, *Nature* **501**, 395 (2013)
J. Huang et al., Adv. Mater. 2014
Longo and Bolink et.al. ACS Energy Letters (2018)

High defect tolerance in perovskites

- **Primary negative impact**: Structural Non-radiative **Recombination Centers**:
    - Defects act as **trap states for photogenerated electron-hole pairs** (excitons). Instead of the electrons and holes being collected at the electrodes to generate electricity, they recombine at these defect sites without producing light (non-radiative recombination). This leads to: lower V_{oc}, $J_{sc,}$ FF

- Due to the antibonding nature of VB and CB, the **energy levels introduced by defects** (which often involve undercoordinated atoms or broken bonds) are more likely to be energetically aligned within or **very close to the existing valence or conduction bands**.

High defect tolerance in perovskites



Jin et al., *Mater. Horiz.*, 2020, 7, 397-410;
DOI: 10.1039/C9MH00500E

- When **captured on shallow traps** a charge can be thermally excited back to the transport band
- Deep traps hinder detrapping and can facilitate non-radiative recombination pathways
- Charge trapping is most influential while the system is illuminated by relatively low-intensity light, as higher intensities increase the concentration of excited carriers which fill the traps, reducing their influence on the carrier transport.

How about processing?

Hybrid Perovskite can be **grown from solution**

One of the major drivers of the research

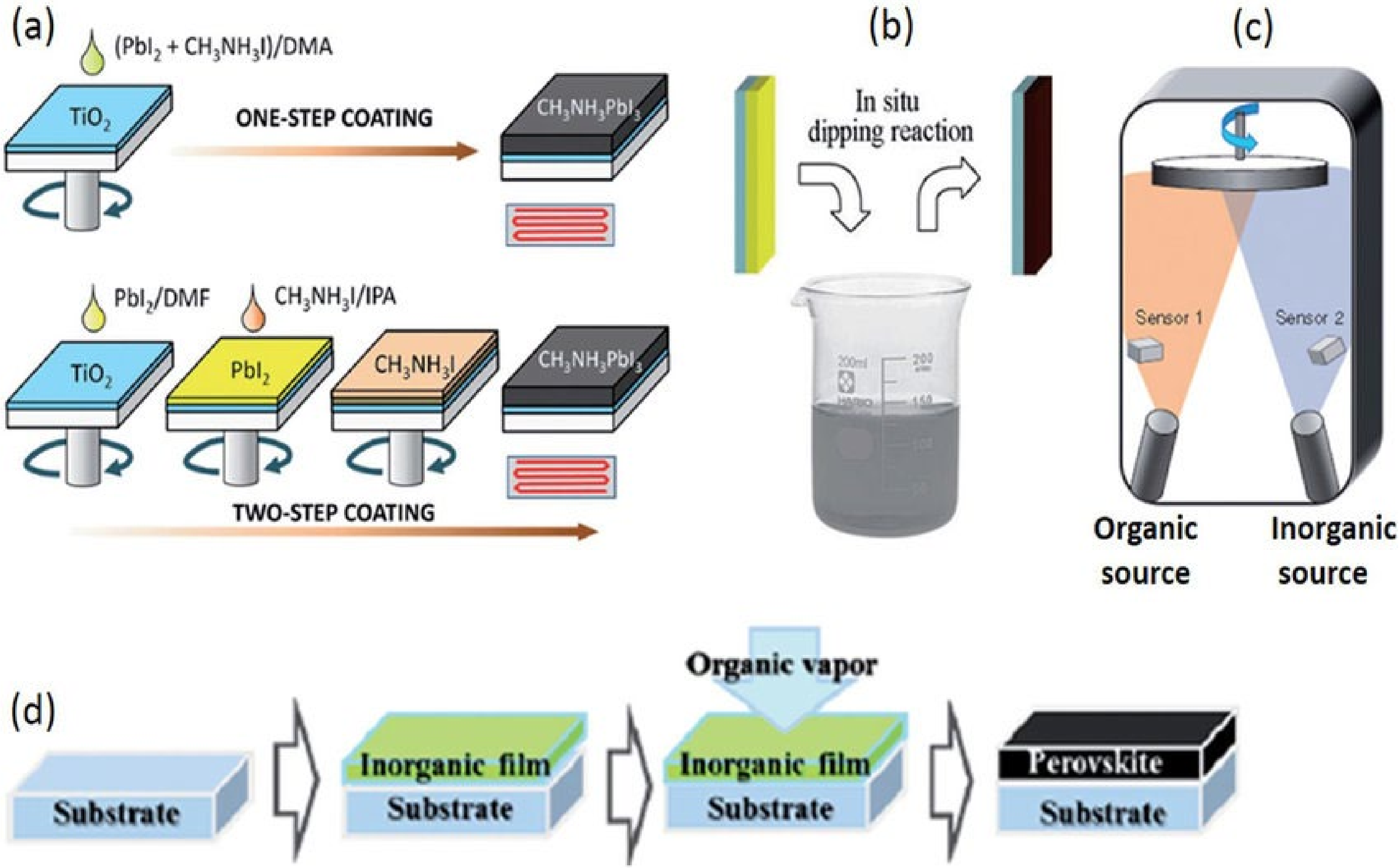
The deeper underlying reason: the material’s hybrid character

- ☐ Relatively **ionic bonding:** interact substantially through Coulomb interactions. The bonding is weaker, less directional, more flexible.
- ☐ **Low formation energies for crystallization**
- ☐ Typical precursors like PbI_2, MAI, FAI**, dissolve readily in polar solvents** such as DMF, DMSO, GBL.
- ☐ When solvent evaporates: ions reorganize spontaneously, the perovskite lattice **self-assembles** into the thermodynamically favorable perovskite phase.

Growth methods of perovskite films

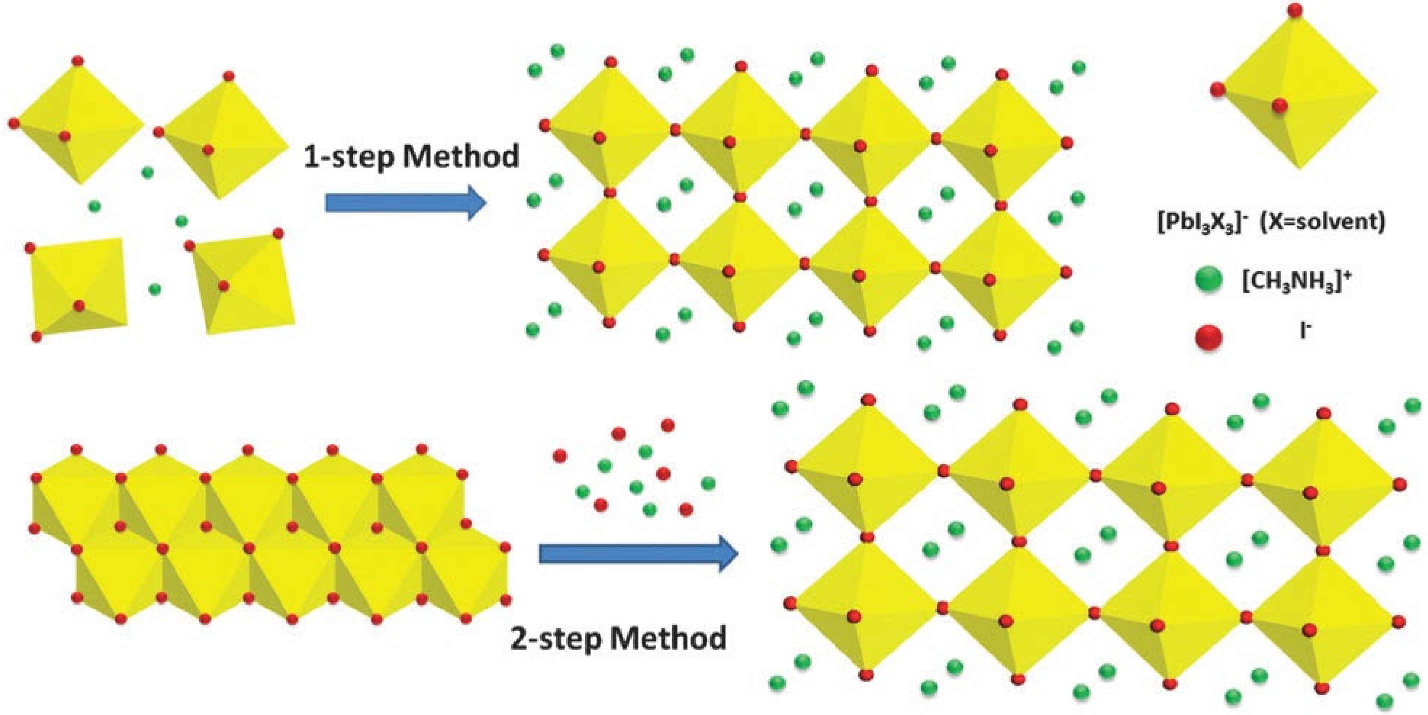
- Allows for composition / growth engineering
- The perovskite film in a working solar cell is not a single crystal. It is a **polycrystalline thin film** grown from solution, and the quality of that crystallization — grain size, orientation, boundary passivation — has an enormous influence on device performance.
- Larger grains mean fewer boundaries, fewer defects, longer carrier diffusion lengths. Modern deposition protocols targeting large-grain, preferentially oriented (100) crystal films have become the standard for high-efficiency cells.

Growth methods of perovskite films



Journal of Photochemistry and Photobiology C: Photochemistry Reviews 35 (2018) 1–24

One-step and two-step solution growth method of perovskite films

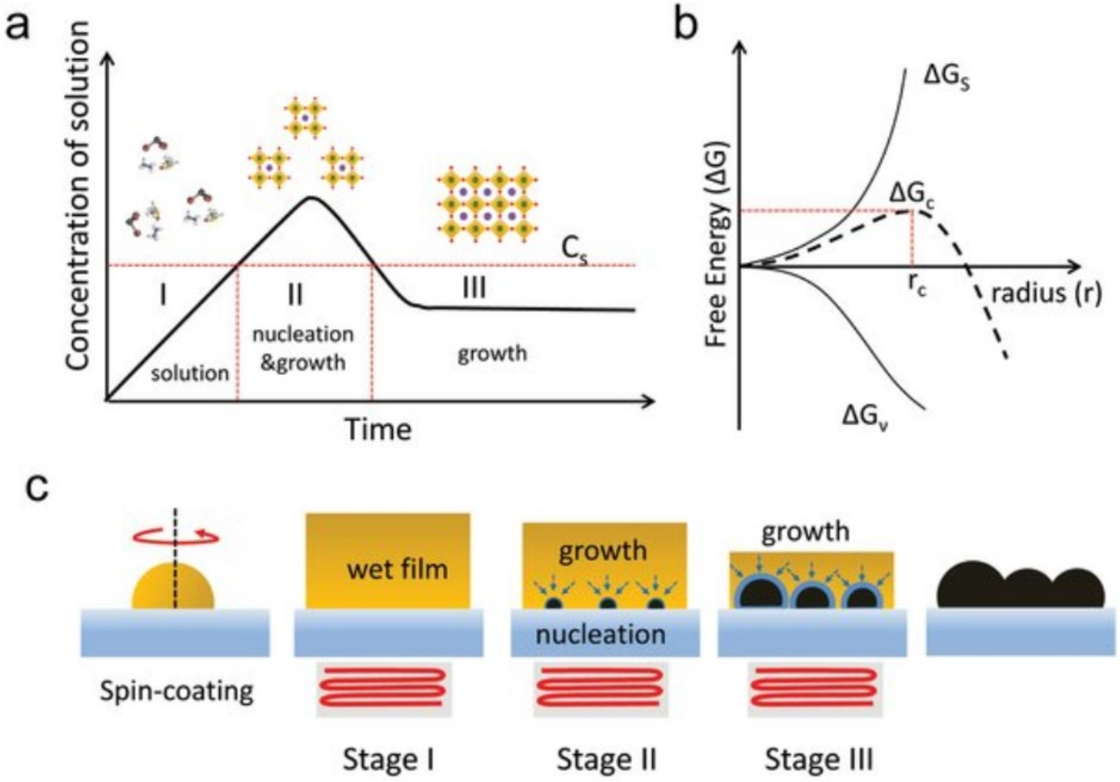


- ☐ Today almost exclusively the 2-step method is used
- ☐ Applied for planar films, but also in mesoscopic structures

Y. Zhao, *Chem. Soc. Rev.*, 2016, 45, 655--689

Control of crystal growth of perovskite films

- Three different stages for crystallization of perovskite films according to the La Mer mechanism.



- Crystal growth of perovskite films can be tuned by control of either nucleation or crystal growth

Advanced Functional Materials 29(47),1807047, 2018
DOI: 10.1002/adfm.201807047

Typical recipe for a two-step solution growth method of perovskite films

1) Lead Iodide (PbI2) Precursor Layer Deposition:
A 1.3 M solution of PbI_2 in N,N′-dimethylformamide (DMF) is spin coated onto the substrate. Both the PbI_2 solution and the substrate are held at 60 °C.
The spincoating speed is set to 3000 rpm for 60 seconds.

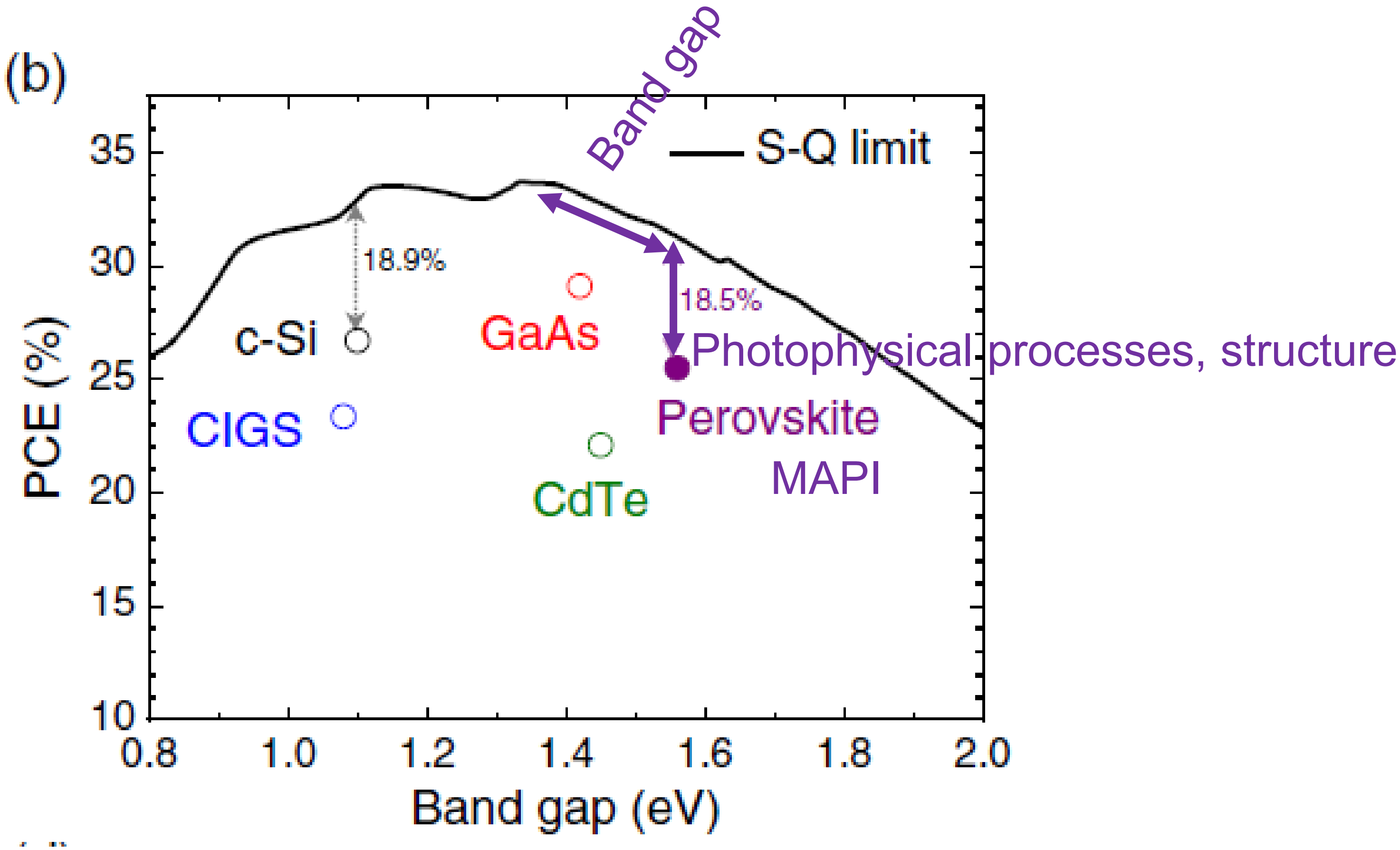
2) Methylammonium Iodide (MAI) Conversion
A 1 M MAI solution in 2-propanol (Isopropanol, IPA) is spin coated onto the PbI_2 film.

3) Antisolvent treatment:
5 seconds after initiating the MAI solution spin; 50 µl of Chlorobenzene (CB) are applied to the substrate by spincoating

4) Annealing
The perovskite film is then annealed for 20 minutes at 100 °C.

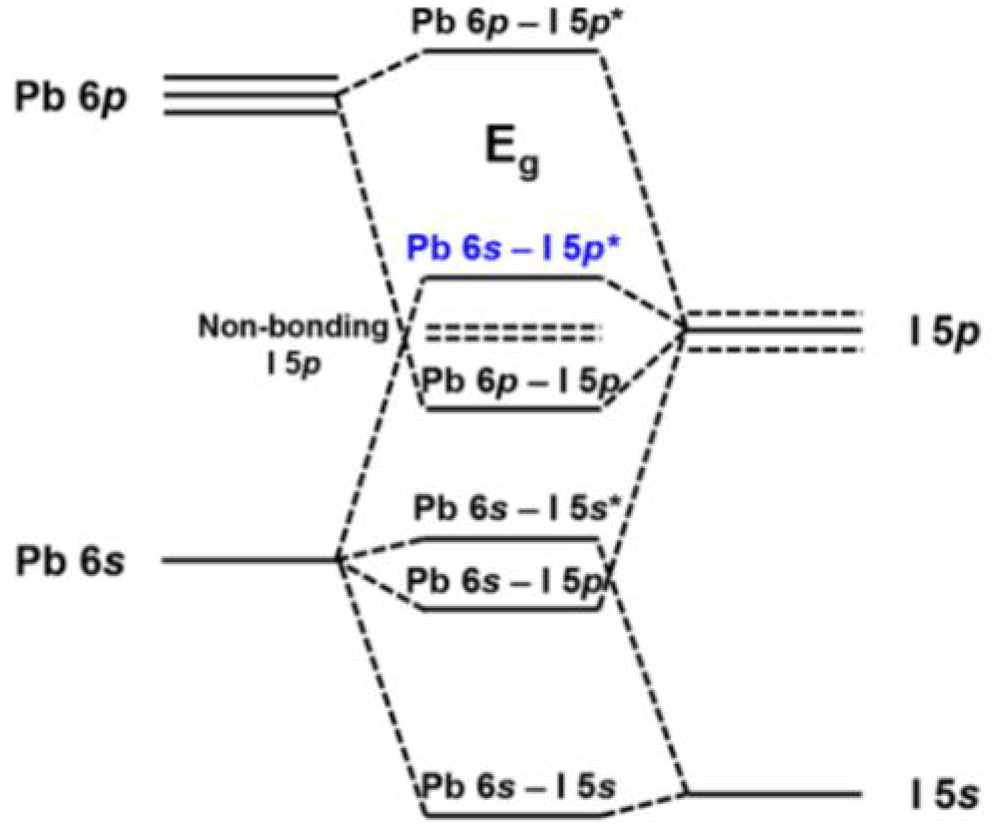
Tunable bandgap - efficiency improvement

- How much better can we get?



Sol. RRL 2022, 6, 2100455

Bandgap engineering



- ☐ How?

Subject of one exercise

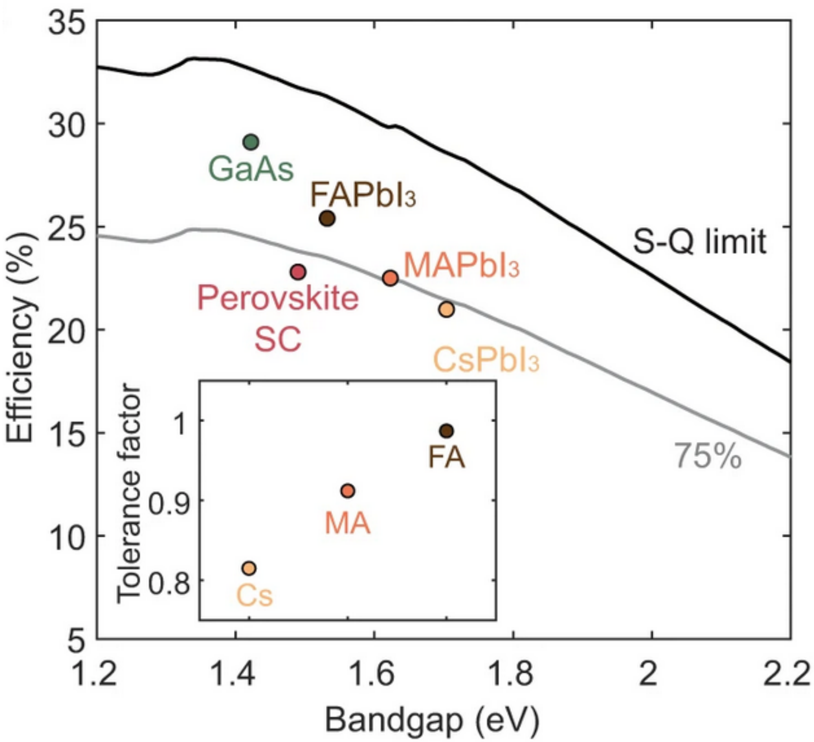
VB: Antibonding hybridization of the B-site metal's s orbitals and the X-site halide's p orbitals (Pb 6s and I 5p).

CB: Antibonding Pb 6p hybridized with I 5p orbitals.

Ideal bandgap

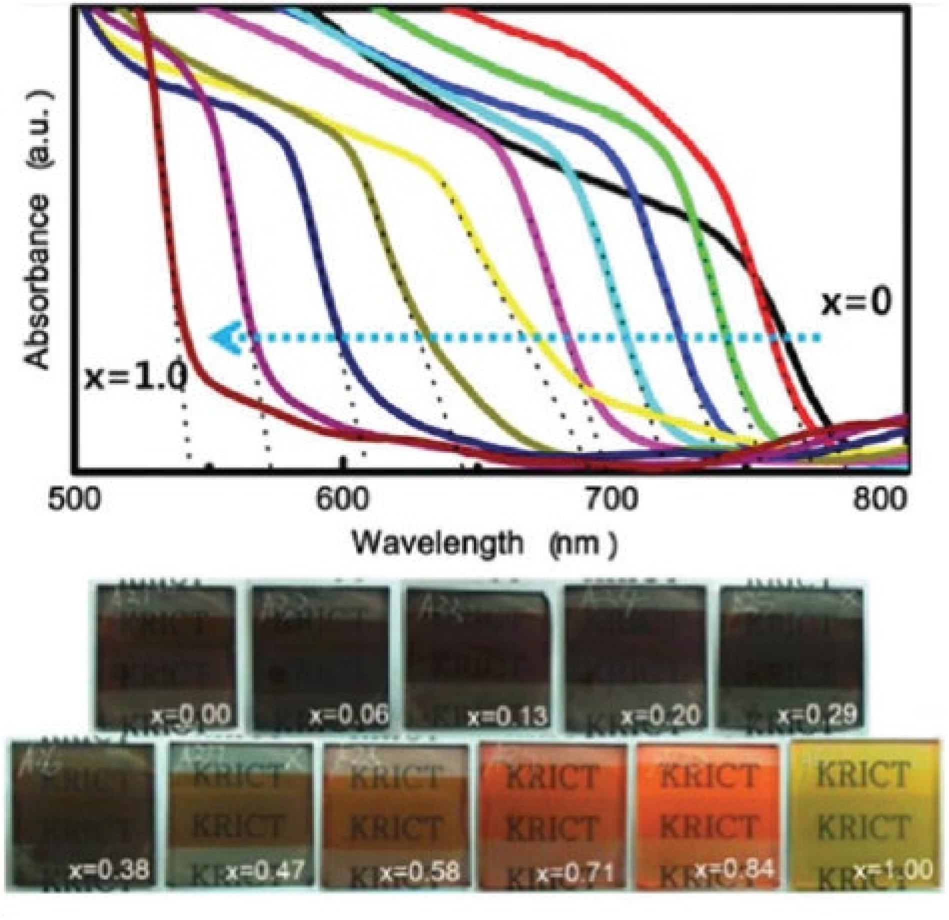
- ☐ Compositional engineering to narrow the bandgap of perovskite towards **ideal bandgap of 1.34 eV** raises the upper efficiency limit of perovskite solar cells

- ☐ Compositional engineering route has reached the limit of the Goldschmidt tolerance factor **(stable Perovskite phase)**

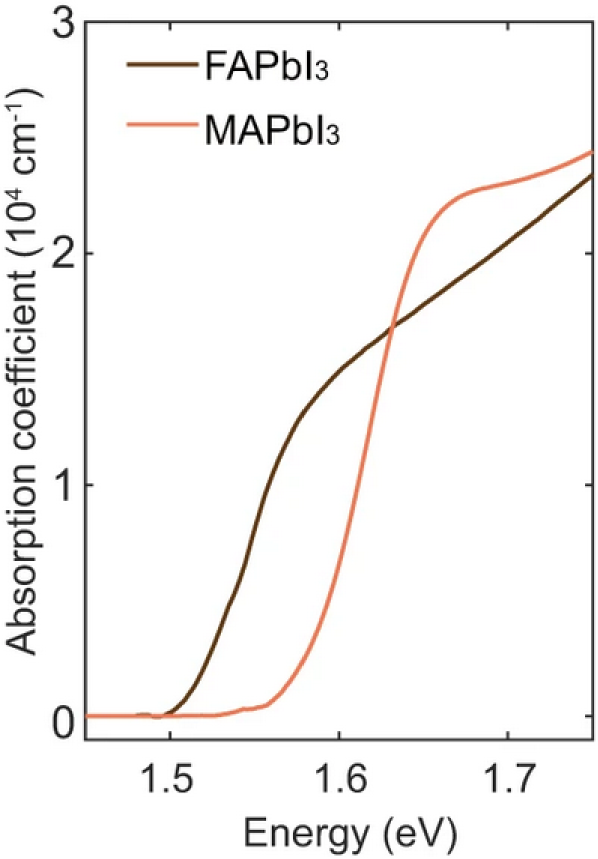


Feng, J., Wang, X., Li, J. et al. Resonant perovskite solar cells with extended band edge. Nat Commun 14, 5392 (2023). DOI:10.1038/s41467-023-41149-1

Bandgap engineering of $MAPb(I_{1-x}Br_x)_3$ perovskites

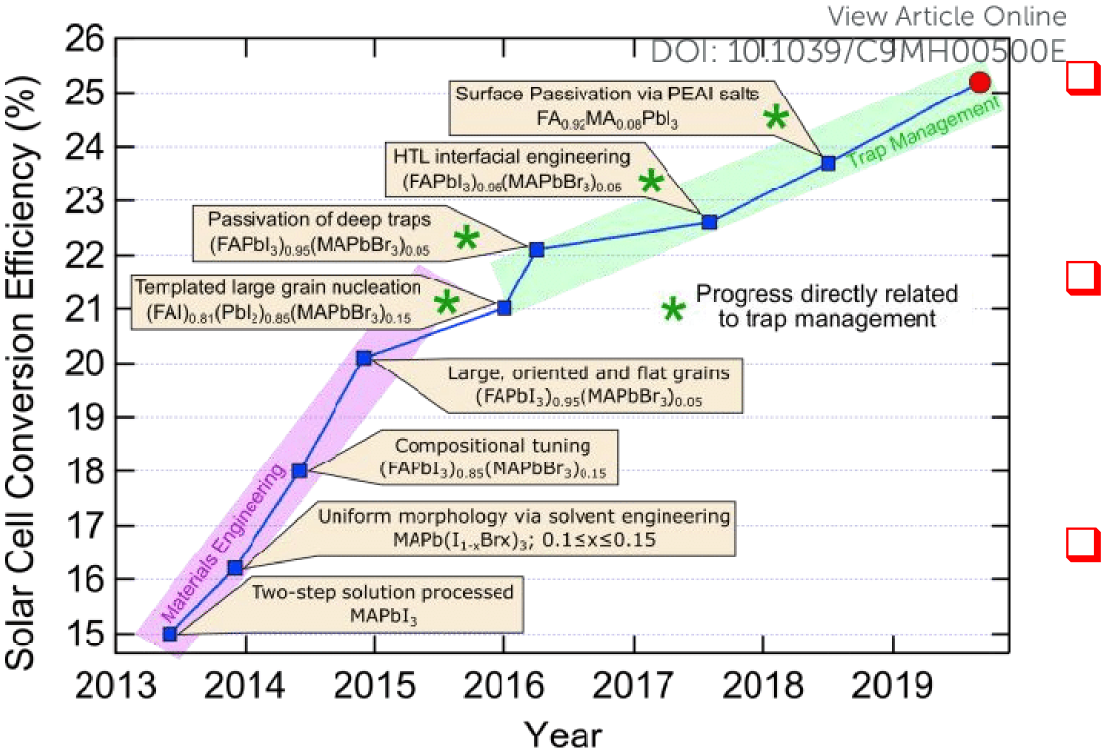


J. H. Noh, S. H. Im, J. H. Heo, T. N. Mandal and S. I. Seok, Nano Lett., 2013, 13, 1764–1769.



Feng, J., Wang, X., Li, J. et al. Resonant perovskite solar cells with extended band edge. Nat Commun 14, 5392 (2023). DOI:10.1038/s41467-023-41149-1

Efficiency improvement

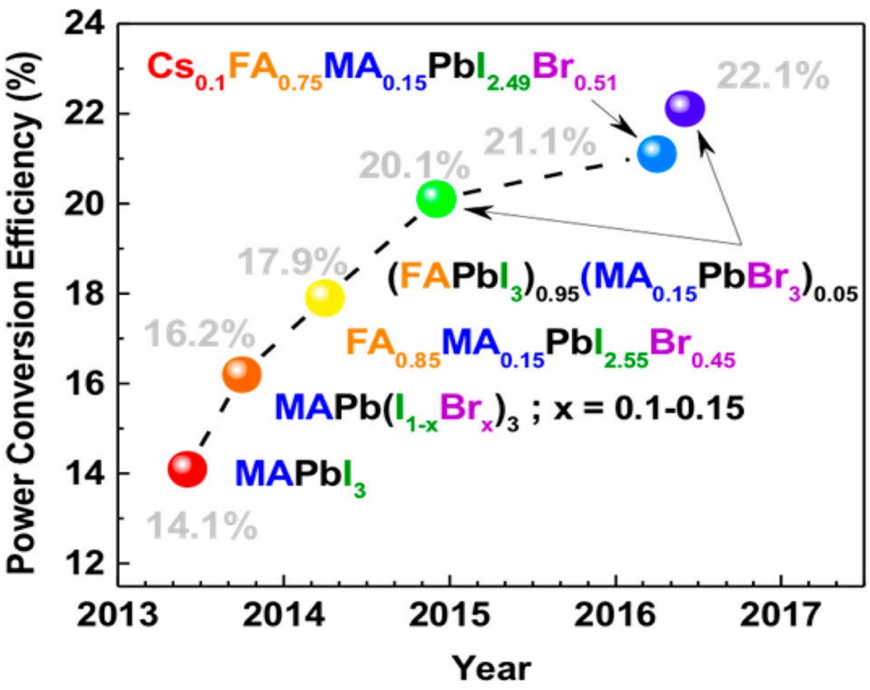


General strategies:

- Control of crystallization (reduce number of defects)
- Compositional engineering (improve optical and electrical properties)
- Additives for defect passivation

H. Jin, E. Debroye, M. Keshavarz, I. Scheblykin, M. B. Roeffaers, J. Hofkens and J. Steele, Mater. Horiz., 2019, DOI:10.1039/C9MH00500E.

Composition engineering



- Electronic characteristics are mainly determined by the B cations and X anions (they determine conduction and valence band)

- A, B and/or X ion substitution and mixing also affect carrier transport, crystal structure and material stability

- The role of the additional cations as well as the mixed halides is yet to be fully understood

- Similar size cation/anion, acts as defect passivator.

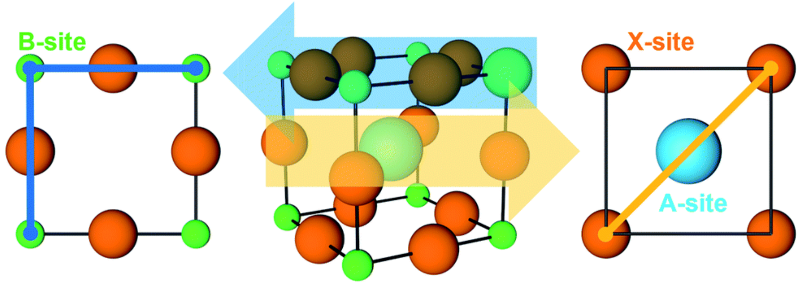
- A cations indirectly affect electronic characteristics via dielectric constant and lattice parameters

- Hypothesis: complementary size cations may help stabilizing the perovskite phase by tuning tolerance factor

DOI:10.1021/acsami.7b06001

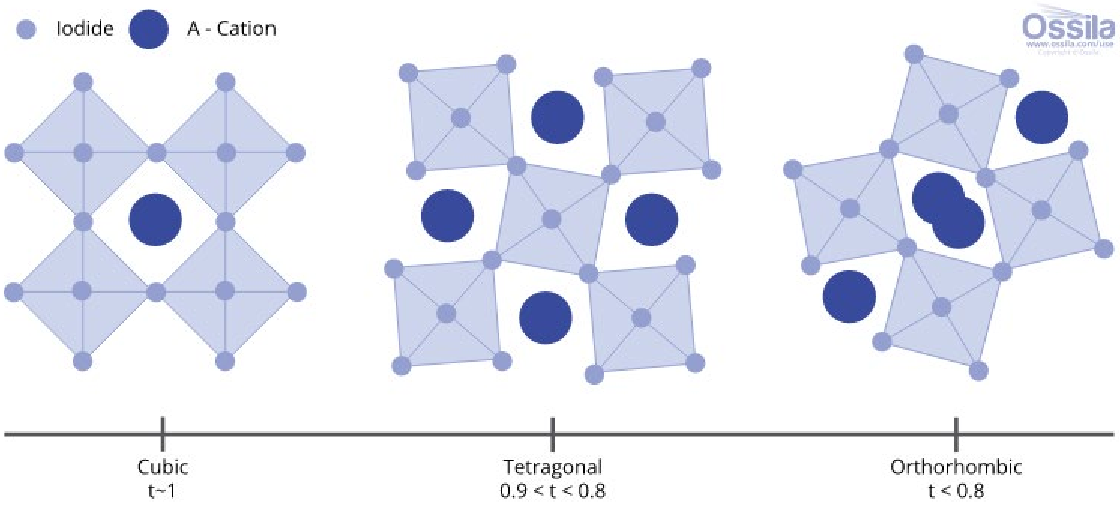
Stability of Perovskite crystal structure

- Empirical finding: primarily defined by the **Goldschmidt tolerance factor (TF)** and the octahedral factor $\mu = r_b/r_x$. For $0.87 < TF < 1.11$ and $0.44 < \mu < 0.90$ the perovskite structure forms.



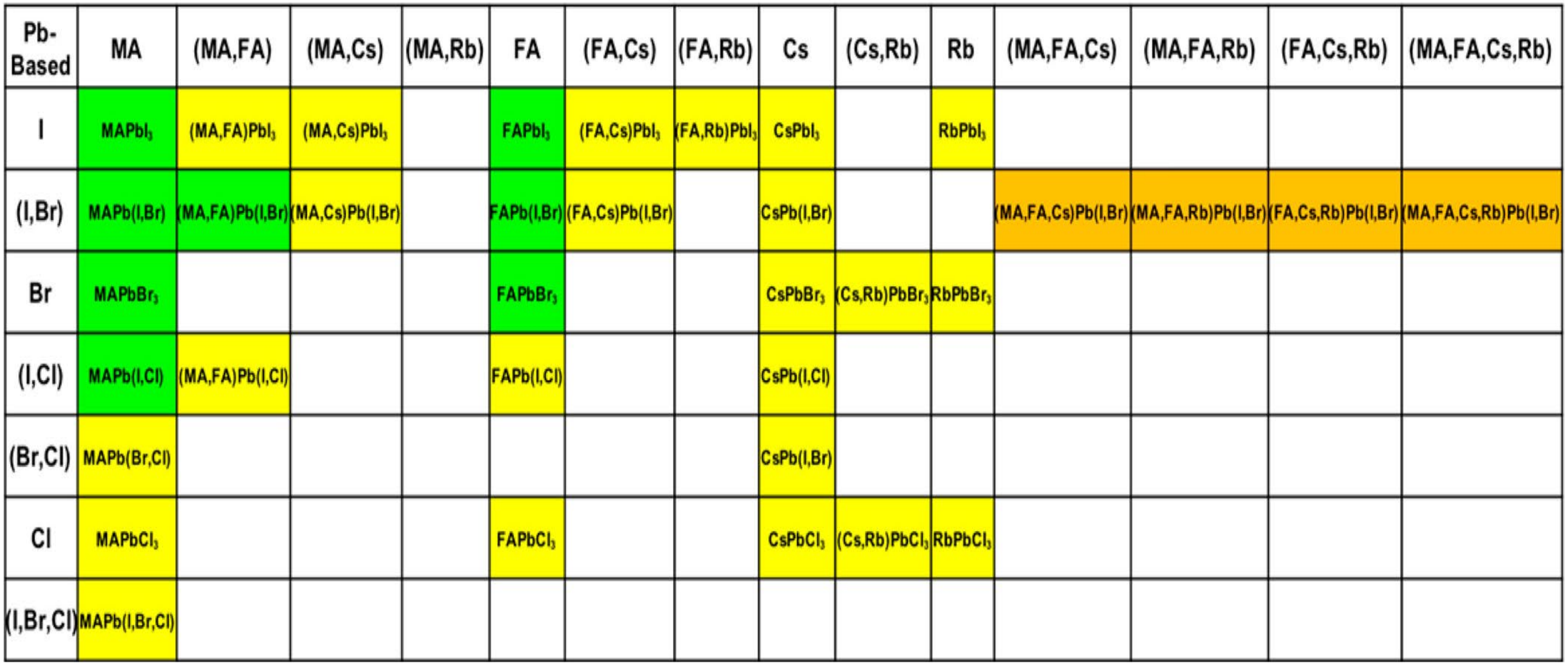
$$a = b = 2r_B + 2r_X \rightarrow TF = \frac{c}{\sqrt{2}a} \leftarrow c = 2r_A + 2r_X$$

Subject of one exercise



DOI: 10.1039/C8TA05794J

Composition engineering

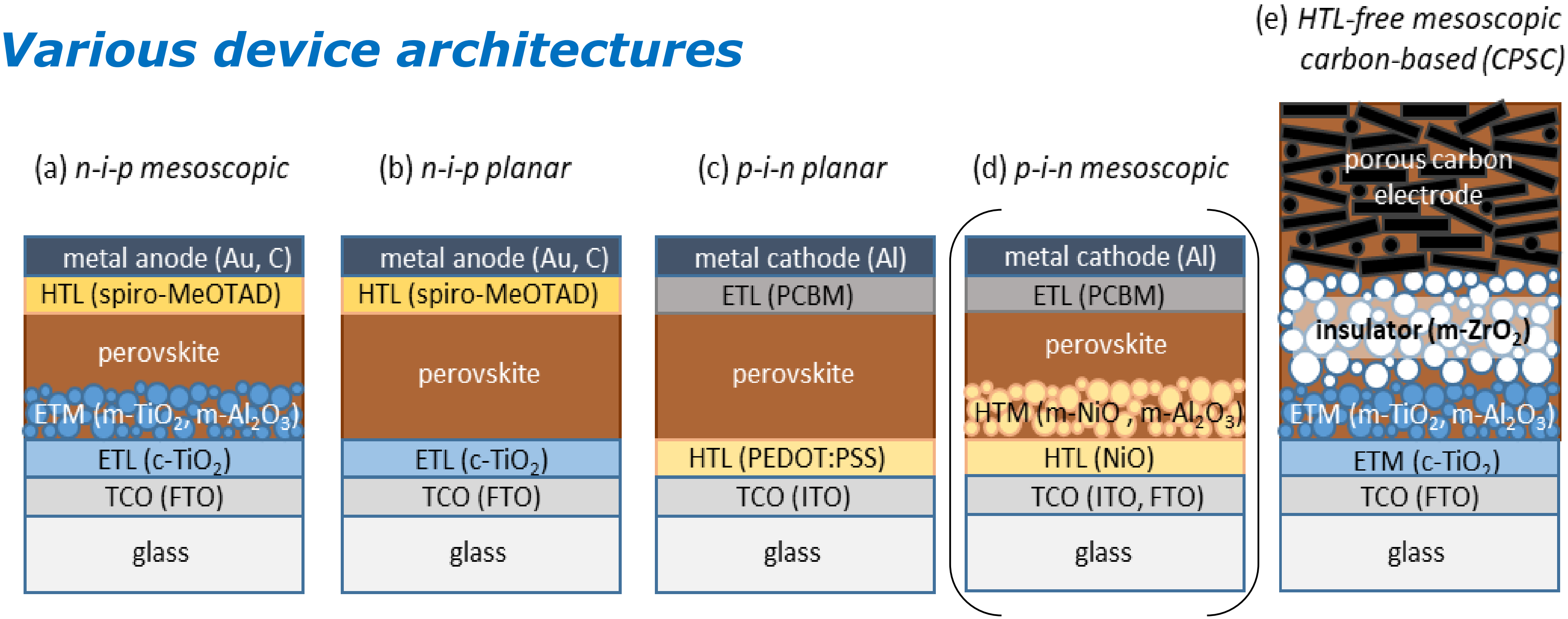


Pb-Based	MA	(MA,FA)	(MA,Cs)	(MA,Rb)	FA	(FA,Cs)	(FA,Rb)	Cs	(Cs,Rb)	Rb	(MA,FA,Cs)	(MA,FA,Rb)	(FA,Cs,Rb)	(MA,FA,Cs,Rb)
I	$MAPbI_3$	$(MA,FA)PbI_3$	$(MA,Cs)PbI_3$		$FAPbI_3$	$(FA,Cs)PbI_3$	$(FA,Rb)PbI_3$	$CsPbI_3$		$RbPbI_3$				
(I,Br)	MAPb(I,Br)	(MA,FA)Pb(I,Br)	(MA,Cs)Pb(I,Br)		FAPb(I,Br)	(FA,Cs)Pb(I,Br)		CsPb(I,Br)			(MA,FA,Cs)Pb(I,Br)	(MA,FA,Rb)Pb(I,Br)	(FA,Cs,Rb)Pb(I,Br)	(MA,FA,Cs,Rb)Pb(I,Br)
Br	$MAPbBr_3$				$FAPbBr_3$			$CsPbBr_3$	$(Cs,Rb)PbBr_3$	$RbPbBr_3$				
(I,Cl)	MAPb(I,Cl)	(MA,FA)Pb(I,Cl)			FAPb(I,Cl)			CsPb(I,Cl)						
(Br,Cl)	MAPb(Br,Cl)							CsPb(I,Br)						
Cl	$MAPbCl_3$				$FAPbCl_3$			$CsPbCl_3$	$(Cs,Rb)PbCl_3$	$RbPbCl_3$				
(I,Br,Cl)	MAPb(I,Br,Cl)													

- Typical permutations for Pb-based perovskites are A=(MA, FA, Cs, Rb) and X=(I, Br, Cl) and mixtures thereof.
- The table shows possible combinations (green: widely studied, good performance; yellow:existing literature reports; orange: high potential, current research focus; white: not yet explored)

DOI: (10.1021/acsami.7b06001)

Various device architectures



Planar was mainly driven for easier processing

Planar versus **mesoscopic**: reveals a **fundamental trade-off**:

Planar designs offer **superior bulk transport** and reduced internal recombination due to their larger grain sizes.

Mesoscopic designs, conversely, provide **enhanced interfacial charge extraction** due to their extensive contact area.

Also look at: stability, reproducibility and hysteresis

Architecture Type	Highest Reported PCE	Key Hysteresis Characteristics	Key Stability Characteristics
n-i-p Mesoscopic	26.7% (2025, General Perovskite)	Can exhibit hysteresis	Improving, but large-area stability challenging
n-i-p Planar	26.0% (2023, General Perovskite)	**Major drawback: J-V hysteresis**	Reproducibility challenges
p-i-n Planar	**26.08% (Recent, small area)**	**Negligible hysteresis**	**Excellent operational stability (>92% after 2000h)**
p-i-n Mesoscopic	19.27% (2020)		Good long-term air stability (half a year)

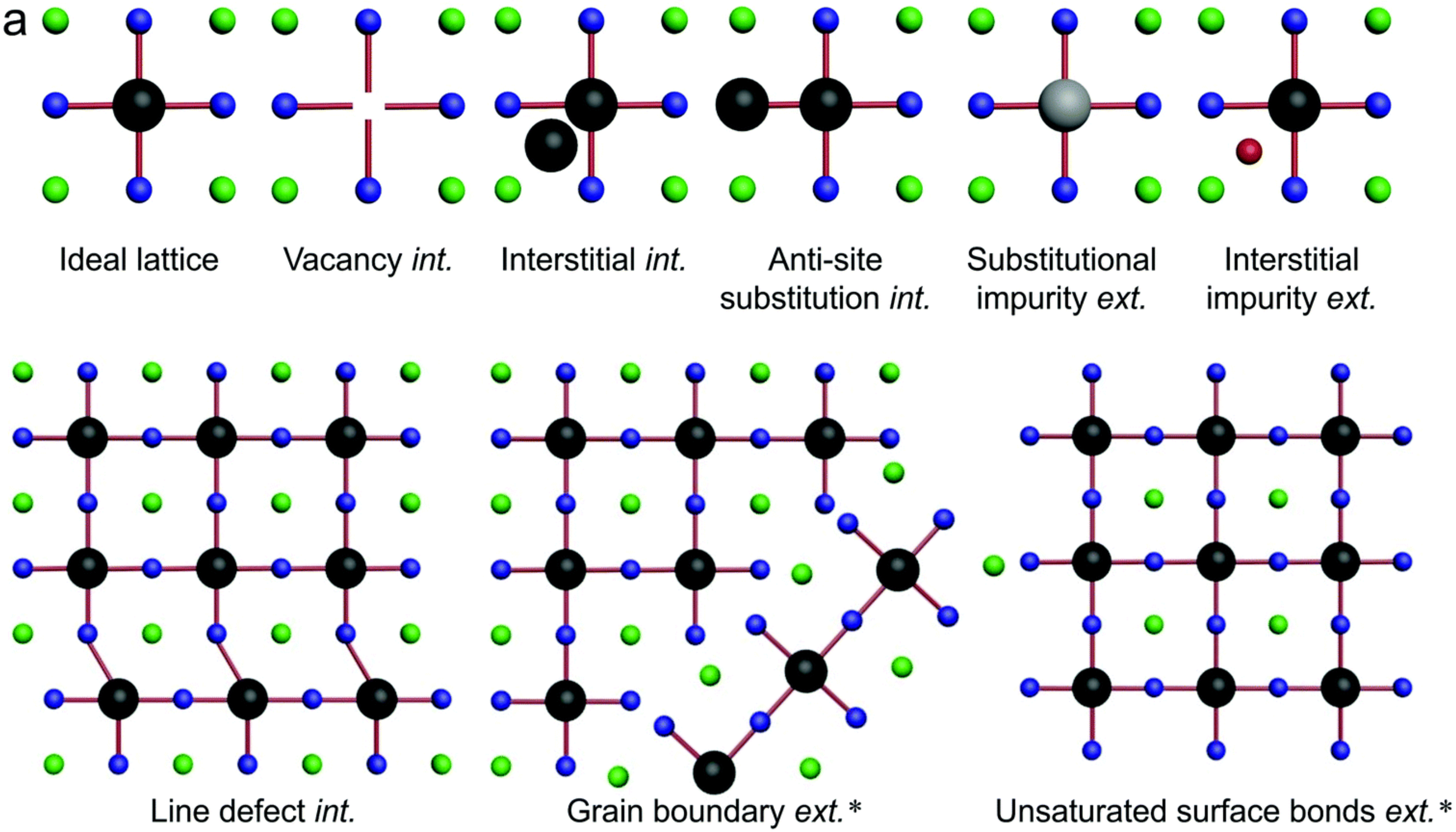
Defects in Perovskites

- ☐ Perovskites’ inherent susceptibility to defect formation during crystallization:
  - ☐ Soft ionic nature
  - ☐ Low formation energy
- ☐ Combined with solution processing
- ☐ Introduces a high defect density to the perovskite films

	Defect denisty [cm^{-3}]
Polycrystalline thin films of lead halide perovskites	10^{15}–10^{16}
In the intrinsic Si for oPV	10^{14}

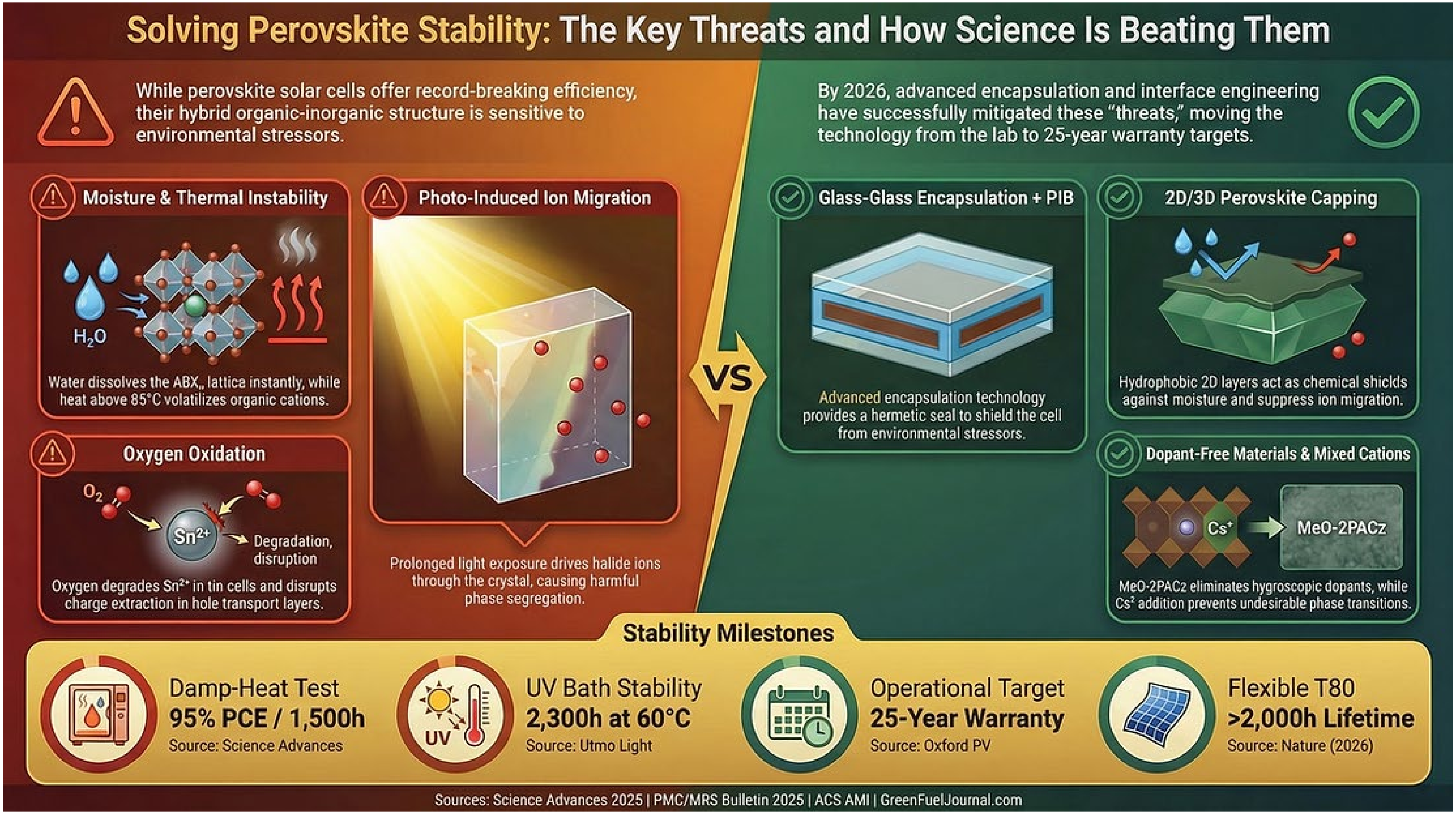
- ☐ Decline in efficiency shortly after fabrication, primarily attributed to the pervasive presence of defects

Defects in Perovskites



Jin et al., *Mater. Horiz.*, 2020, 7, 397-410;
DOI: 10.1039/C9MH00500E

Perovskite degradation



Solving Perovskite Stability: The Key Threats and How Science Is Beating Them

While perovskite solar cells offer record-breaking efficiency, their hybrid organic-inorganic structure is sensitive to environmental stressors.

By 2026, advanced encapsulation and interface engineering have successfully mitigated these "threats," moving the technology from the lab to 25-year warranty targets.

Moisture & Thermal Instability

Water dissolves the ABX,, lattice instantly, while heat above 85°C volatilizes organic cations.

Oxygen Oxidation

Oxygen degrades Sn^{2+} in tin cells and disrupts charge extraction in hole transport layers.

Photo-Induced Ion Migration

Prolonged light exposure drives halide ions through the crystal, causing harmful phase segregation.

Glass-Glass Encapsulation + PIB

Advanced encapsulation technology provides a hermetic seal to shield the cell from environmental stressors.

2D/3D Perovskite Capping

Hydrophobic 2D layers act as chemical shields against moisture and suppress ion migration.

Dopant-Free Materials & Mixed Cations

MeO-2PAC2 eliminates hygroscopic dopants, while Cs^2 addition prevents undesirable phase transitions.

Stability Milestones

Damp-Heat Test
95% PCE / 1,500h
Source: Science Advances

UV Bath Stability
2,300h at 60°C
Source: Utmo Light

Operational Target
25-Year Warranty
Source: Oxford PV

Flexible T80
>2,000h Lifetime
Source: Nature (2026)

Sources: Science Advances 2025 | PMC/MRS Bulletin 2025 | ACS AMI | GreenFuelJournal.com

- We have just learnt: defects facilitate recombination, but what is worse: **in all degradation mechanisms, defects play a role**!

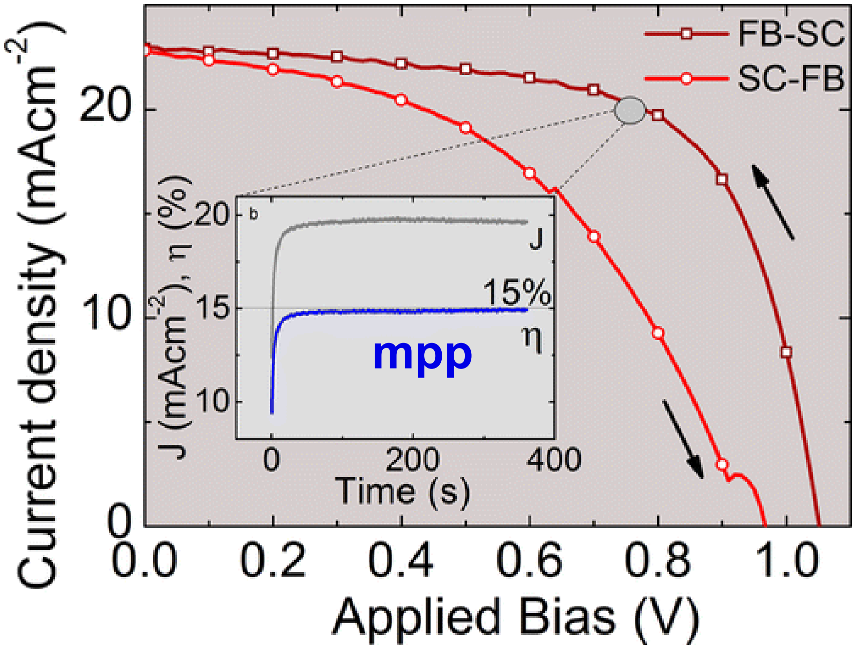
Degradation in Perovskites I - humidity

- Consequence of hybrid nature:
  - Bonding is not purely covalent (weaker)
  - Rich in defects

- Under humidity:
  - **Water penetrates the crystal (along grain boundaries)**
    - Coordinates with Pb^{2+}
      - Pb–I bonds weaken
        - Octahedra distorted
          - Iodide becomes mobile
            - Water solvates MA^{+}
- Heat accelerates
  - Diffusion, Hydration kinetics, Ion migration

Degradation in Perovskites II – photoinduced ion migration

- ❑ Early observation: the **I-V curve** of perovskite solar cells show strong **hysteresis**.
- ❑ **Ion-migration** was considered as the major cause
- ❑ Today: the field has shifted from treating ion migration mainly as a cause of hysteresis to recognizing it as a dominant **driver of light-soaking degradation**, interfacial instability, phase segregation, and field screening losses.



Degradation in Perovskites II – photoinduced ion migration

- ❑ The crystal lattice is relatively "soft" and contains mobile ionic defects
- ❑ Typical **activation energies are unusually low:** halide migration: ~0.1–0.6 eV; organic cation migration: ~0.4–0.8 eV
  - ❑ Under illumination, electrons and holes redistribute internal electrostatic potentials. This changes the **drift force on mobile ions**.
    - ❑ **Migrating ions accumulate** at: ETL/perovskite interfaces, HTL/perovskite interfaces, metal electrodes
      - ❑ Interfacial traps, redox reactions, electrode corrosion, contact delamination
      - ❑ In mixed-halide perovskites: photoinduced phase segregation
- ❑ In addition: Illumination can break Pb–I bonds and generates iodide vacancies, interstitial iodide and iodine molecules I_2

Degradation in Perovskites III & IV

❑ Oxygen degradation

- ❑ Oxygen can strongly affect perovskite stability, particularly under illumination.
- ❑ In common perovskites such as ($MAPbI_3$), oxygen interacts with photo-generated electrons:

$$O_2 + e^- \rightarrow O_2^-$$

The resulting superoxide species (O_2^-) attacks the organic cation (e.g. MA^+).

❑ Phase transformations

- ❑ Phase instability is another central degradation mechanism
- ❑ Perovskites can transform from the desired photoactive phase into non-photoactive or less efficient phases
- ❑ Example: Alpha Phase of $FAPbI_3$ transforming into the non-perovskite yellow δ-phase:

$$\alpha\text{-}FAPbI_3 \rightarrow \delta\text{-}FAPbI_3$$

Subject of one exercise

Stability of Perovskite solar cells

- ☐ **Bad news:** perovskites are intrinsically **unstable** when exposed to **light, heat, or applied voltage.** Their lifespan significantly decrease when exposed to **moisture and oxygen.**

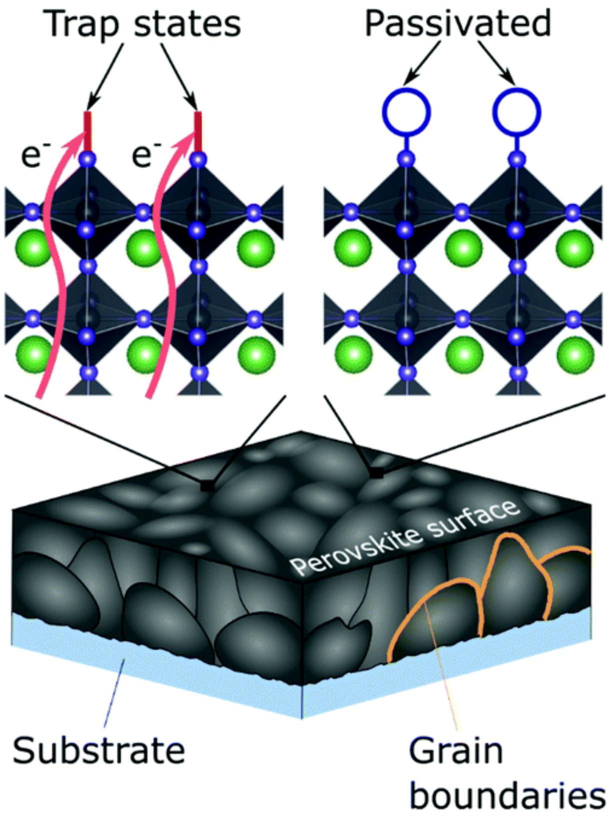
- ☐ The poor stability of perovskite solar cells was the main factor **hampering their industrialization for many years**– they need to competed with Si-technology. The high industry **standard lifespan (25-30 years** for Si-modules) is typically backed up with 25-year production warranties, guaranteeing at least 80% efficiency during that period.

- ☐ **Challenge:** address all degradation mechanisms at once. Standard **accelerated lifetime tests** developed for “other” PV-technologies seem **not very meaningful** for Perovskites.

- ☐ **Good news:** can be solved by **defect passivation** and **encapsulation.**

Defect passivation

- Defect passivation in perovskite solar cells means neutralizing or “healing” imperfections in the perovskite material
- Passivation molecules bind chemically to defects and neutralize their electronic activity

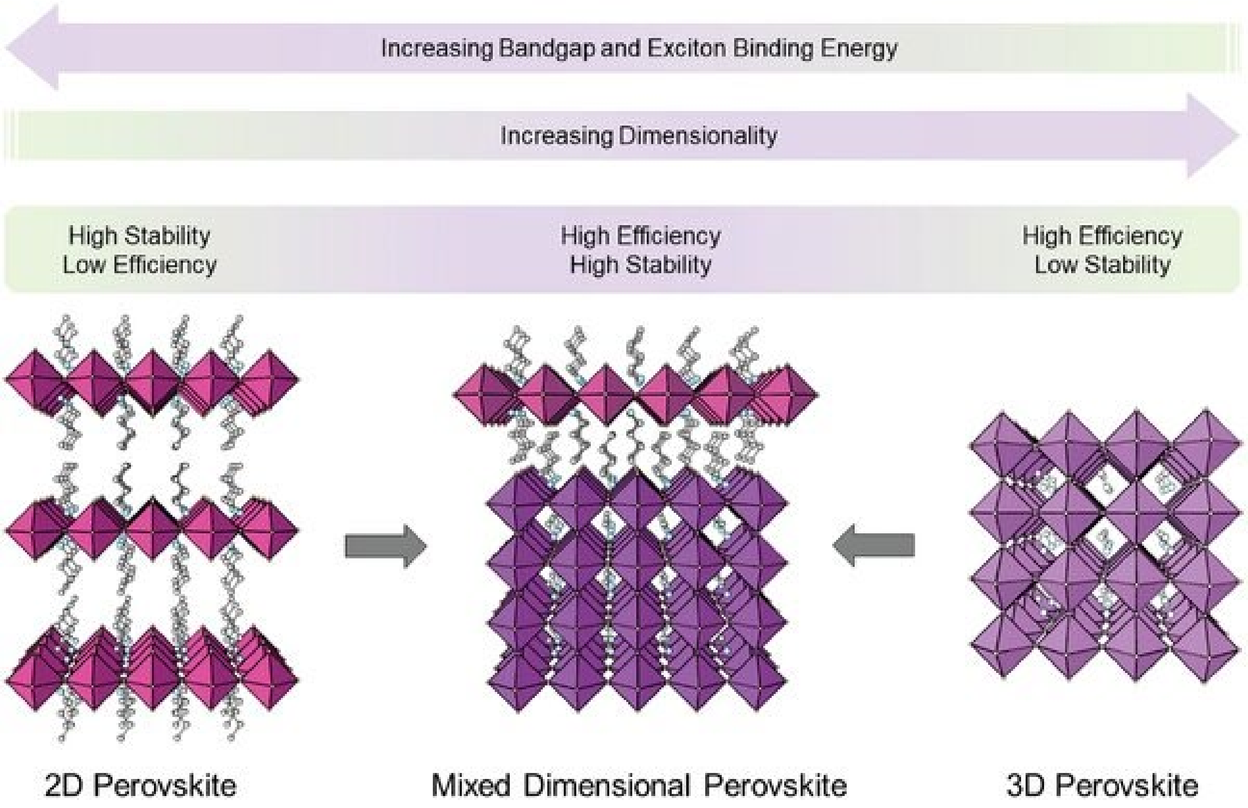


Subject of one exercise

Jin et al., *Mater. Horiz.*, 2020, 7, 397-410;
DOI: 10.1039/C9MH00500E

Defect passivation

- The 2D/3D perovskite heterojunction architecture places a thin layer of two-dimensional (Ruddlesden-Popper phase) perovskite on top of the conventional three-dimensional absorber. This 2D layer acts as a chemical shield: it is highly hydrophobic (water-repelling), resists ion migration, and passivates surface defects.



Surface Passivation Using Two Dimensional Perovskites Towards Efficient and Stable Perovskite Solar Cells.
2022 Advanced Materials 34(8); DOI: 10.1002/adma.202105635

The encapsulation revolution

- **Advanced encapsulation** is proving highly **effective at addressing** most degradation mechanisms simultaneously.
- The key insight is that **perovskite cells are not inherently more fragile than silicon** — they are simply far **more sensitive to their environment**.
- The state of the art in 2026 involves **glass-glass encapsulation** using advanced polymeric interlayers. **Poly-isobutylene (PIB) edge seals** have been demonstrated to prevent moisture ingress effectively for over 200 days in shelf-life tests, while also passing IEC 61215 damp-heat tests at 85°C/85% RH.
- **Epoxy polymer (EP) encapsulant** with self-healing properties showed remarkable results: devices retained 95.17% of initial PCE after 1,500 hours of damp-heat exposure, and 93.53% efficiency after 300 thermal cycling tests — exceeding the IEC 61215 requirement of maximum 5% loss after 200 cycles.

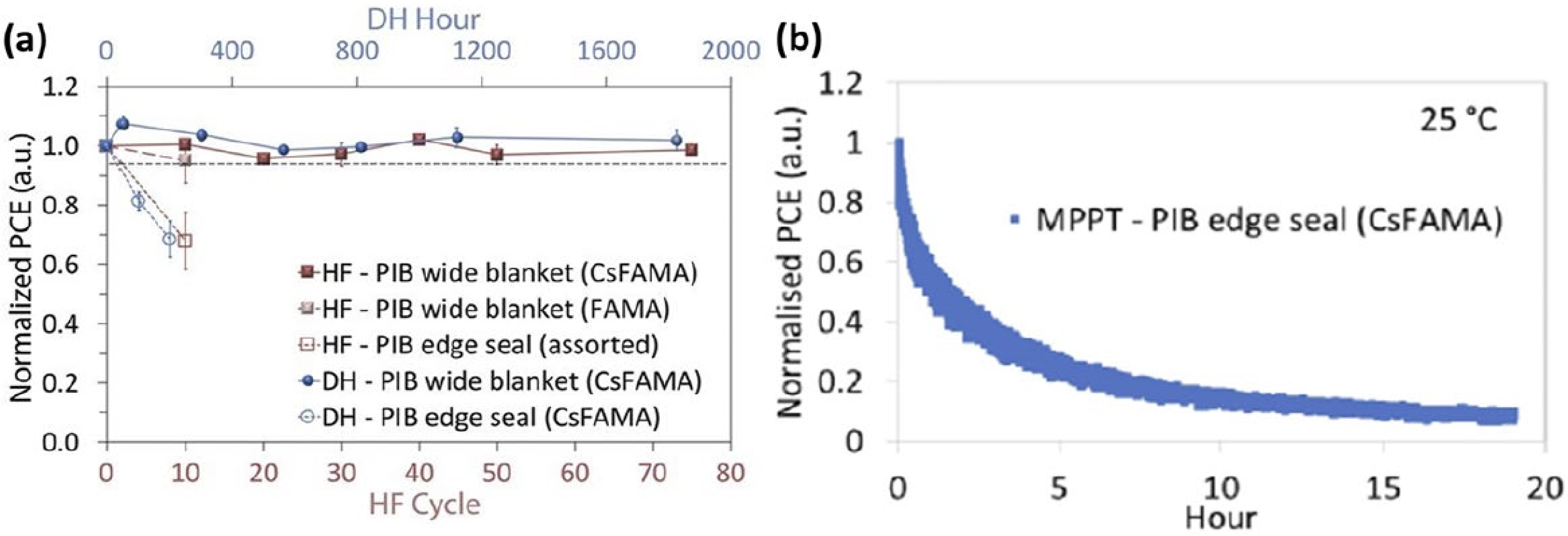
Standardized Stability Assessments: From Lab to Field

“Perovskite stability" is not an absolute concept but must be validated under specific stressors. The International Summit on Organic Photovoltaic Stability (ISOS) protocols, updated in 2023, have become the de facto standard for academic reporting, while industry testing adheres to the more rigorous IEC 61215 standard

Protocol	Conditions	Primary Objective
ISOS-D-1/2	Dark, Ambient to Elevated Temp	Baseline shelf-life and thermal stability
ISOS-D-3	85°C, 85% RH (Damp-Heat)	Accelerated moisture and thermal stress
ISOS-L-1/2	Continuous Light Soaking	Evaluation of photo-stability and ion migration
ISOS-L-3	High Temp + Light Soaking	Combined operational stress (Worst-case scenario)
ISOS-T-3	Thermal Cycling	Resistance to thermomechanical delamination
ISOS-O	Outdoor Testing	Real-world validation with diurnal cycles

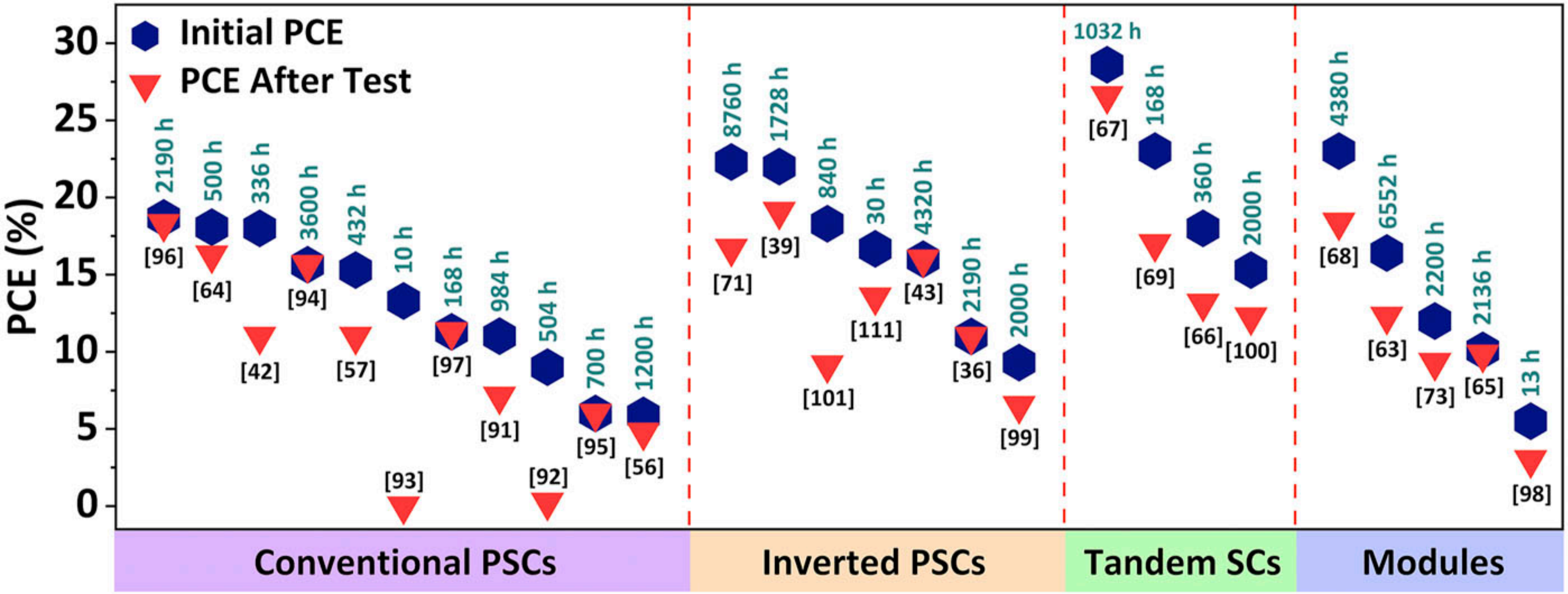
Stability tests:

- Typical stress test: 1000 hours continuous illumination at an intensity equal to one sun (light soak test) ; 1000 hours exposure to a high humidity relative humidity of 85 %) combined with exposure to a temperature of 85°C (damp-heat test); 50 thermal cycles from -40 o C to 85 o C (thermal cycling test)



Shi et al., Science 368, 2412 (2020).

Outdoor stability testing of perovskite solar cells

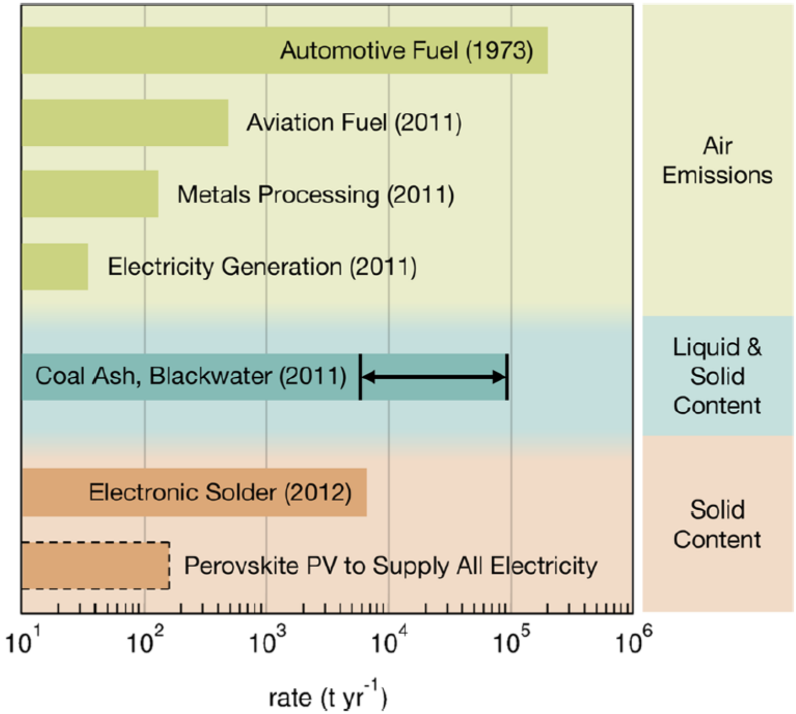


8760 h = 1 year
The majority of the cells subjected to outdoor tests have been encapsulated. Reports of outdoor tests on cells without encapsulation show that mesoscopic structures are more stable than planar devices, that eventually completely degraded in 10 h.

APL Energy. 2023;1(2). doi:10.1063/5.0155845

Environmental issues

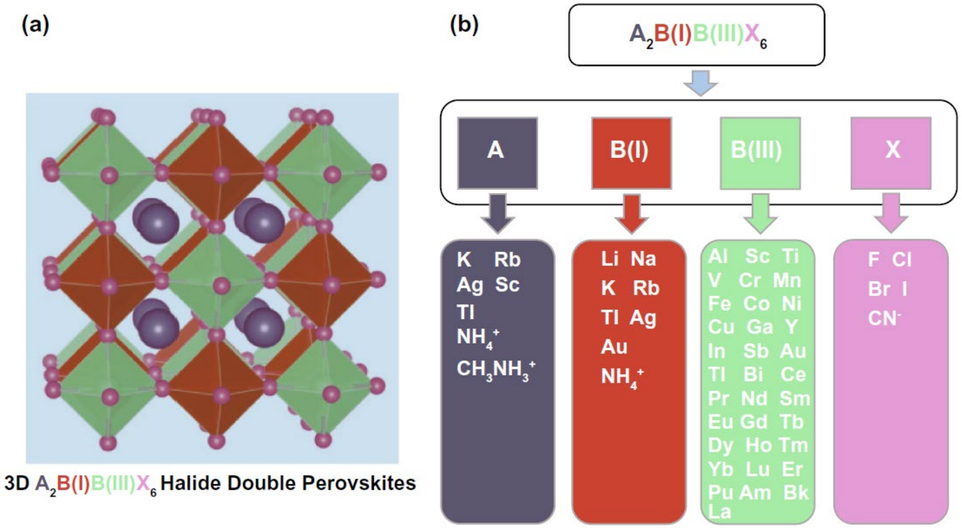
- ❑ The lead content intrinsic to PSCs raises significant concerns not only during device operation but also at the end of their lifecycle
- ❑ **Lead salts** are **water soluble**
- ❑ **Toxicity of lead salts** is of high concern. Intake of lead by the human body affects the liver, kidney and nervous tissues leading to various forms of intoxication
- ❑ Lead has a relatively short half-life in the latter soft tissues, but is eventually deposited in the skeleton where it fixates as lead phosphate.



D. Fabini et al., J. Phys. Chem. Lett. 2015, 6, 3546−3548
B. Hailegnaw et al., J. Phys. Chem. Lett. 2015, 6, 1543−1547
A. Babayigit, A. Ethirajan, M. Muller, B. Conings, Nature Materials 2016, *15*, 247.

Possible remedies

- ❑ PSCs hold the potential to accelerate energy transitions by lowering the expense and broadening the applicability of solar technology, especially in regions where cost-sensitive solutions are needed. Ensuring the safe use of lead within PSC systems aligns with broader sustainability goals, integrating environmental protection, public health, and renewable energy advancement into a coherent framework.
- ❑ Chemical and physical containment
- ❑ Alternative perovskite compositions



3D $A_2B(I)B(III)X_6$ Halide Double Perovskites

- ❑ But: Sn is also toxic.

-> Explore «double perovskites»

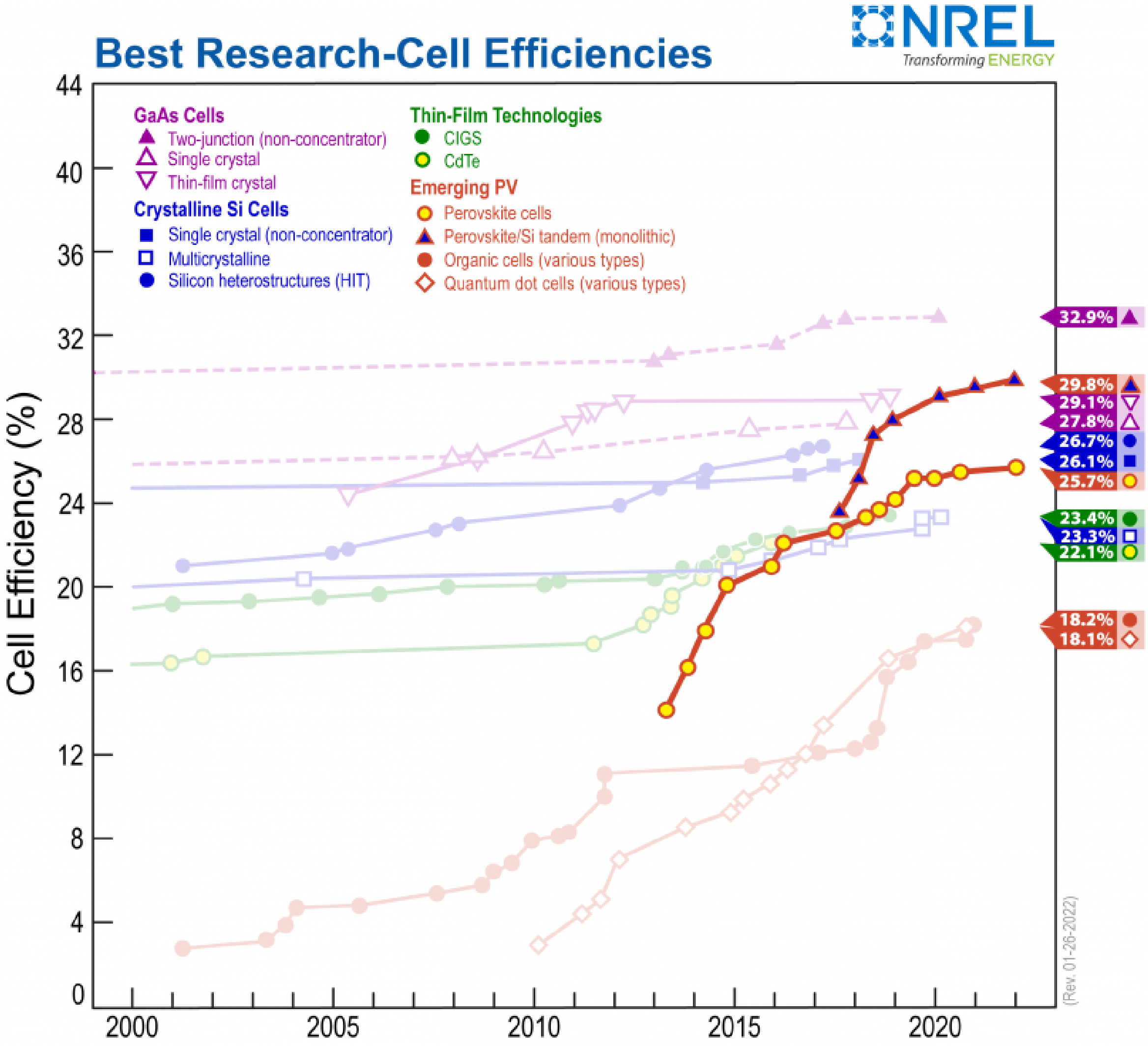
$Cs_3Bi_2I_9$ (PCE of a few %)

M. Wang et al., Nano-Micro Lett. (2021) 13, 62

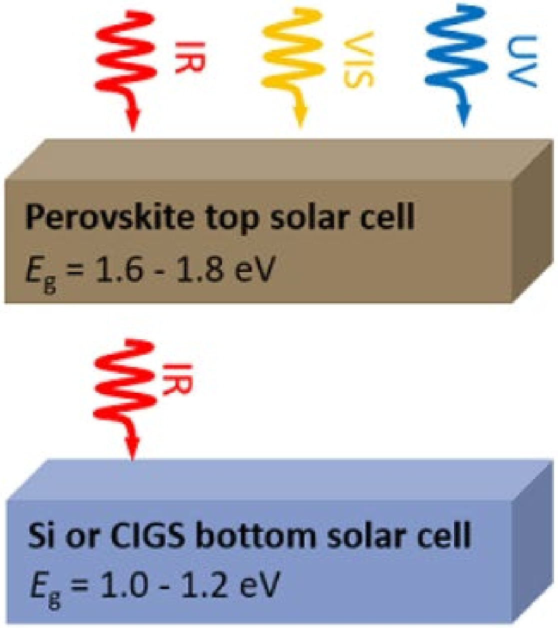
B. W. Park et al, 2015, Adv. Mater, 27, 43

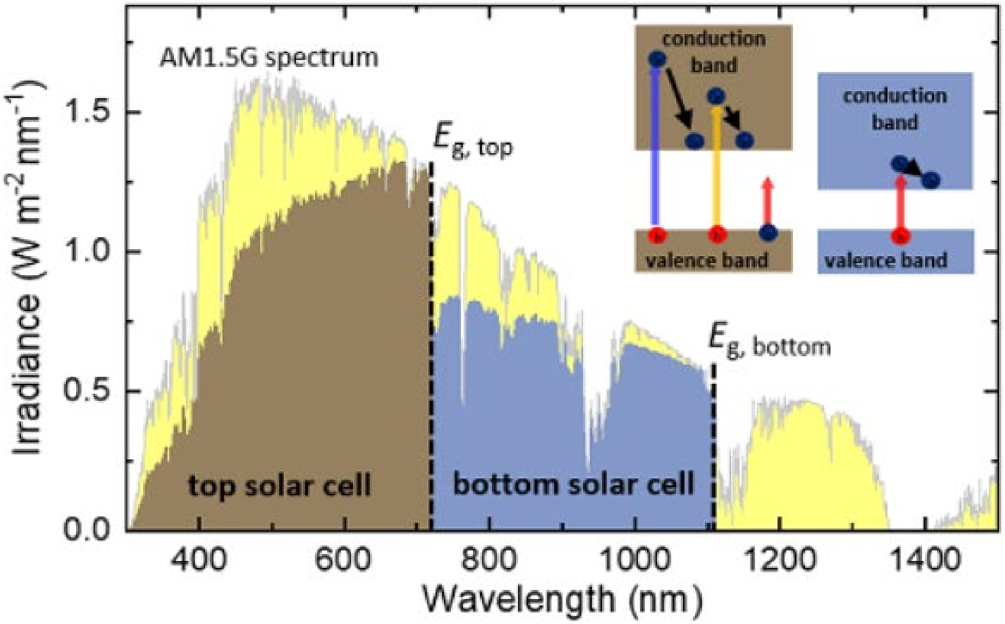
J. Li et al., Nano Energy 2021, 80, 105526

Tandem cells or another reason for band gap engineering



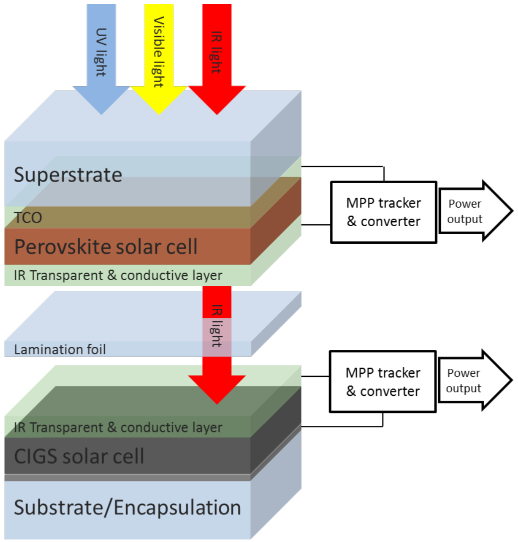
Tandem cells or another reason for band gap engineering

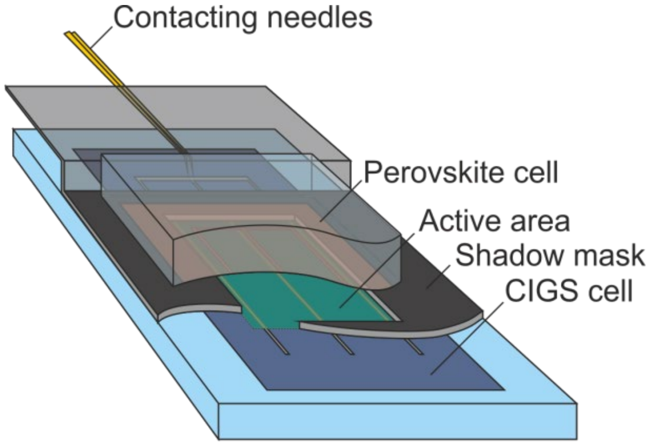


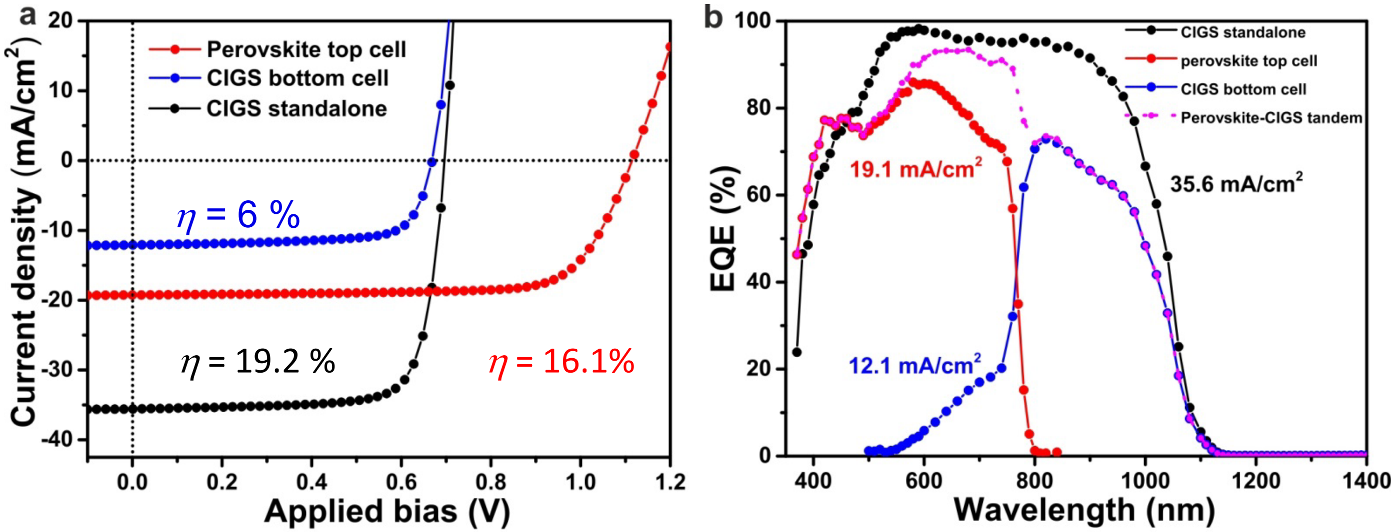


https://www.lti.kit.edu/english/9042.php

22.1% 4-terminal perovskite/CIGS tandem cells

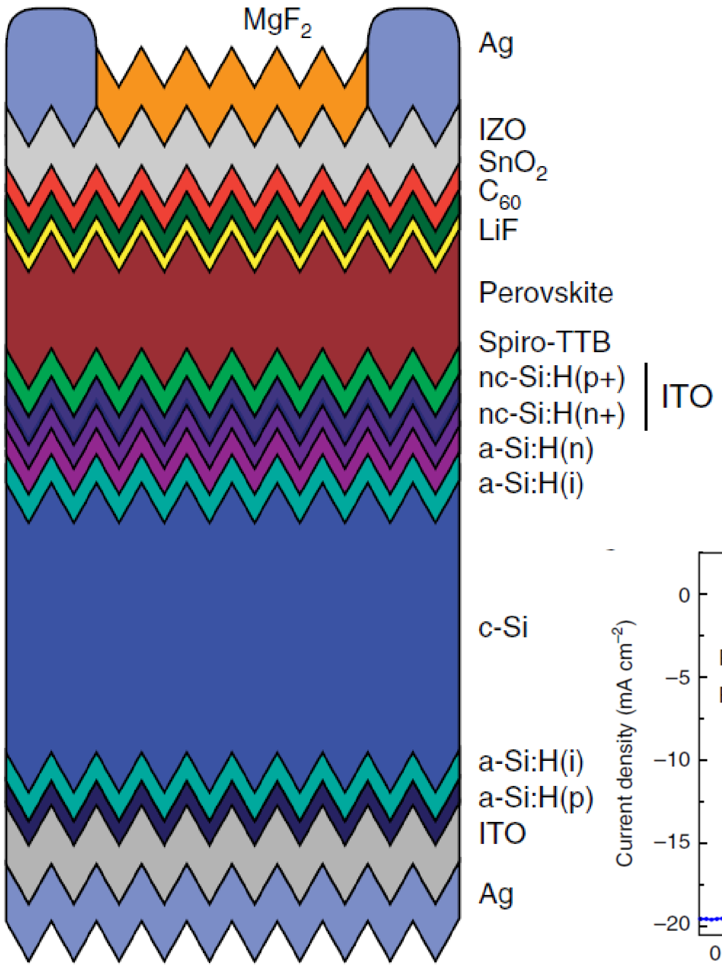


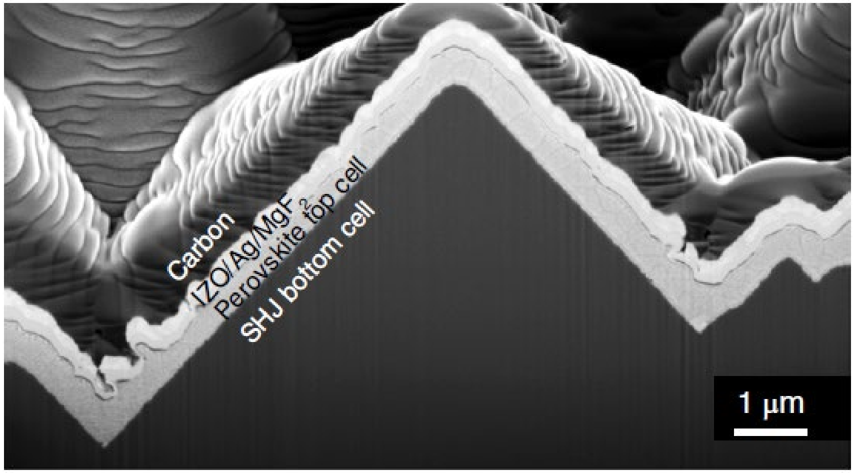


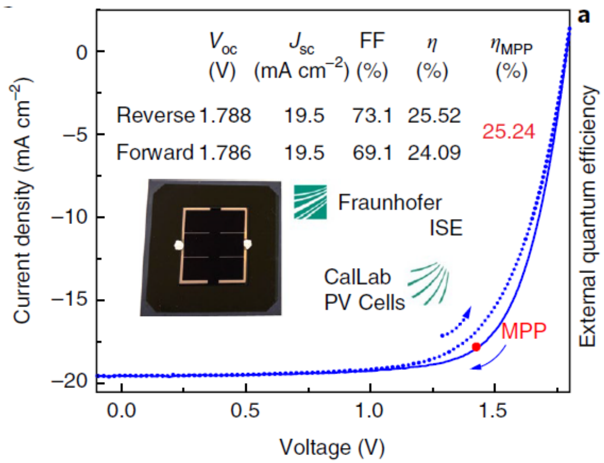


F. Fu, S. Buecheler, A.N. Tiwari et al., *Nature Energy,* 2, 16190 (2016)

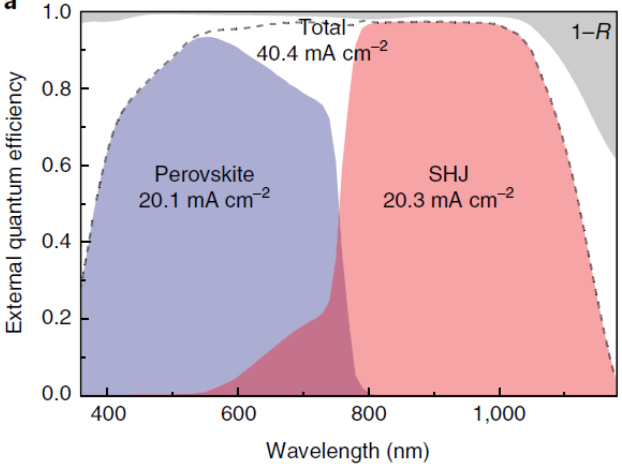
25.2% 4-terminal perovskite/Si tandem solar cells







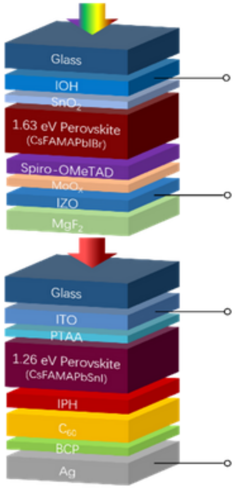
	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	η (%)	η_{MPP} (%)
Reverse	1.788	19.5	73.1	25.52	25.24
Forward	1.786	19.5	69.1	24.09	

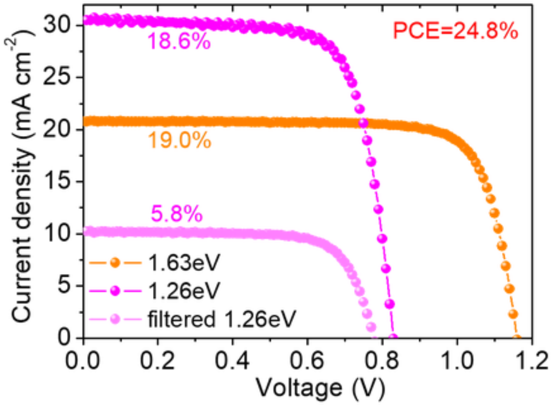


Sahli and Werner et al., *Nat. Mat.*, 2018, 1 (2), pp 474–480

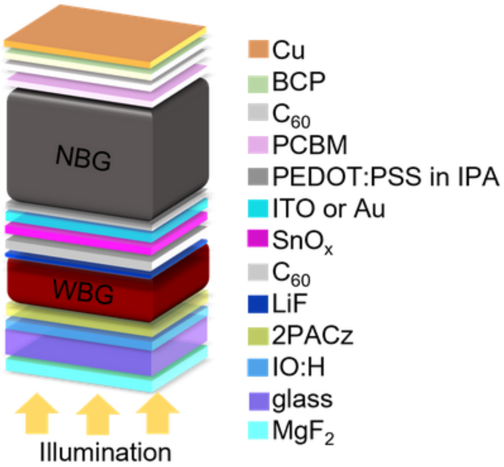
All perovskite tandem solar cells

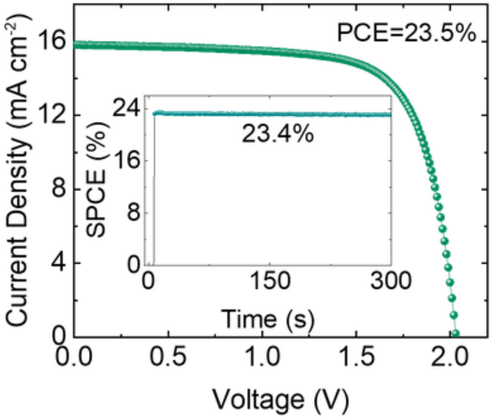
Four-terminal all-perovskite tandems





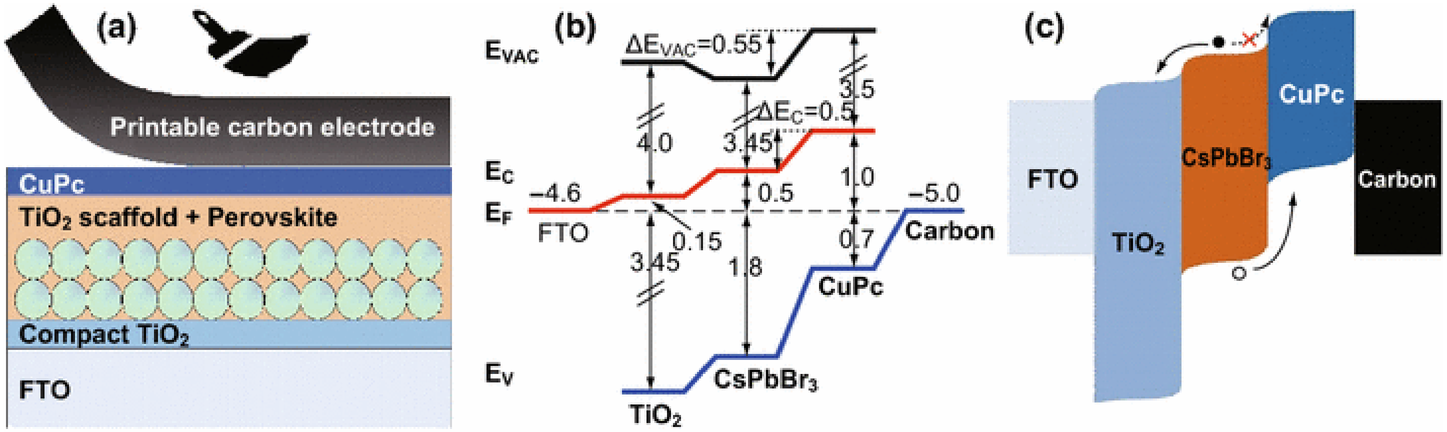
Two-terminal all-perovskite tandems

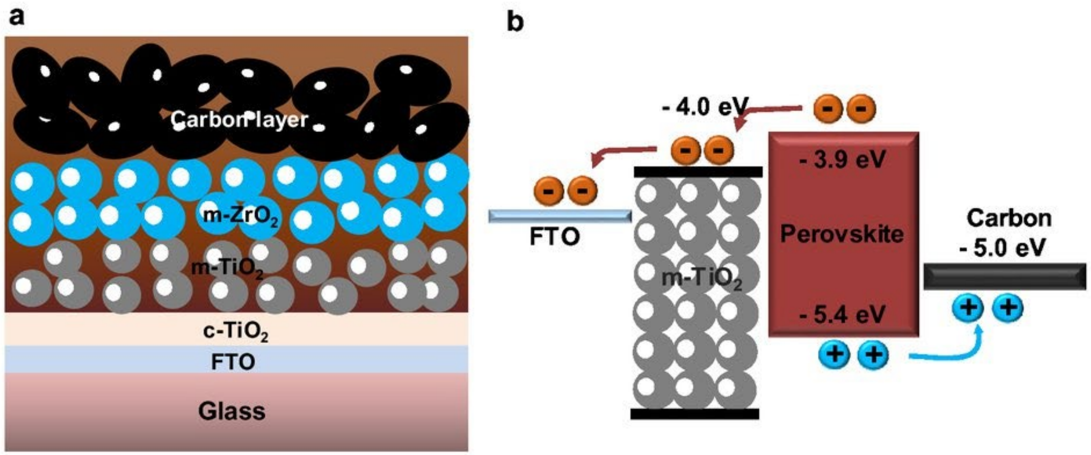




https://www.lti.kit.edu/english/9042.php

Carbon based perovskite solar cells



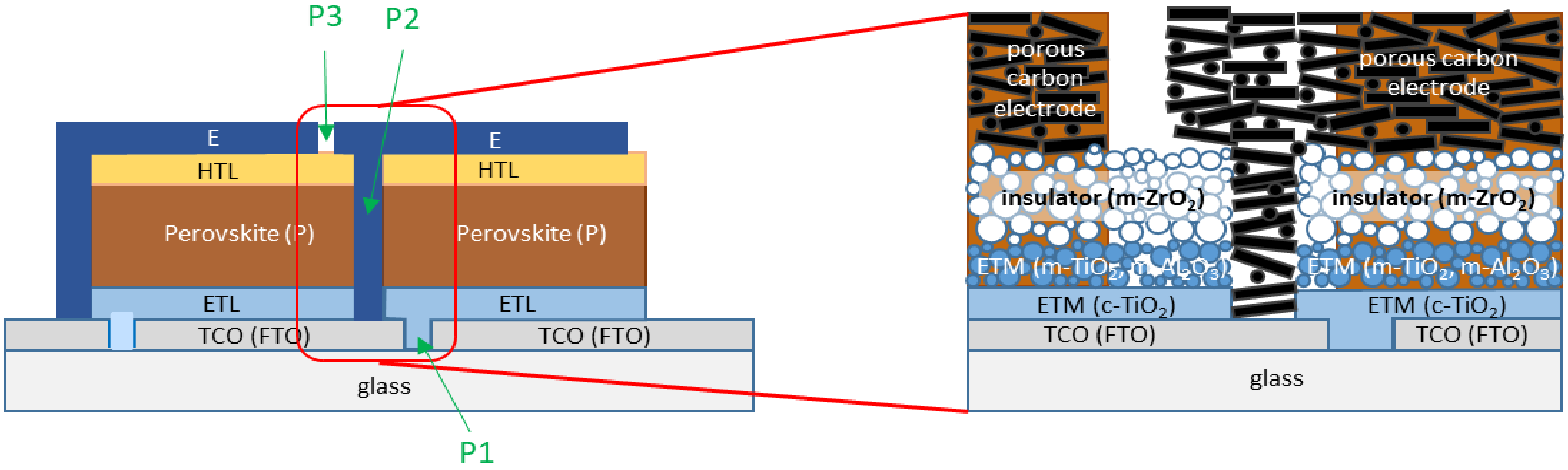


- Good air stability
- High low light intensity efiiciency
- Completely printable
- But: low efficiency ~ 13.83 %

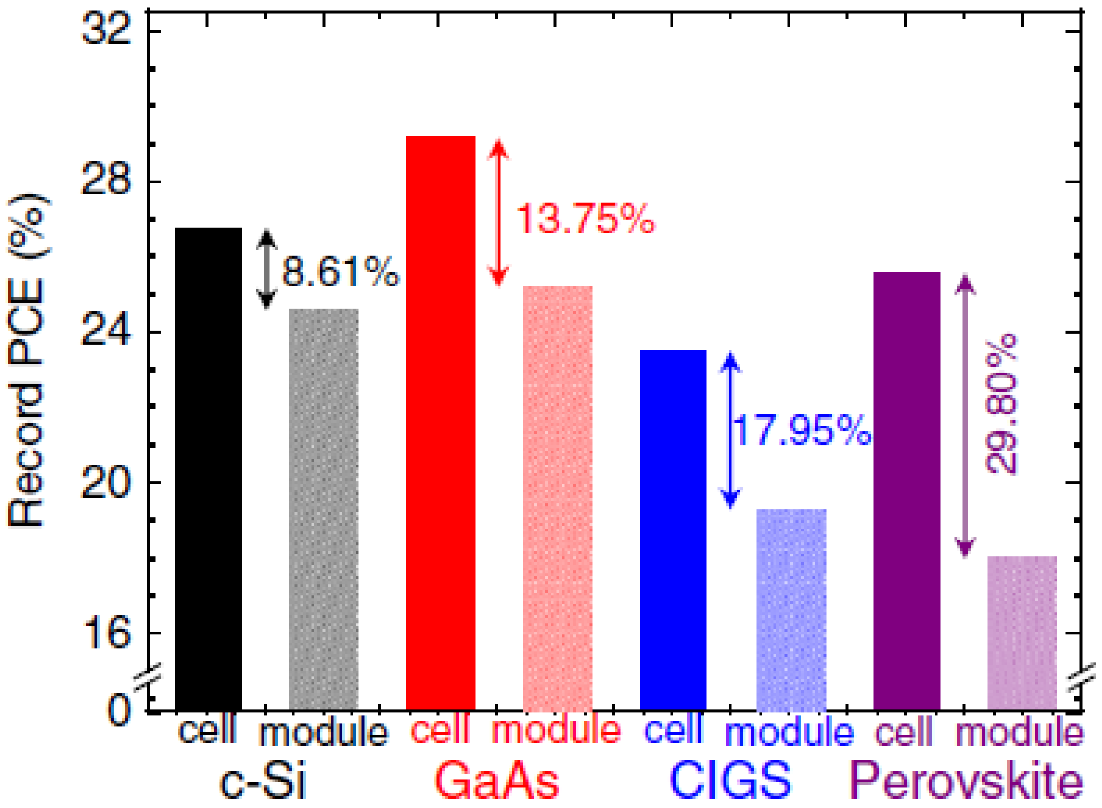
Liu et.al. Nano-Micro Letters (2018)
Duan SPIE (2018)

Uniqueness of the mesoscopic PSC architecture

- Crystal growth uniform over the full surface using inkjet
- Robust thick structure is less sensitive to surface defects
- Cell interconnect does not create interfacial defects since the active material is added after the scribing step



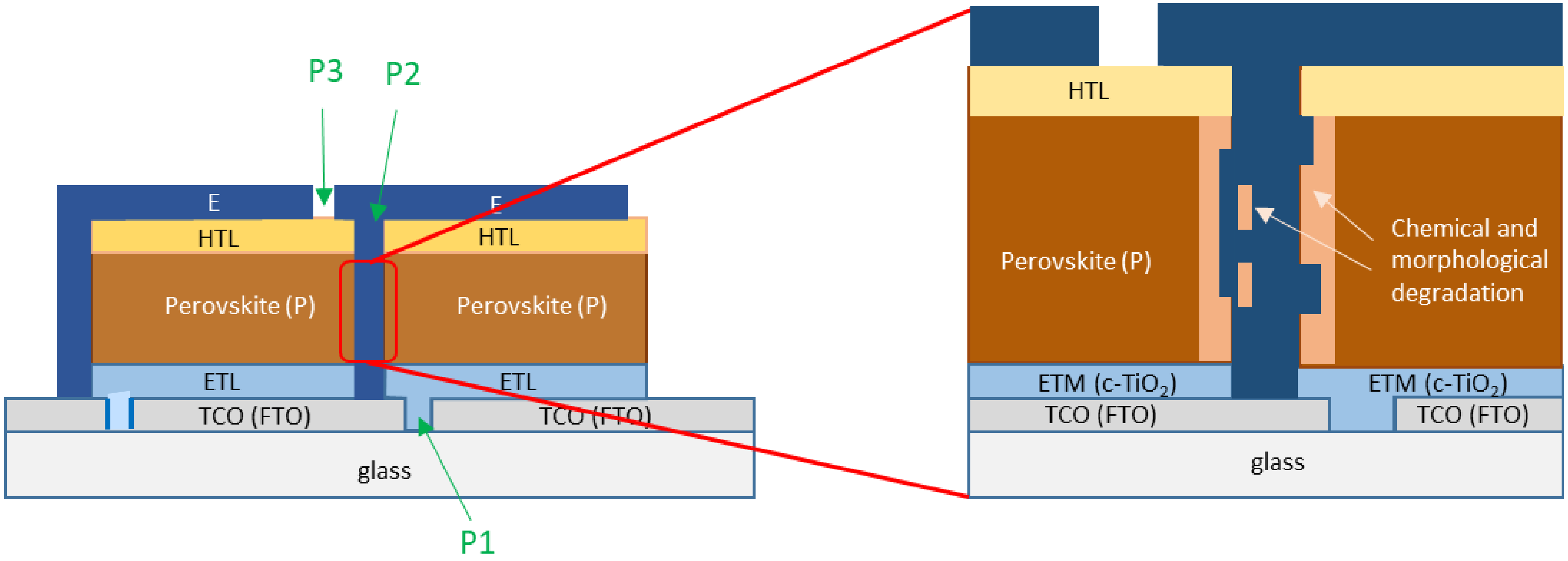
Up-scaling - Efficiency loss in modules



Sol. RRL 2022, 6, 2100455

The challenge of series interconnect

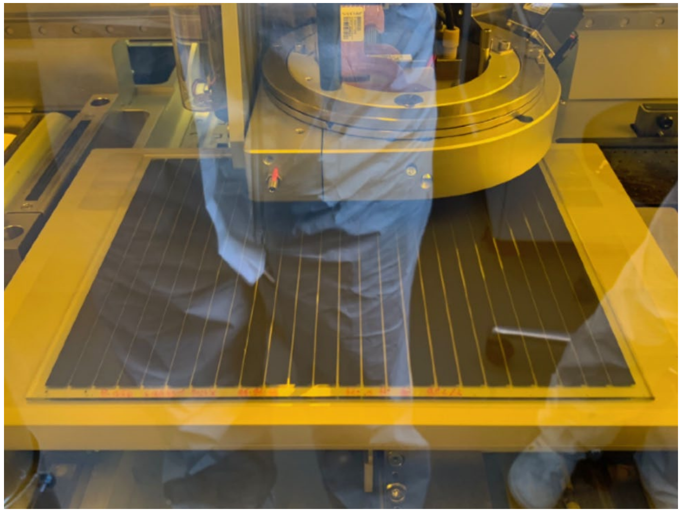
- ❑ Laser or mechanical scribing
  - ❑ Structural deterioration
  - ❑ Chemical degradation

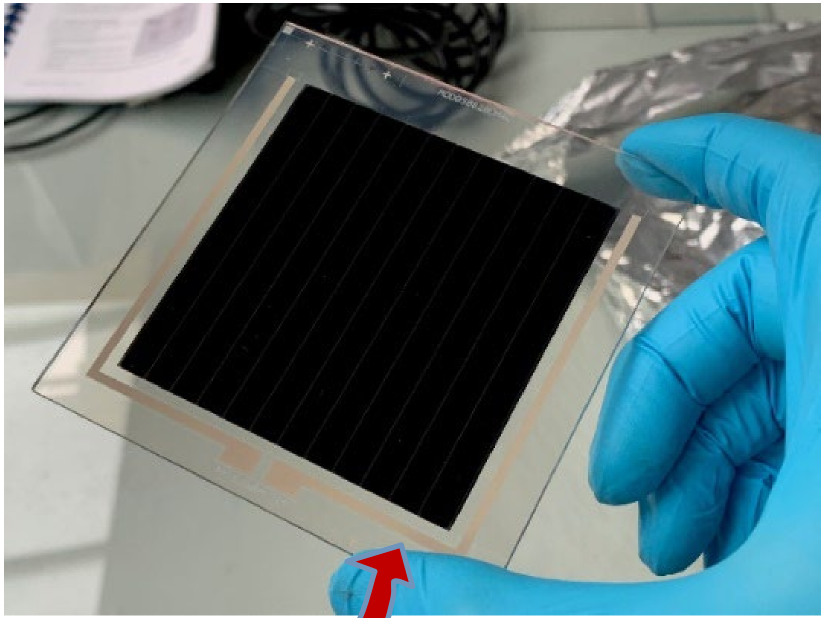


J. Werner et al.,Energy & Environmental Science 2020, *13* (10), 3393-3403

Uniqueness of the mesoscopic PSC architecture

- Slot-die coating of porous scaffold.
- Inkjet infiltration of the perovskite precursor.

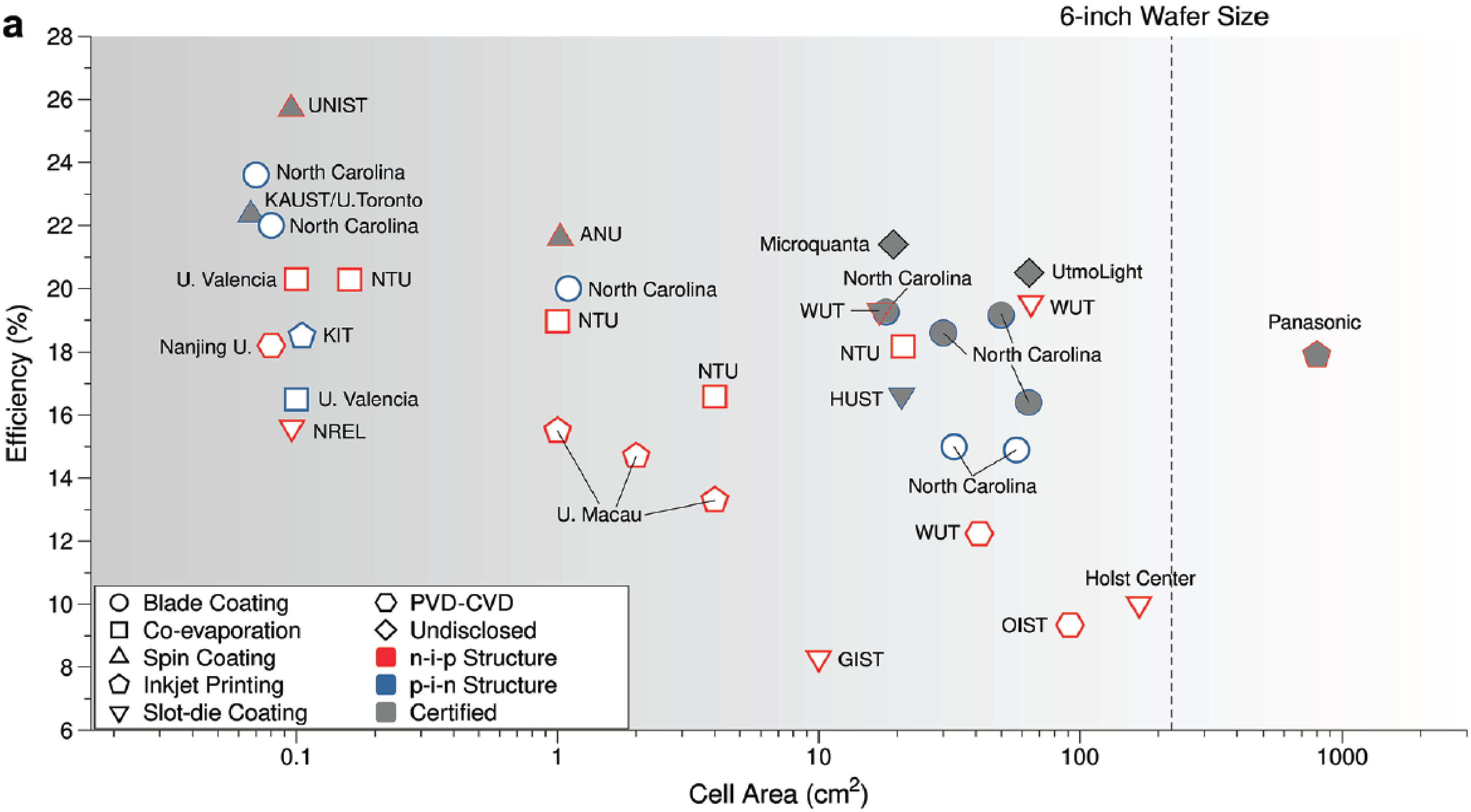




A. Verma et al, J.Mater.Chem.C, 2020,8,6124
A. Verma et al, Materials Advances, 2020, DOI: 10.1039/d0ma00077a

Both have a PCE of 13 %

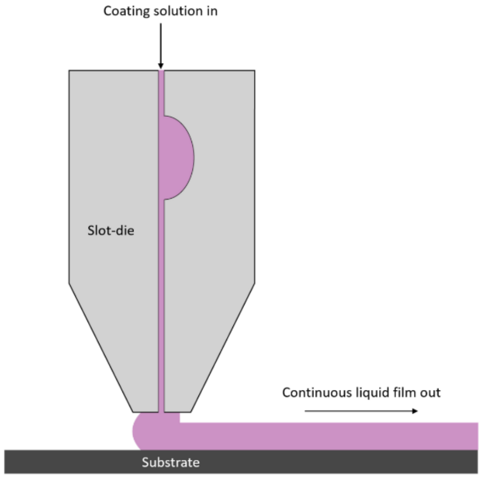
Towards industrialization – from labscale to modules

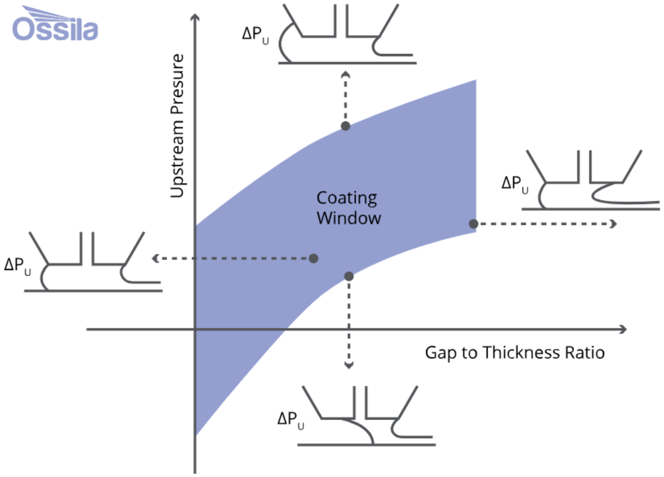


- Evaporation: ideal for tandem cells, integrate into existing infrastructure
- **From solution: potentially much cheaper**

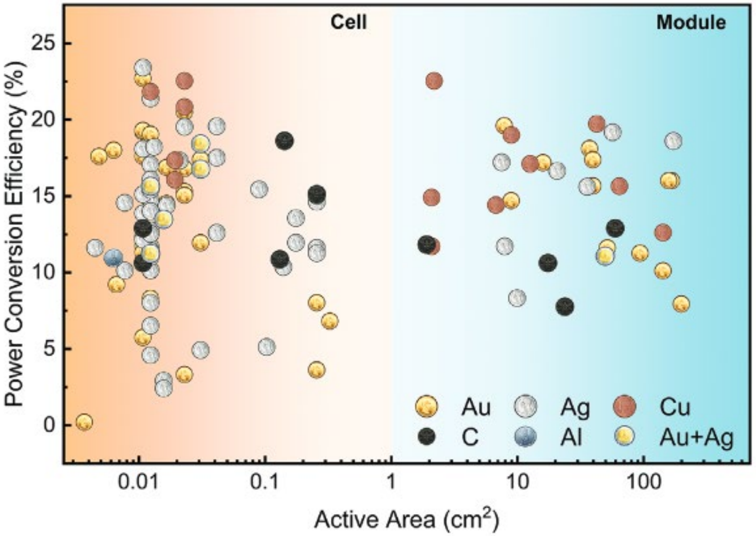
Adv. Mater. 2022, 2106540

Towards industrialization – slot die coating



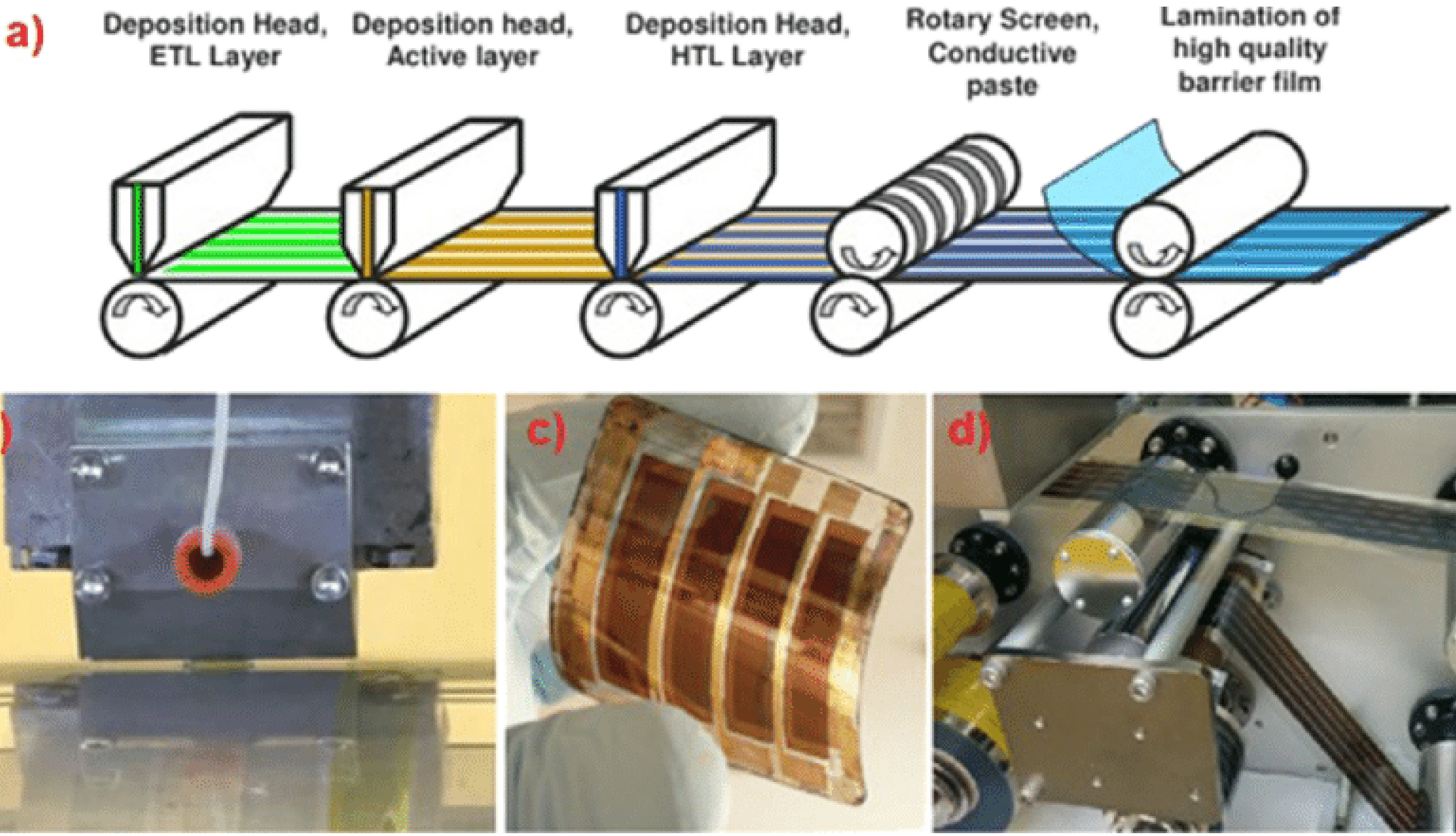


- ☐ New challenge: solvent evaporation differs significantly from spin-coating => crystallization also differs significantly



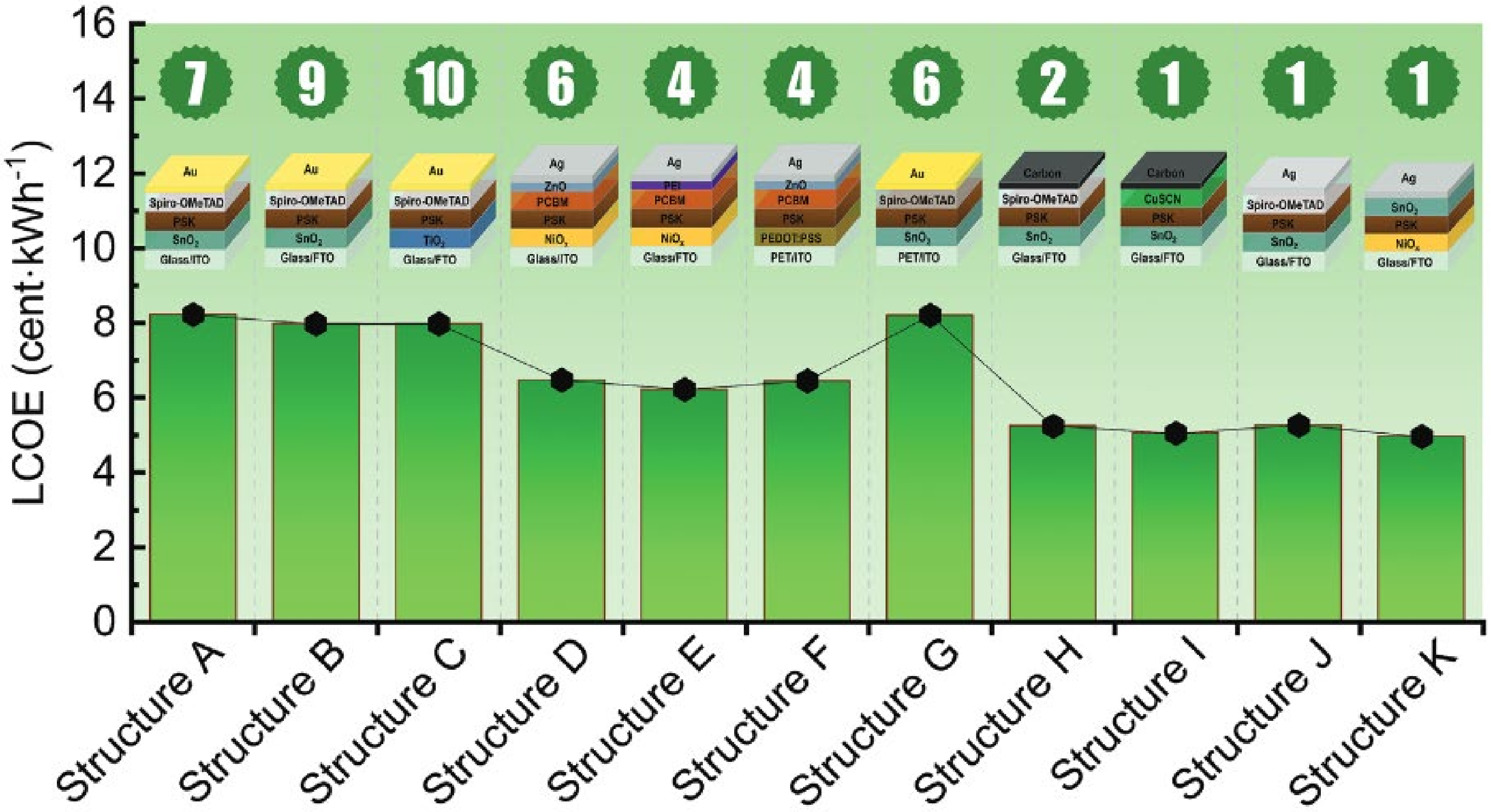
K. K.Shin Thant, et al. Adv. Energy Mater.2025, 15, 2403088. https://doi.org/10.1002/aenm.202403088

Fully printed Perovskite solar cells



Research Update: Large-area deposition, coating, printing, and processing techniques for the upscaling of perovskite solar cell technology, Stefano Razza, Sergio Castro-Hermosa, Aldo Di Carlo, and Thomas M. Brown , APL Mater. 4, 091508 (2016)

Towards industrialization – slot die coating



K. K.Shin Thant, et al. Adv. Energy Mater.2025, 15, 2403088. https://doi.org/10.1002/aenm.202403088

Commercial Readiness Timeline

Timeline	Development Stage	Key Milestone	Leading Organizations
2009–2019	Laboratory Discovery	PCE grows from 3.8% → 25%+	Miyasaka, Grätzel (EPFL), Park (SKKU)
2020–2023	Pilot-Scale Prototyping	First pilot lines; PCE >26%; tandem cells >33%	Oxford PV, LONGi, Saule Tech, GCL
2024	Early Commercial	Oxford PV ships 24.5% modules to U.S.; Qcells reaches 28.6%	Oxford PV, Hanwha Qcells, LONGi
2025–2026	Active Commercial	LONGi 35% tandem record; GCL passes IEC 61215; modules 24–29%	LONGi, GCL, Utmo Light, Oxford PV
2027–2028	Mass Production Target	IEC certification widespread; Qcells mass production; 30%+ commercial	Qcells (H1 2027), LONGi, JinkoSolar
2029–2032	Grid-Scale Deployment	Utility bankability achieved; LCOE parity with premium silicon	Multiple players globally
2035+	Technology Maturity	25-year warranties standard; >32% commercial modules possible	Industry-wide

Lifecycle Assessment Summary

Environmental Parameter	Perovskite PSC	Crystalline Silicon	CdTe Thin-Film	Coal Power
Energy Payback Time	0.2–0.5 years	1.0–2.5 years	0.5–1.0 years	N/A (ongoing)
GHG Intensity	10–25 gCO_2eq/kWh	20–50 gCO_2eq/kWh	15–30 gCO_2eq/kWh	820+ gCO_2eq/kWh
Toxic Material Content	0.4–1.5 g/m² Pb	Low (Si, Al, Ag)	Cadmium (toxic)	Heavy metals in ash
Manufacturing Temperature	<150°C	~1,500°C	~500–600°C	~1,400°C (combustion)
Recycling Status	Developing (R&D)	Established (EPD)	Established (First Solar)	Partial (ash)
End-of-Life Protocol	Closed-loop (proposed)	Mechanical + chemical	Manufacturer take-back	Landfill (ash)

Companies working on Perovskite modules (no claim of completeness)

Company Name	Primary Technology Focus	Recent Commercialization /Products	Reported Module/Cell Efficiency (Public)	Manufacturing Scale/Plans
Oxford PV (UK)	Perovskite-Silicon Tandem	Shipped commercial tandem panels (Sept 2024); utility-scale deployment.	24.5% (module, commercial); 28.6% (cell, 2023); 26.9% (module record)	Pilot line (Brandenburg, 125MW initial); plans for GW scale.
Hanwha Qcells (KR/DE)	Perovskite-Silicon Tandem (scalable)	Achieved 28.6% on M10 tandem cell (Dec 2024); focus on mass manufacturing.	28.6% (M10 tandem cell)	R&D pilot line in Germany; significant R&D investment for commercialization.
UtmoLight (CN)	Perovskite Modules (large area)	18.1% efficiency on 0.72-m^2 modules (Mar 2025); supplying commercial projects.	18.1% (0.72-m^2 module)	150-MW pilot line operational.

Companies working on Perovskite modules (no claim of completeness)

Company Name	**Primary Technology Focus**	**Recent Commercialization /Products**	**Reported Module/Cell Efficiency (Public)**	**Manufacturing Scale/Plans**
Tandem PV (US)	Perovskite-Silicon Tandem (US-made)	Secured $50M funding (Mar 2025) to build US plant.	28% (current panels); aiming for >30% (late 2025)	Building commercial-scale US mfg. facility.
LONGi Green Energy (CN) LONGi	Perovskite-Silicon Tandem (cell R&D)	World record tandem cell efficiency (June 2024).	34.6% (tandem cell)	Major silicon PV mfg; R&D focus, commercial PSC plans not detailed.

Companies working on Perovskite modules (no claim of completeness)

Company Name	Primary Technology Focus	Recent Commercialization /Products	Reported Module/Cell Efficiency (Public)	Manufacturing Scale/Plans
JinkoSolar (CN)	Perovskite-Silicon Tandem (cell R&D)	High-efficiency tandem cell results (May 2024).	~33.8% (tandem cell)	Major silicon PV mfg; R&D focus, commercial PSC plans not detailed.
Microquanta Semiconductor (CN)	Perovskite Modules	Introduced commercial-scale module "α" (May 2022) with 12-year warranty.	Not specified.	Commercial-scale production via solution printing process.
Perovskia SA Perovskia	Hole conductor free carbon based, ink jet printing	Niche market: indoor electronic appliances	13 %	Setting up pilot plant in Aubonne, VD

Companies working on Perovskite modules (no claim of completeness)

QW SOLAR

Subsidiary of the listed company Quanwei Technology, is a provider of solar modules, energy storage, and new energy solutions.

脉络能源
MELLOW ENERGY

China-based perovskite solar module manufacturer

Grape Solar®
Clean Power. Today.

Grape Solar (US) is a retail solar brand with over a decade of experience providing grid-tied, grid-interactive and off-grid solar systems to businesses and individuals

First Solar

Solar is an American solar technology company and global provider of responsibly produced, eco-efficient solar modules

Companies working on Perovskite modules (no claim of completeness)

Halocell Energy	Australia, former GreatCell
PSI Perovskite Inspired Technology	Indian startup incubated at the Tides Business Incubation Center within IIT Roorkee
仁烁光能 RENSHINE SOLAR	RenShine Solar is a Chinese developer of perovskite solar cells
VOLTEC solar	Voltec Solar is a France-based producer of photovoltaic panels

Learning outcome

- What are Perovskite solar cells?
  - *Based on the perovskite structure,* ABX_3
  - *A = An organic monovalent cation – methylammonium* ($CH_3NH_3^+$) *or formamidinium* ($NH_2CHNH_2^+$); *B = A inorganic divalent cation – usually lead(II)* (Pb^{2+}); X_3 *= A slightly smaller halogen anion – usually chloride* (Cl^-) *or iodide* (I^-)
  - *Most researched is* $MAPbI_3$
- Why are they so good?
  - *High absorption: Bandgap originates from the inorganic corner-sharing* PbX_6 *octahedral network: direct bandgap, transition from antibonding into antibonding state*
  - *Partially due to the hybrid character:*
    - *Low exciton binding energy: dielectric screening, small effective electron mass*
    - *Long charge carrier diffusion: good crystallinity*
    - *High defect tolerance: mainly «shallow traps»*

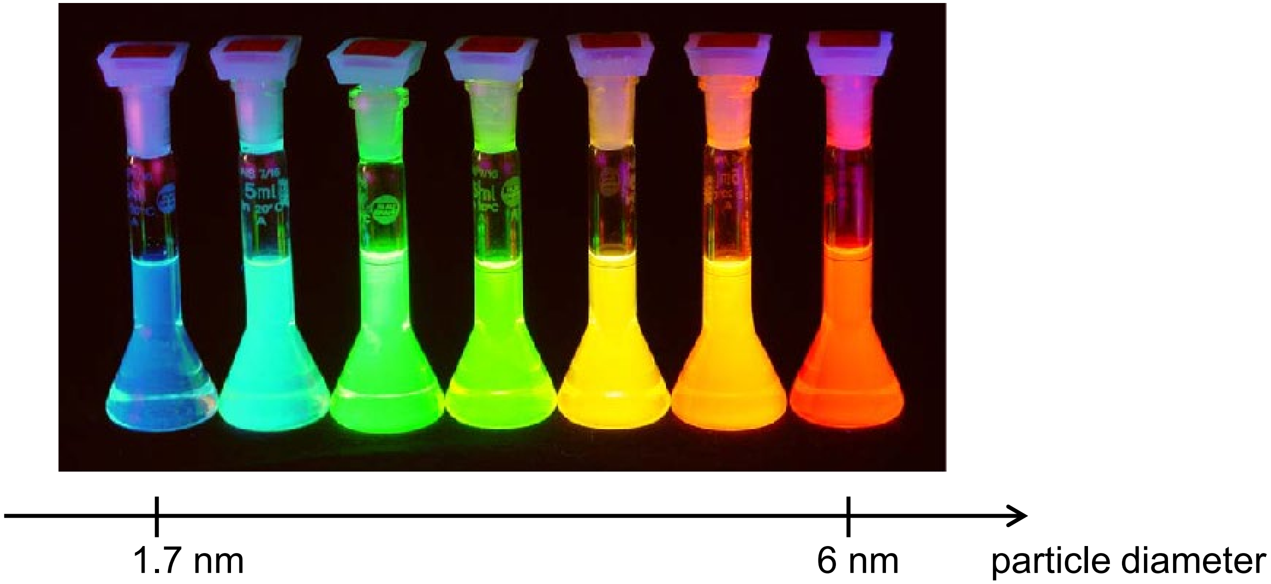
Learning outcome

- Processing:
  - *Perovskite solar cells can be processed from solution: one of the major advantages over other PV technologies*
- Strategies for efficiency improvement
  - *Control of crystallization*
  - *Optimize the bandgap:*
    - *Compositional engineering*
  - *Minimize recombination, optimize charge extraction*
    - *Controlled crystallization, composition engineering, defect passivation*
- Architectures? How are they made?
  - *Mesoscopic and planar; n-i-p or p-i-n; solution processing or evaporation*

Learning outcome

- Stability of Perovskite Solar cells
  - *Real challenge, inherent to material because of soft ionic nature and low formation energy; many degradation mechanisms*
  - *Combining defect passivation and proper sealing strategies*
- Lead content is an issue
  - Sofar no good alternative
- Tandem solar cells
  - *As top cell in combination with Si, CIGS or all perovskite*
- Industrialization
  - *Huge advantage: solution processability*
  - *Efficiency loss upon up-scaling*
  - *Slot die coating as preferred manufacturing technology*
  - *Commercial readiness timeline: Commercial module shipments began in earnest in 2024, with full mass-market deployment expected between 2026 and 2029.*
  - *The LCA picture is distinctly positive compared to fossil energy, and generally competitive with silicon PV*

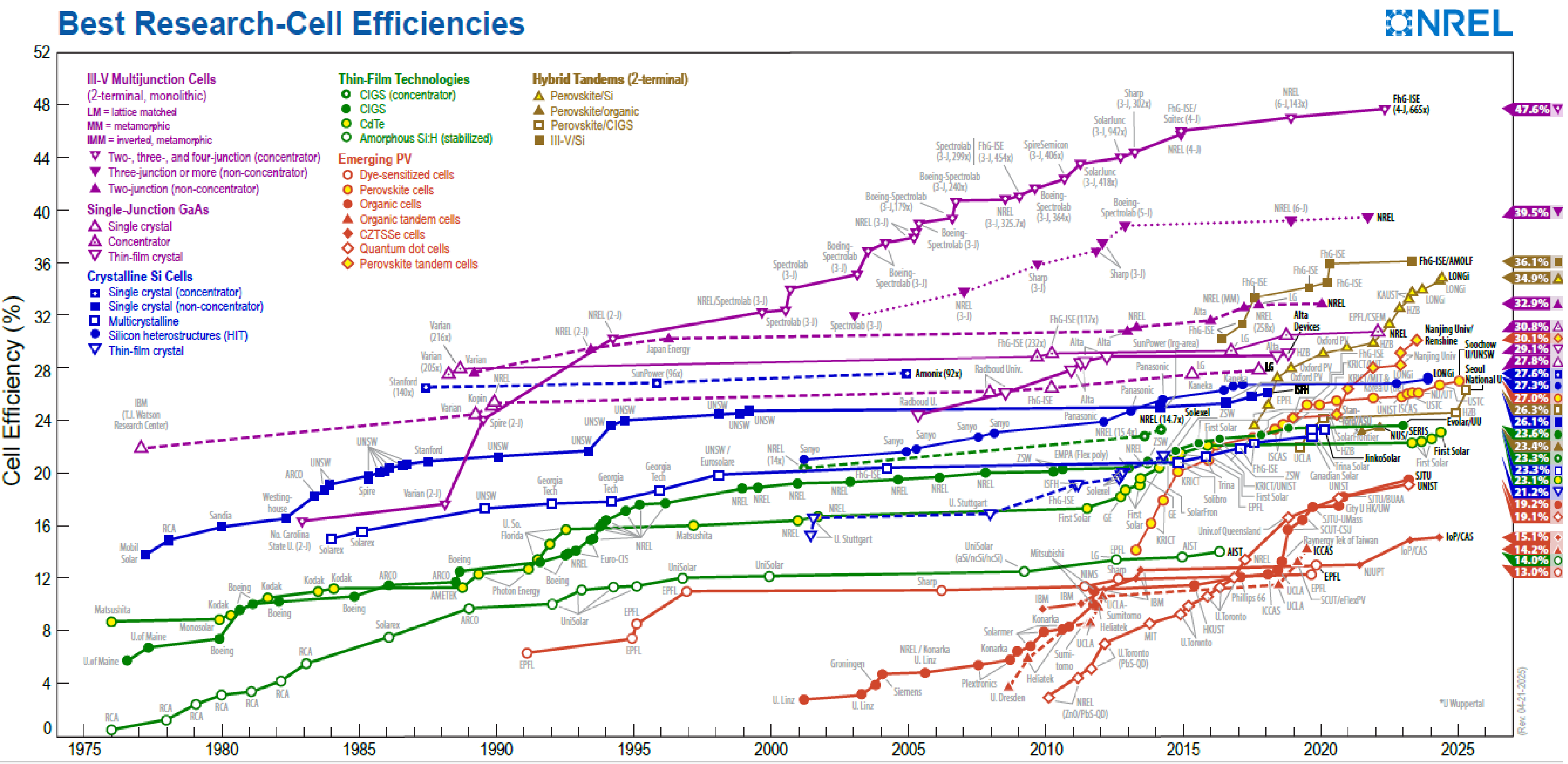
2.3B Hybrid solar cells - Quantum dot



Nanoproperties: change in properties of due to its physical size. The image shows CdSe-CdS core-shell nanoparticles with various diameters.

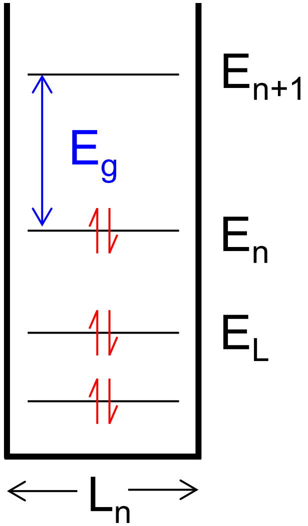
E. Roduner, *Size matters: why nanomaterials are different* , Chem. Soc. Rev., 2006,35, 583–592

NREL Efficiency Chart



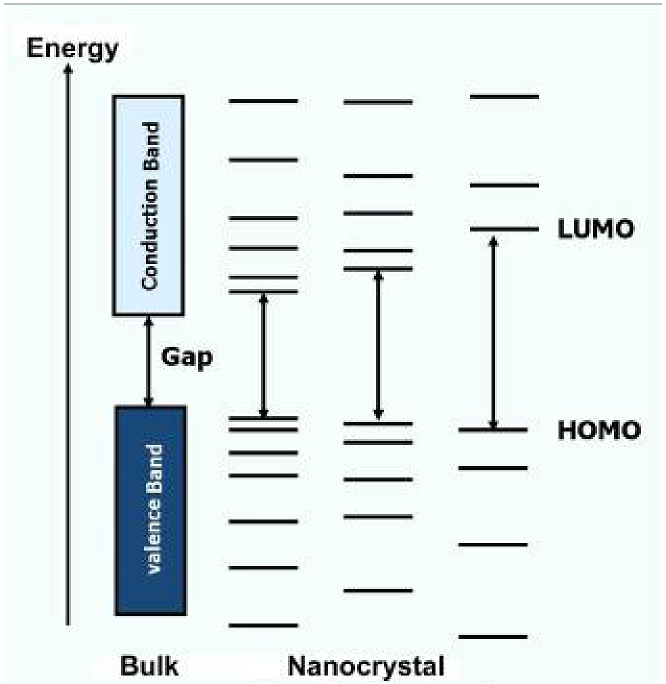
Quantum Confinement Effect

Particle in a box model



$$E_n = \frac{n^2 h^2}{8 m_e {L_n}^2}$$

where, $L_n \approx n \cdot L_0$
(for large enough box length)



$$n_1 > n_2 > n_3$$

$$Band\ gap\ (E_g) = E_{n+1} - E_n$$

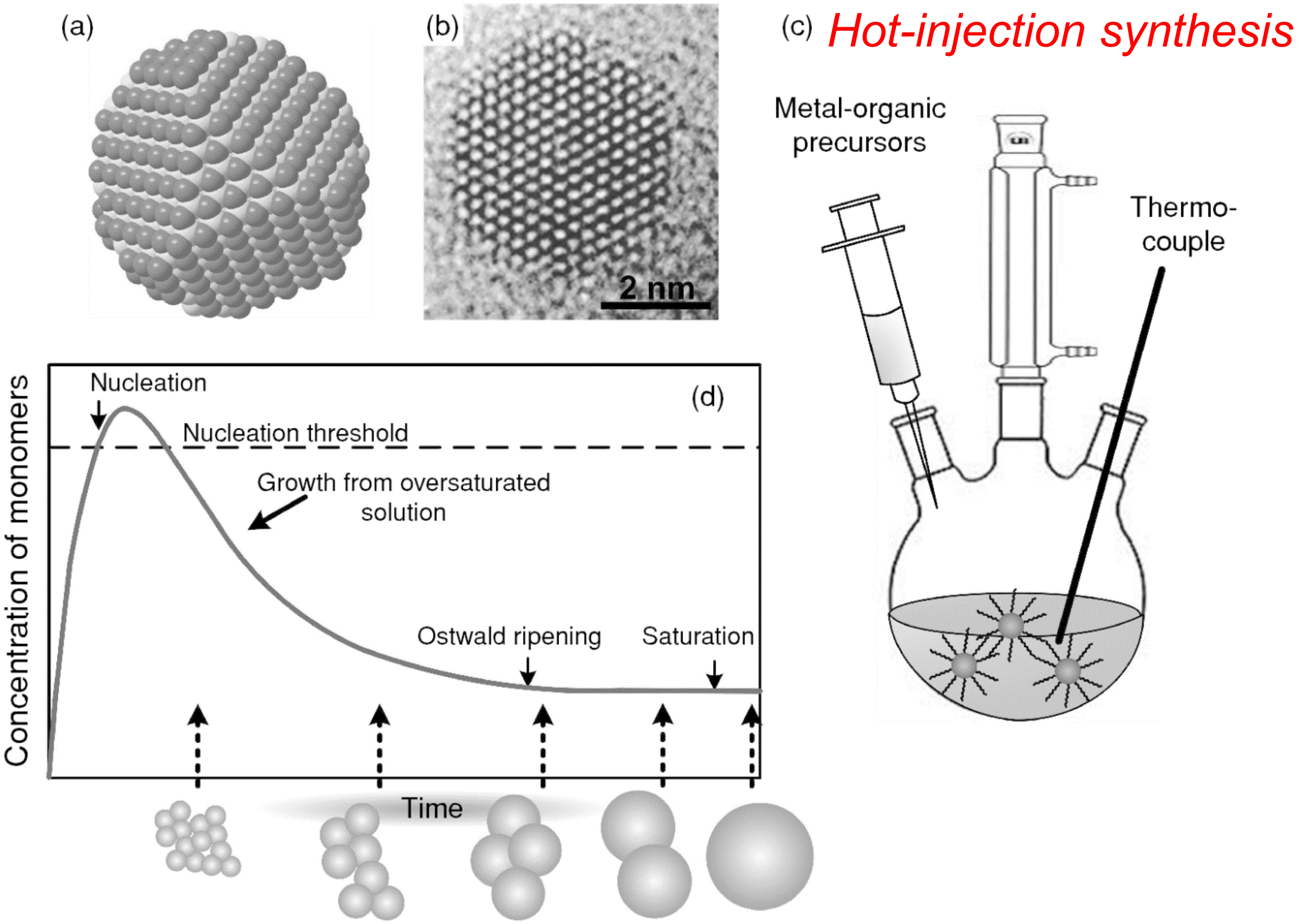
$$= \frac{(n+1)^2 h^2}{8 m_e {L_n}^2} - \frac{n^2 h^2}{8 m_e {L_n}^2} = \frac{h^2}{8 m_e {L_n}^2}\left((n+1)^2 - n^2\right)$$

$$= \frac{h^2}{8 m_e (n.L_0)^2}\ (2\mathrm{n} + 1)$$

$$E_g = \frac{h^2}{8 m_e (L_0)^2}\ \left(\frac{2}{n} + \frac{1}{n^2}\right)$$

$$\boxed{E_g \propto \frac{1}{n}}$$

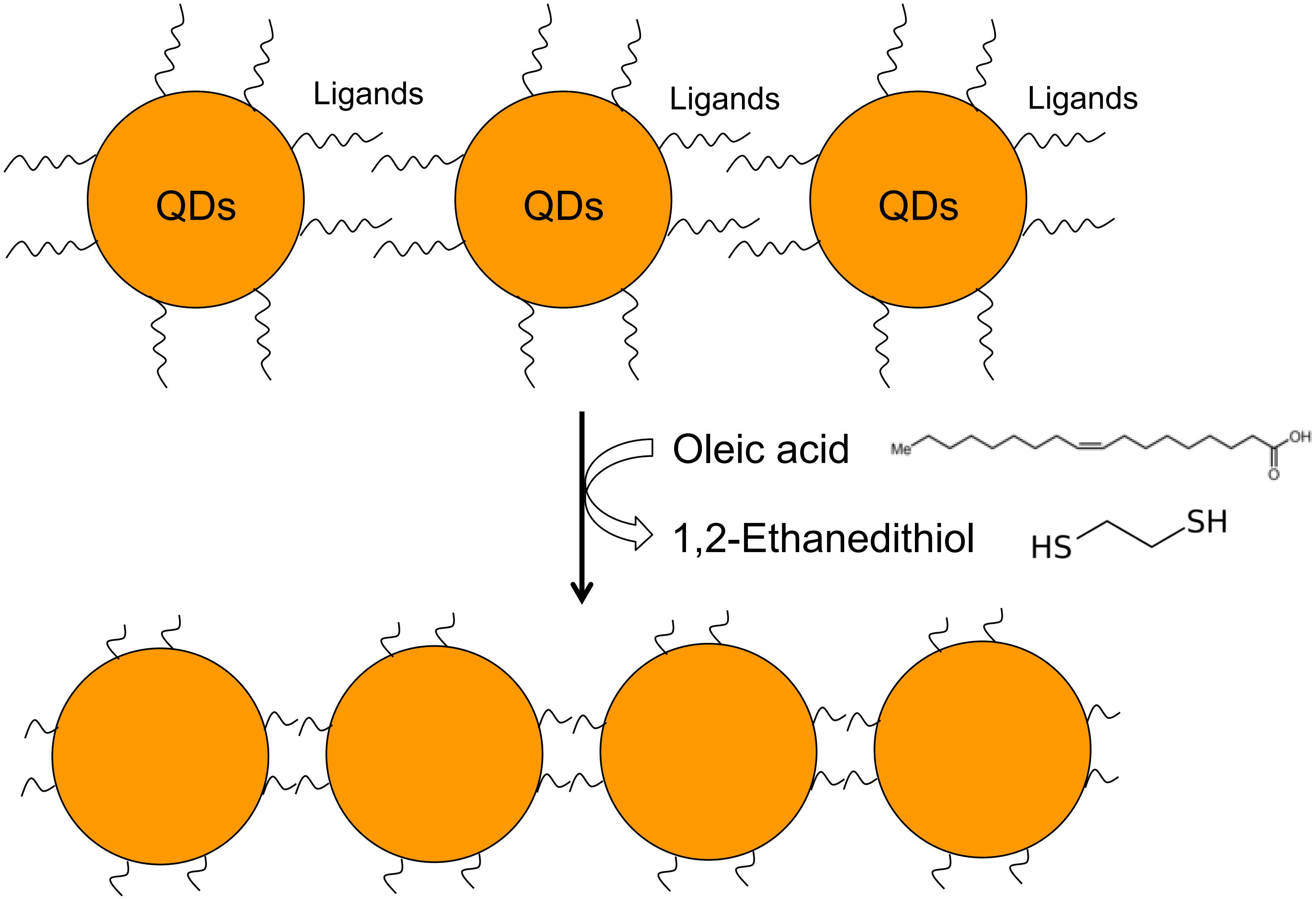
Thermodynamics and Kinetics in QDs Synthesis



Hot-injection synthesis

Bodnarchuk, M., & Kovalenko, M. (2013). *Colloidal Quantum Dot Optoelectronics and Photovoltaics* (pp. 1-29). Cambridge University Press.

Ligand Exchange

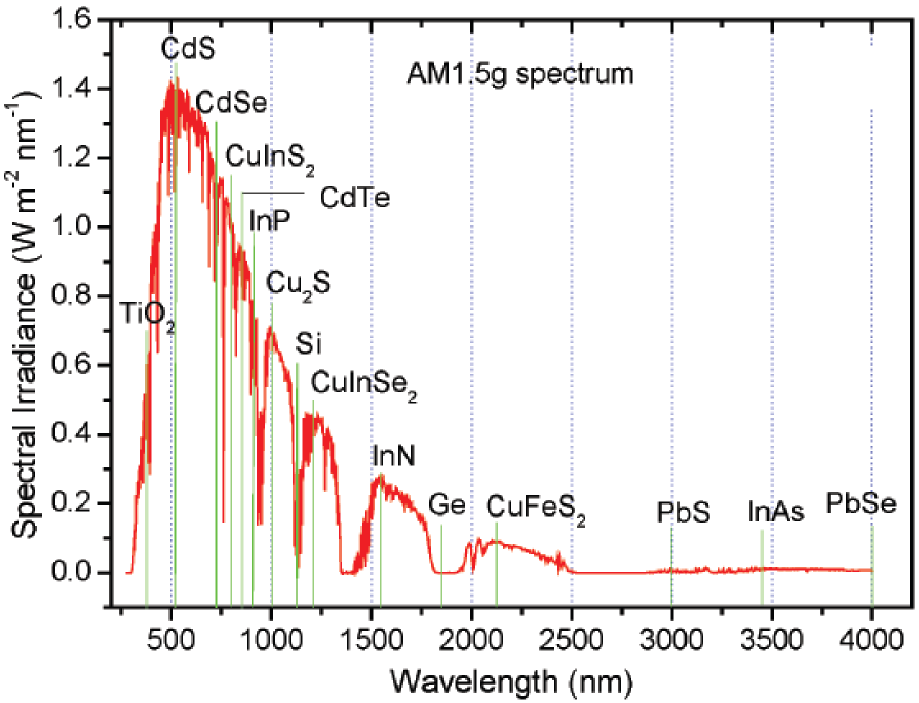


Oleic acid

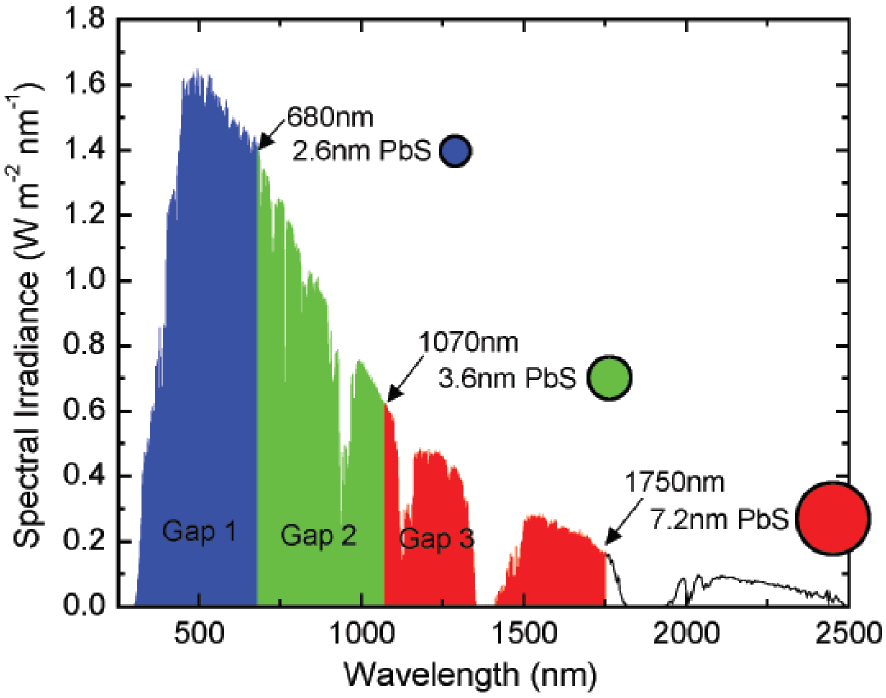
1,2-Ethanedithiol

Band gap tunability in QDs

Changing the material of nanocrystals

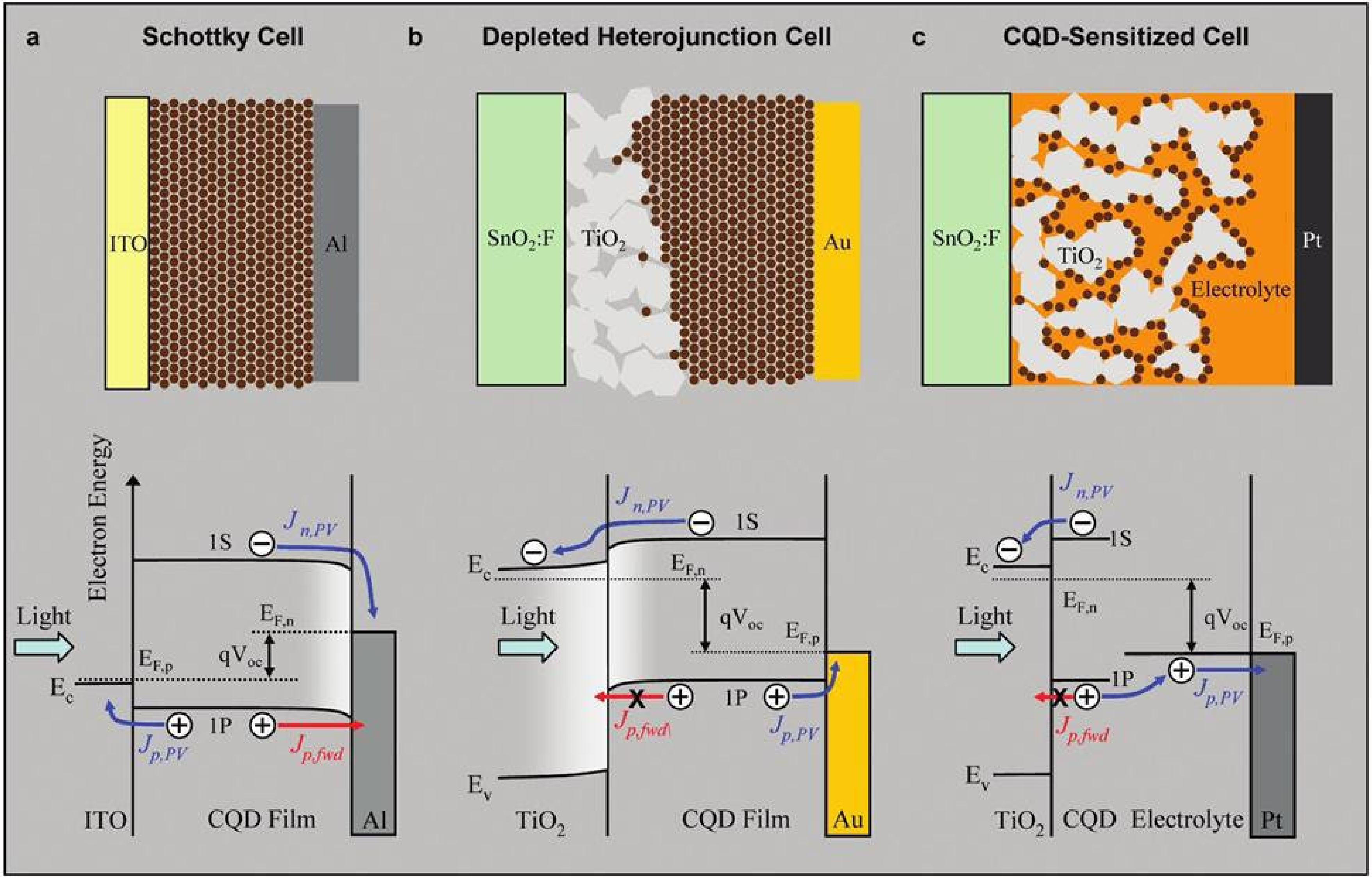


Changing the radius of nanocrystals - quantum confinement effect



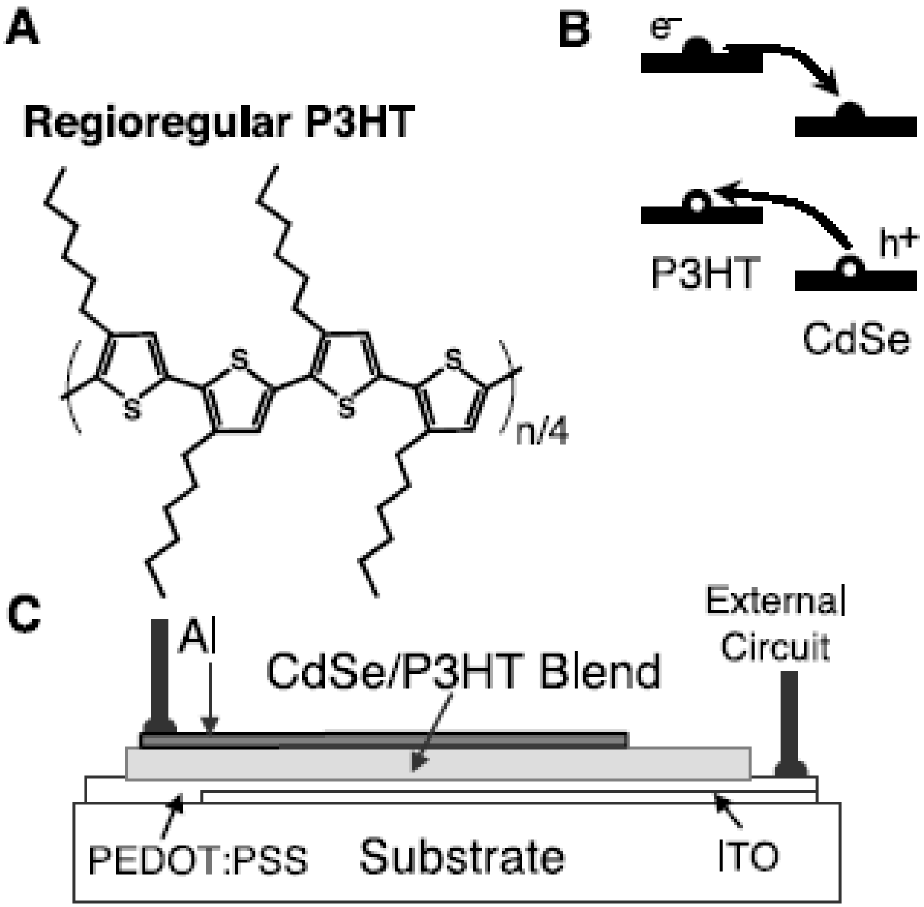
→ J. Tang, E.H. Sargent, *Adv. Mater.* **13**, 12 (2011)

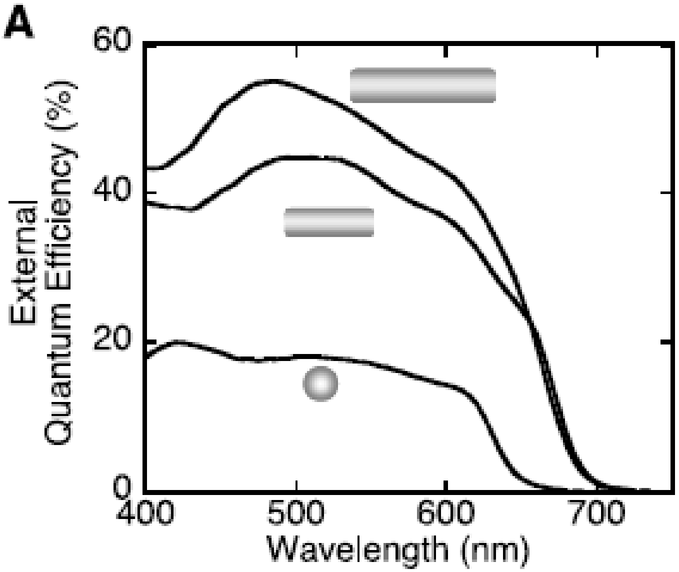
Design of „real“ QD solar cells



Uni Toronto, Sargent`s group web-site, 2012

Hybrid QD-polymer cells

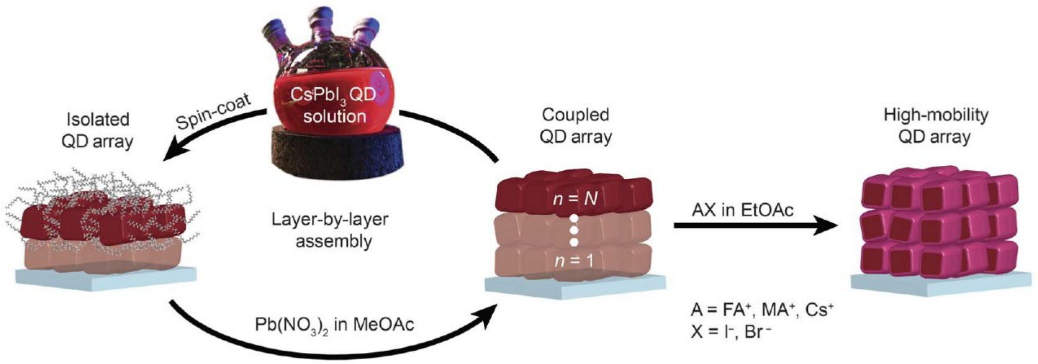




Efficiency is higher for nanorods due to better charge transport (1.7%)

W. U. Huynh *et al.*, Science **295**, 2425 (2002)

Perovskite Quantum Dot Solar Cells



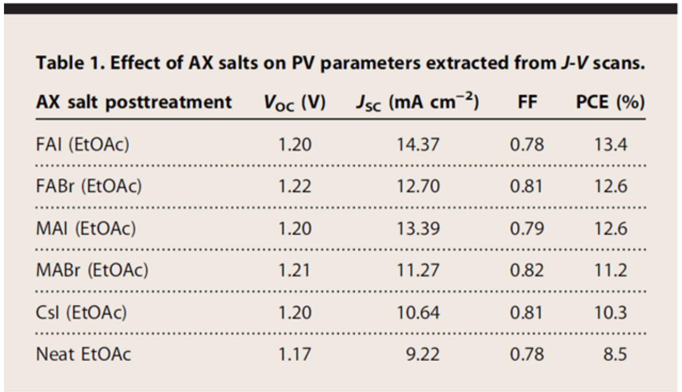
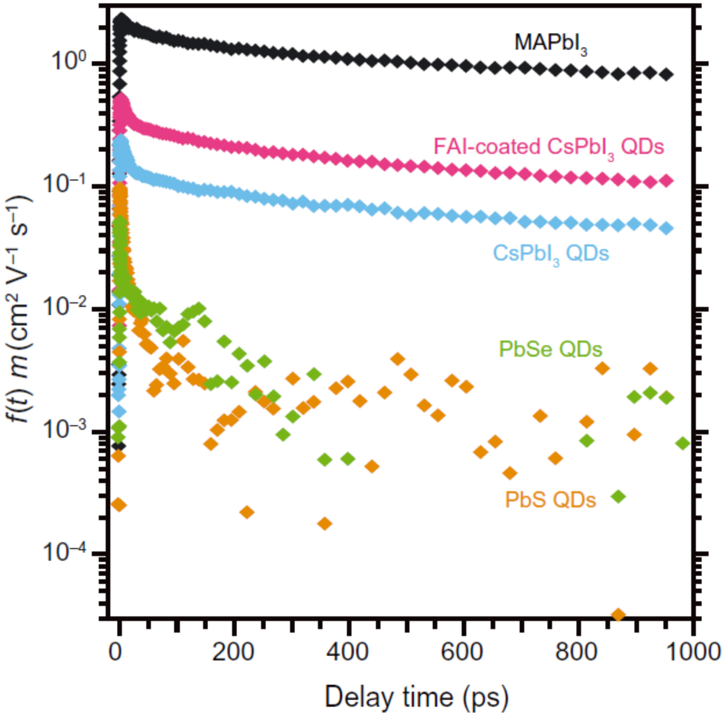
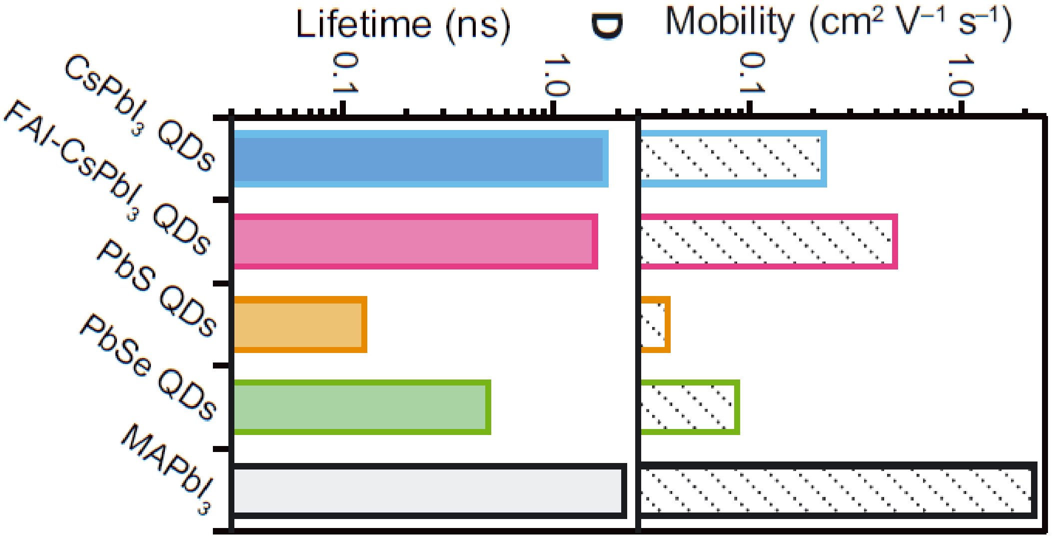


Table 1. Effect of AX salts on PV parameters extracted from *J-V* scans.

AX salt posttreatment	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	PCE (%)
FAI (EtOAc)	1.20	14.37	0.78	13.4
FABr (EtOAc)	1.22	12.70	0.81	12.6
MAI (EtOAc)	1.20	13.39	0.79	12.6
MABr (EtOAc)	1.21	11.27	0.82	11.2
CsI (EtOAc)	1.20	10.64	0.81	10.3
Neat EtOAc	1.17	9.22	0.78	8.5





Sanehira et al., Sci. Adv. (2017) 3

Upcoming Materials

- Transition metal dichalcogenides or 2D materials
- Perovskite quantum dot solar cells
- 2D perovskites
- Hybrid Perovskite QDs on Silicon cells
- and more….