

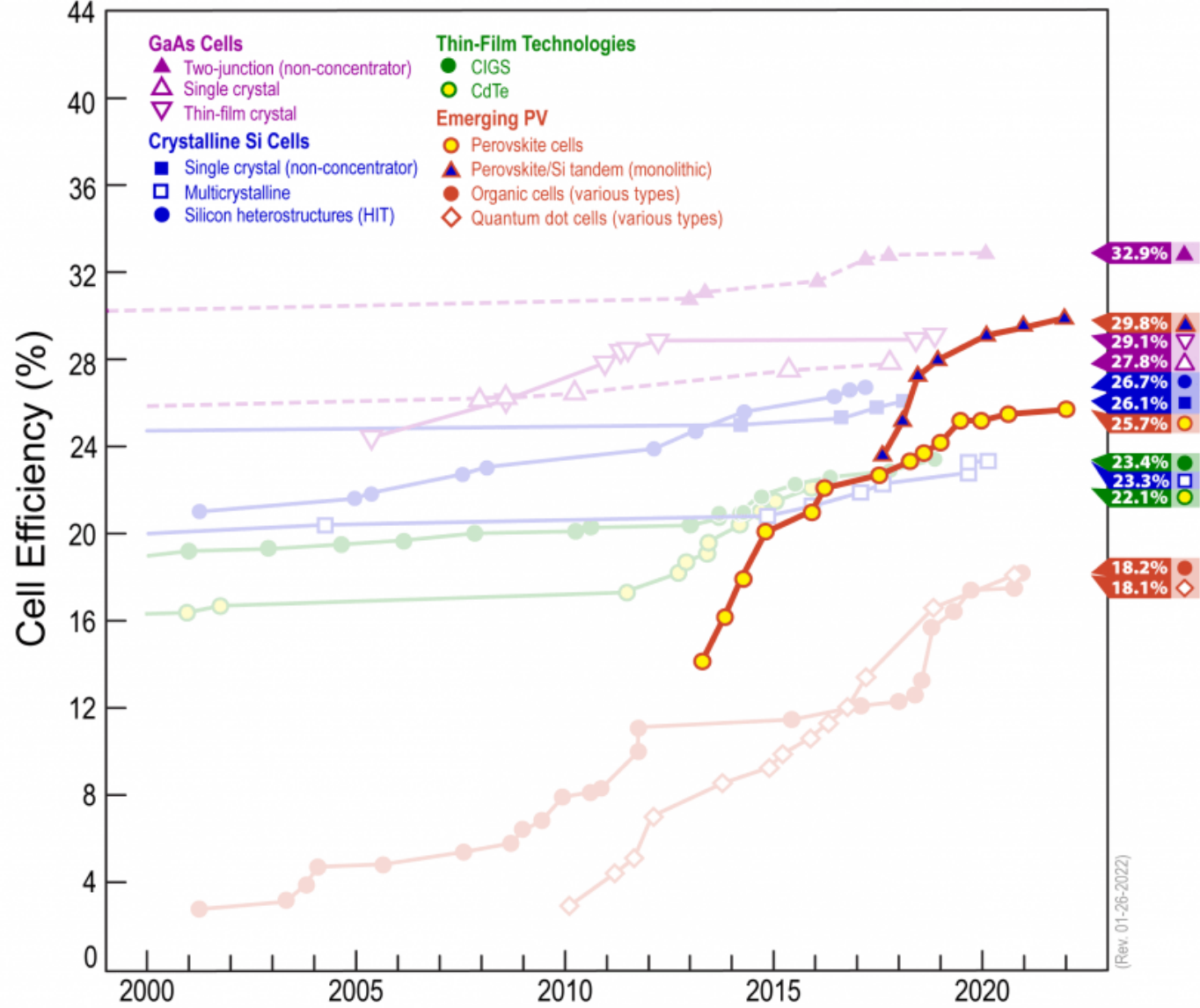
3.3A Hybrid solar cells - Perovskites

Learning goals

- ❑ What are Perovskite solar cells?
- ❑ Why are they so good?
- ❑ Architectures? How are they made?
- ❑ Strategies towards high efficiency cells
- ❑ Tandem cells
- ❑ Challenges towards industrialization
 - ❑ Stability
 - ❑ Lead
 - ❑ Up-scaling



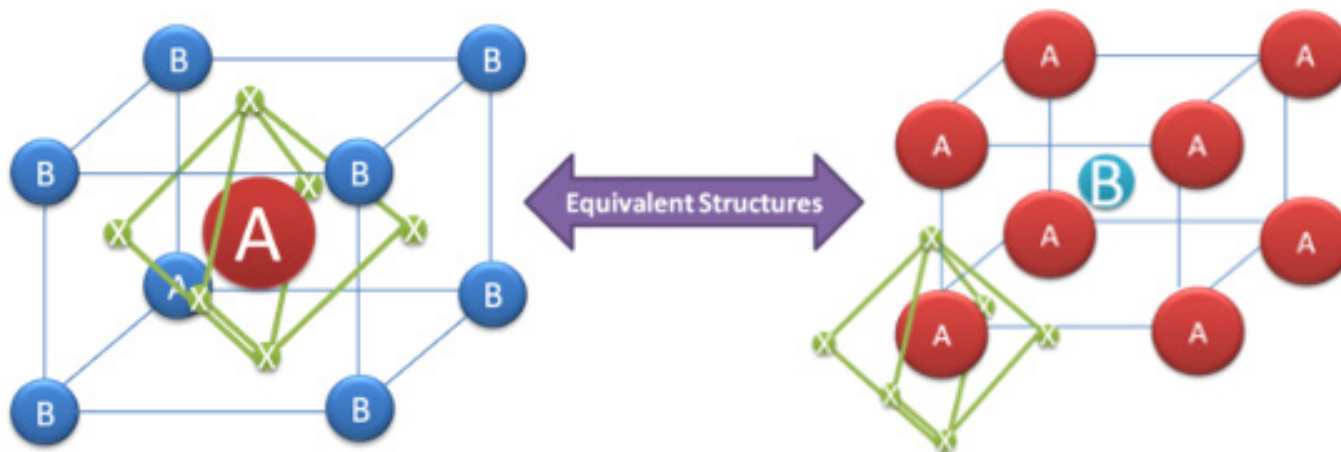
Best Research-Cell Efficiencies



(Rev. 01-26-2022)

Perovskite

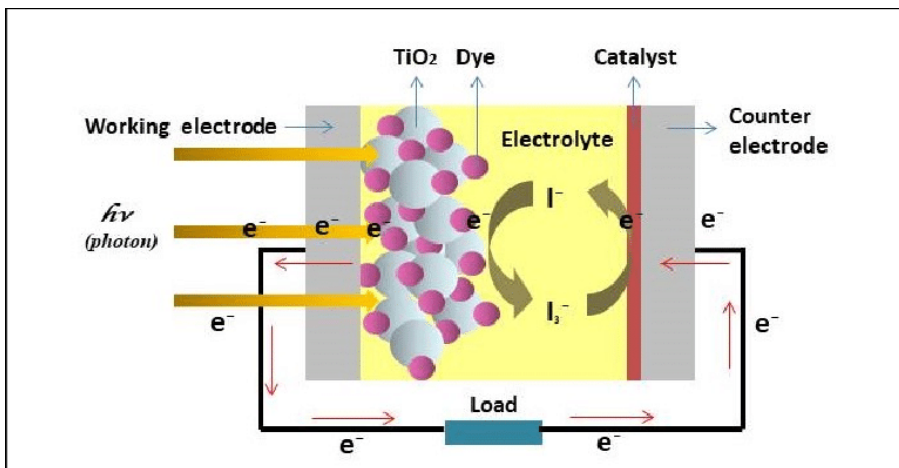
- ❑ The original **perovskite** (the mineral) is composed of calcium, titanium and oxygen in the form CaTiO_3 .
- ❑ Today: any crystal structure of the form ABX_3



❑ Typically:

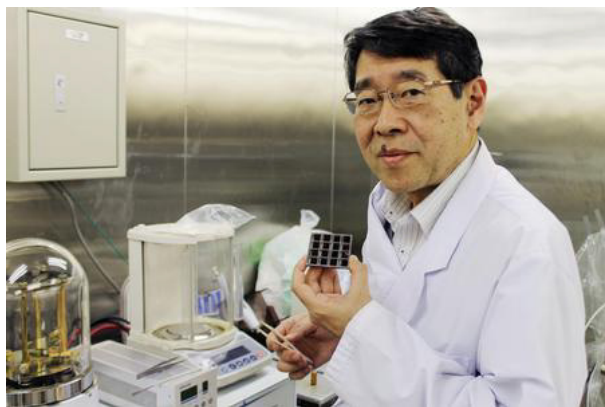
- ❑ A = An organic cation – methylammonium (CH_3NH_3^+) or formamidinium ($\text{NH}_2\text{CHNH}_2^+$)
- ❑ B = A big inorganic cation – usually lead(II) (Pb_2^+)
- ❑ X_3 = A slightly smaller halogen anion – usually chloride (Cl^-) or iodide (I^-)

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

MAPbI₃ 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)

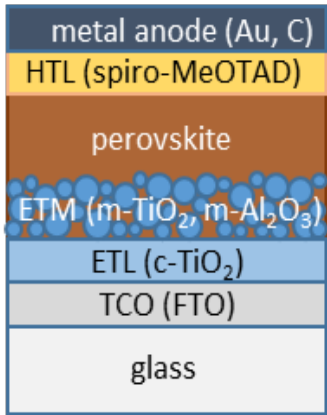
Why do perovskite solar cells work so well?

- ❑ **Good crystallinity**, large grains (few defects, reduced grain boundary scattering)
- ❑ High **absorption coefficient** (direct bandgap semiconductor)
- ❑ Low **exciton binding energy** (thermal generation of charge carriers)
- ❑ Long **carrier diffusion length**
- ❑ High **defect tolerance**
- ❑ **Tunable bandgap** allows for the fabrication of tandem or multi-junction cells, where two or more PSCs with different band gaps are stacked on top of each other, or on top of a silicon or thin-film solar cell (**tandem cells**)

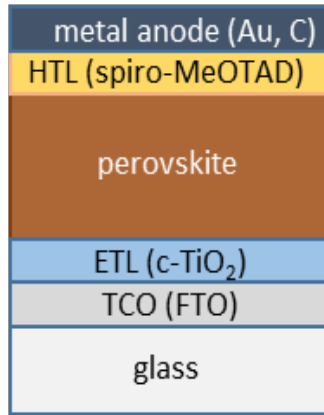
Various device architectures

(e) HTL-free mesoscopic carbon-based (CPSC)

(a) *n-i-p mesoscopic*



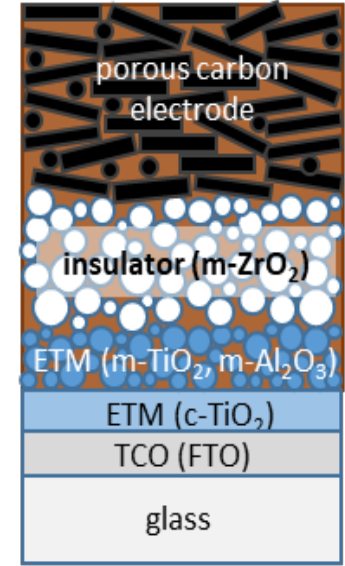
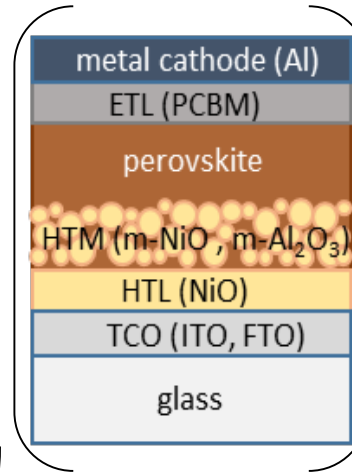
(b) *n-i-p planar*



(c) *p-i-n planar*



(d) *p-i-n mesoscopic*



No high sintering temperatures

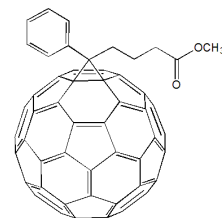
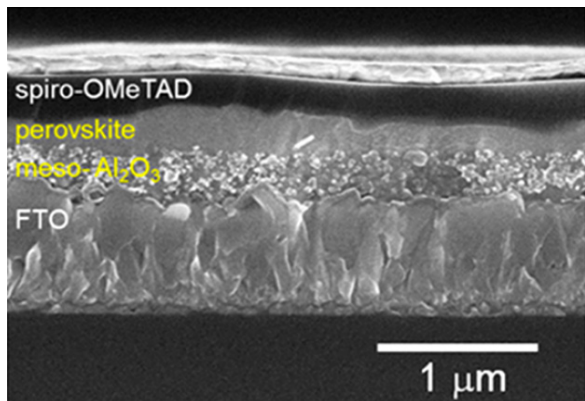
All architectures showed high efficiencies

Planar: higher charge mobilities and slower trap-mediated recombination

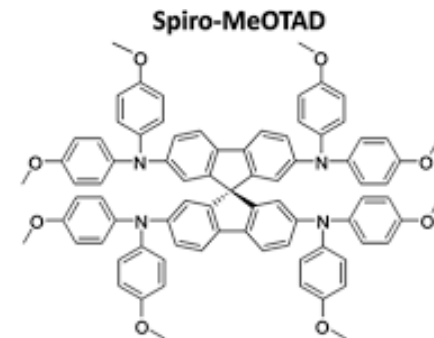
Mesoscopic: less interfacial recombination at ITO electrode

Examples of typical cell architectures

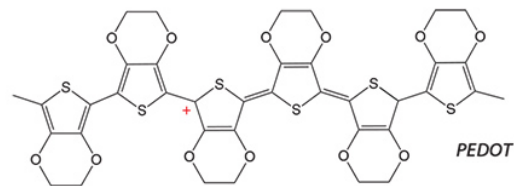
«mesoscopic n-i-p (Al_2O_3)»



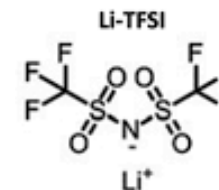
PCBM



Spiro-MeOTAD

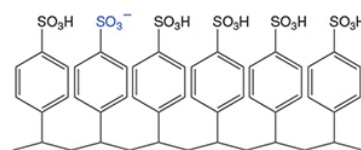


PEDOT+



Li-TFSI

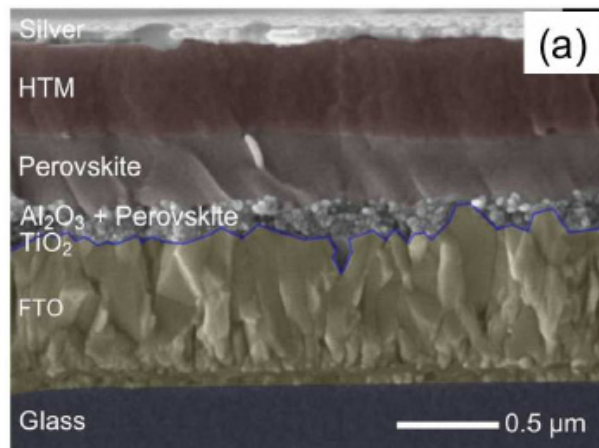
Li+



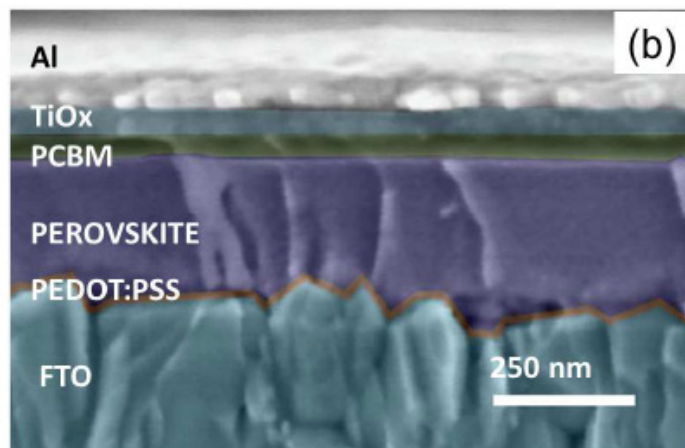
PSS-

PEDOT:PSS

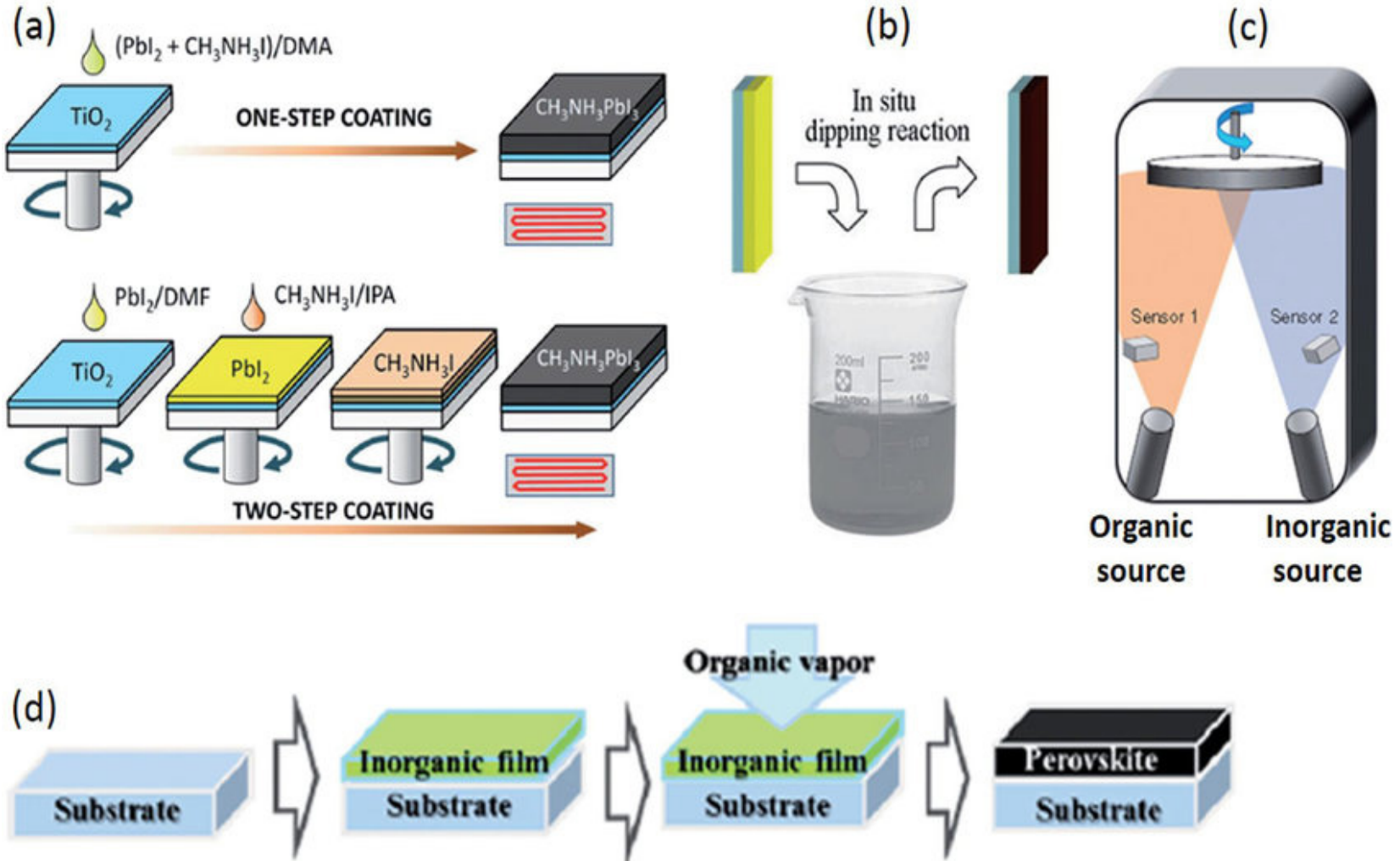
«mesoscopic n-i-p (TiO_2)»



«planar p-i-n»

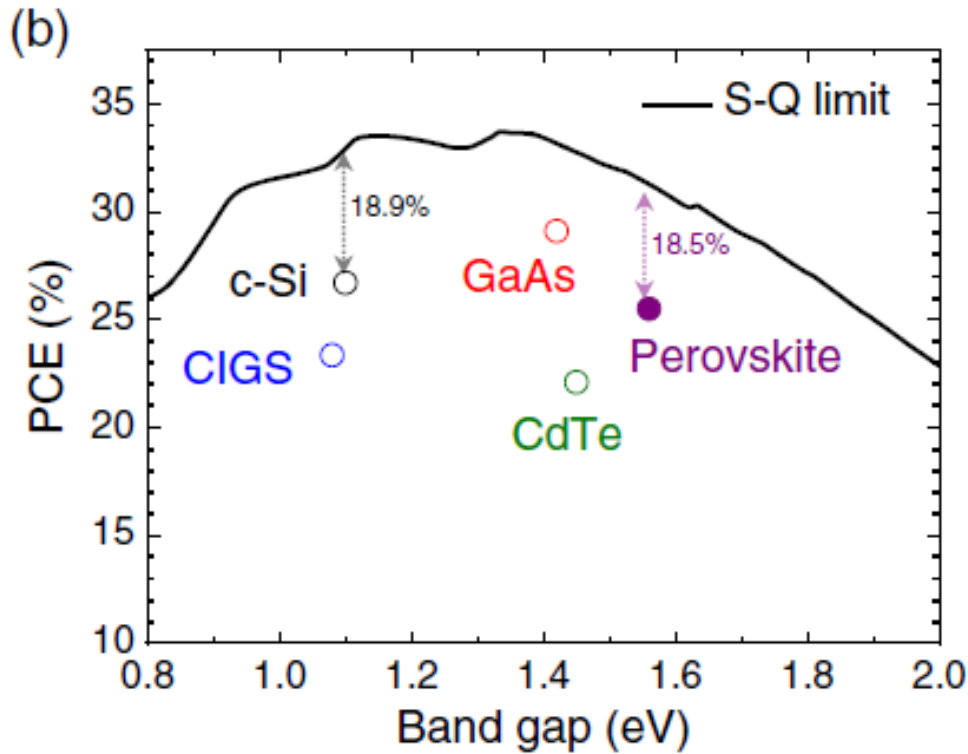


Growth methods of perovskite films



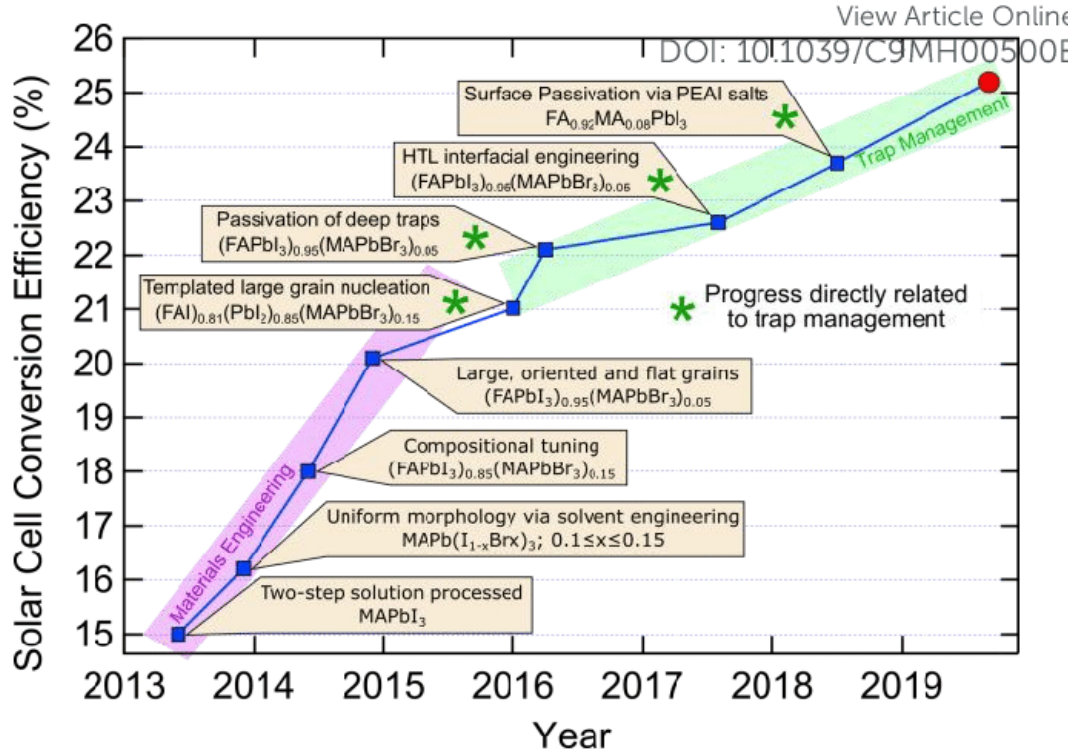
Efficiency improvement

How much better can we get?



Typical cell size 5 cm²; efficiency measurement on 0.1 cm²

Efficiency improvement



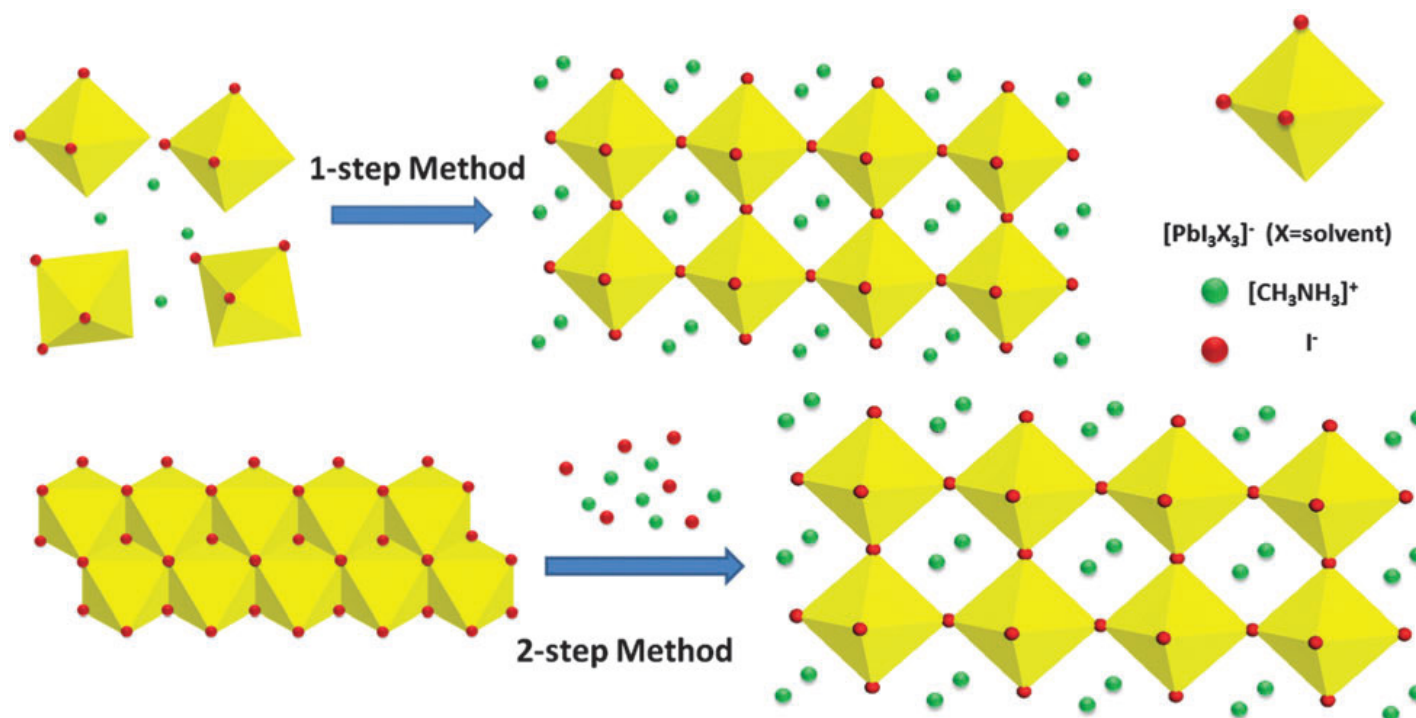
General strategies:

- 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.

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

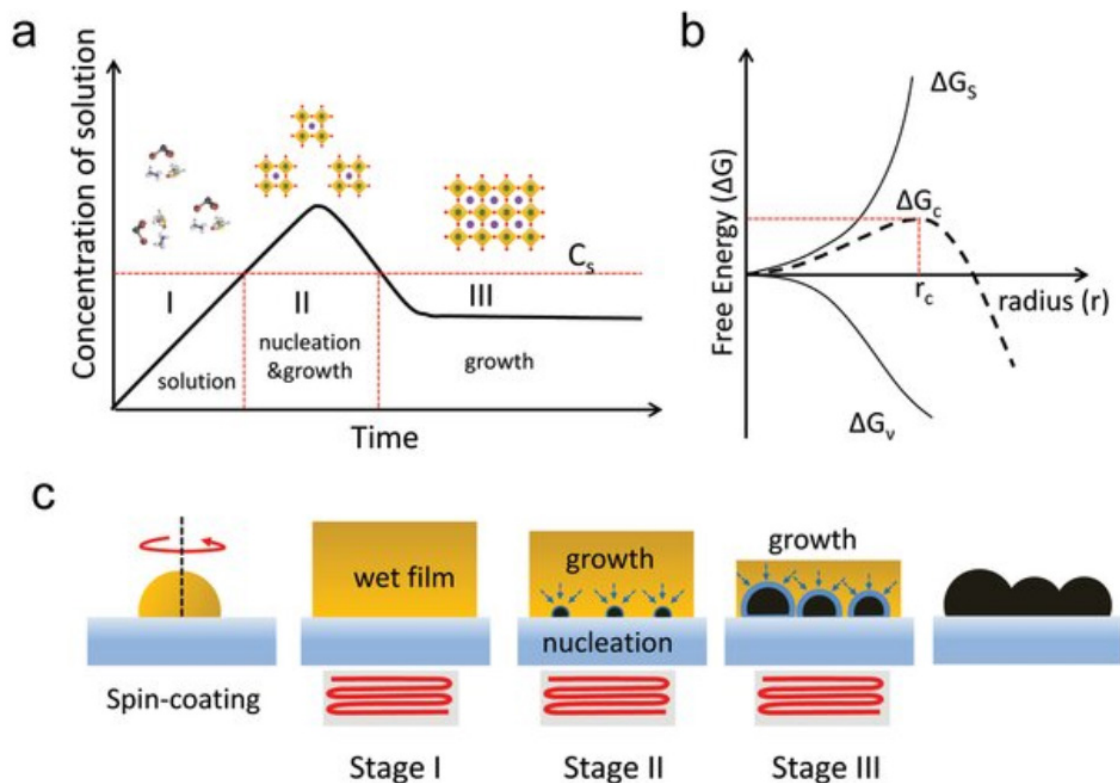
- Perovskite crystals can be grown from solution



- Both deposition methods have successfully produced devices with efficiency exceeding 23%
- Advantage of 2-step method: does not need inert atmosphere

Control of crystal growth of perovskite films

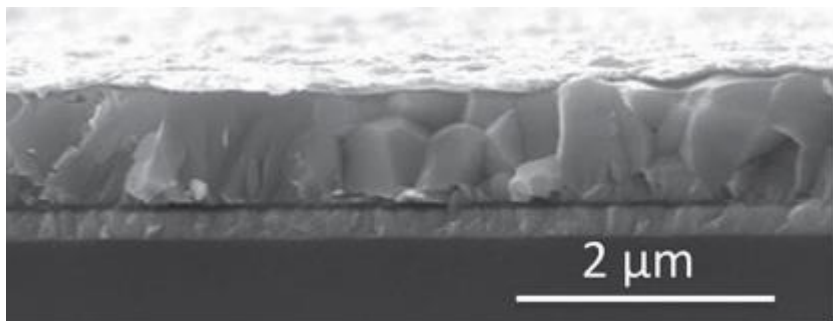
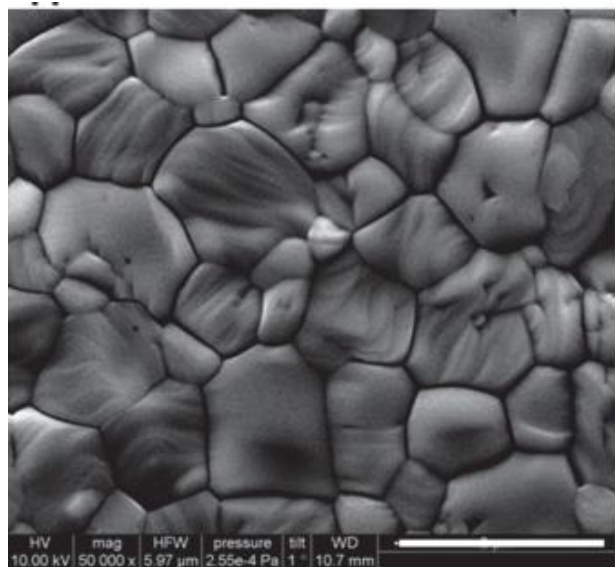
- Three different stages for crystallization of perovskite films according to the La Mer mechanism.



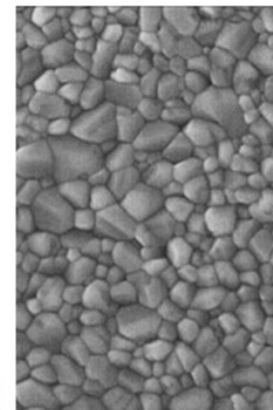
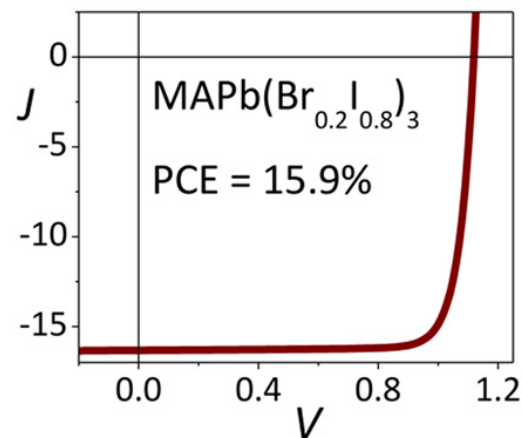
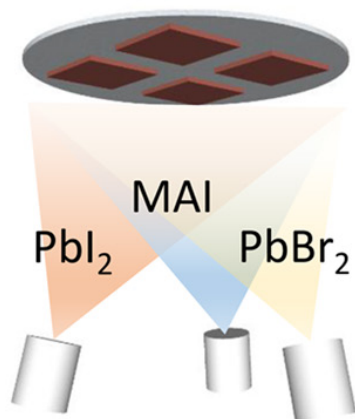
- Crystal growth of perovskite films can be tuned by control of either nucleation or crystal growth

Good crystallinity and large grains

Solution-processed



Vacuum-processed



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

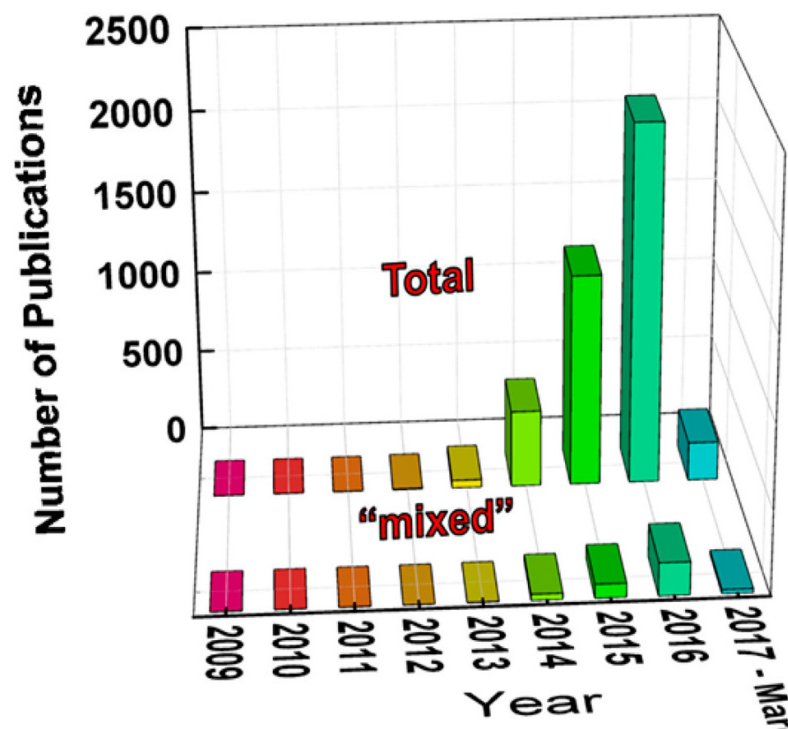
Snaith et al, *Nature* **501**, 395 (2013)

J. Huang et al., *Adv. Mater.* 2014

Longo and Bolink et.al. *ACS Energy Letters* (2018)

Composition engineering

- ❑ The most widely studied Perovskite for solarcell applications is methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) or MAPI for short

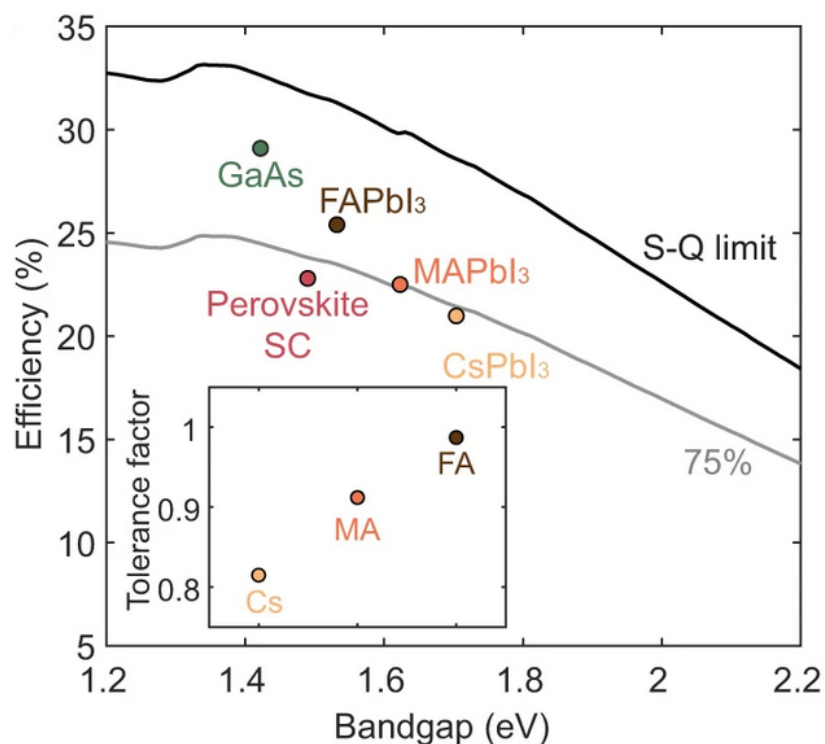


- ❑ Why composition engineering?

- ❑ A, B and/or X ion substitution affect the band gap, carrier transport, crystal structure and material stability
- ❑ Electronic characteristics are mainly determined by the B cations and X anions (they determine conduction and valence band)
- ❑ A cations indirectly affect electronic characteristics via dielectric constant and lattice parameters
- ❑ Trend: mixture of respective anions and cations

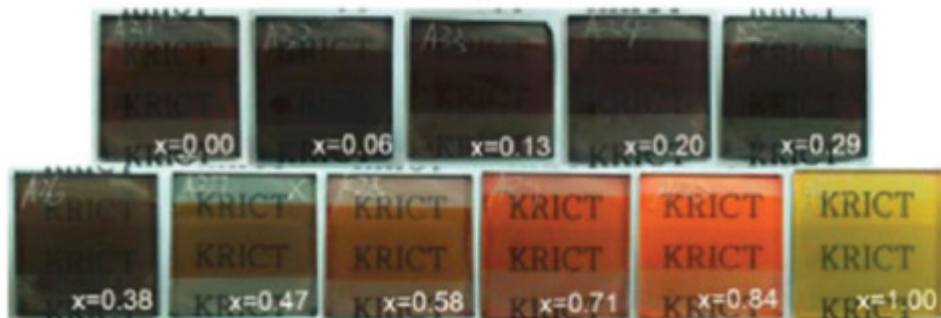
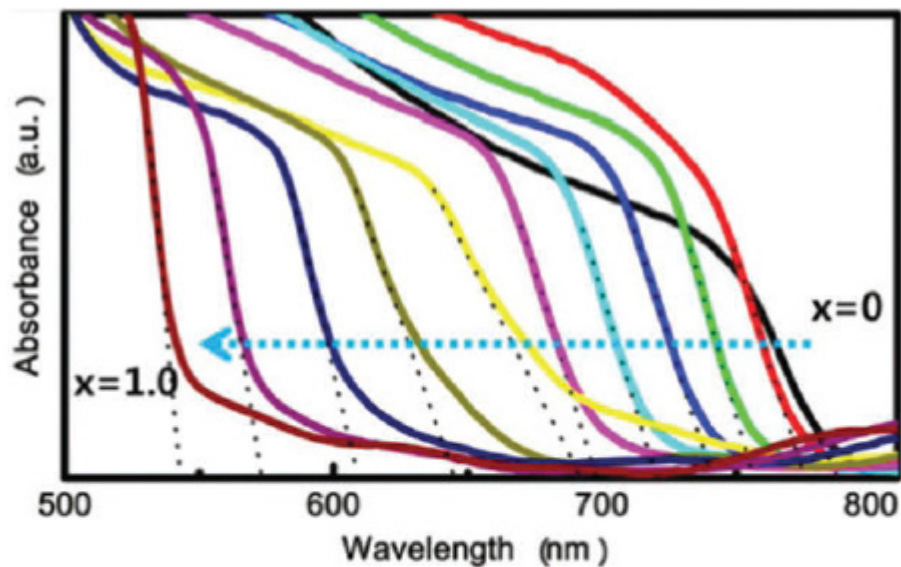
Ideal bandgap

- ❑ 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**)

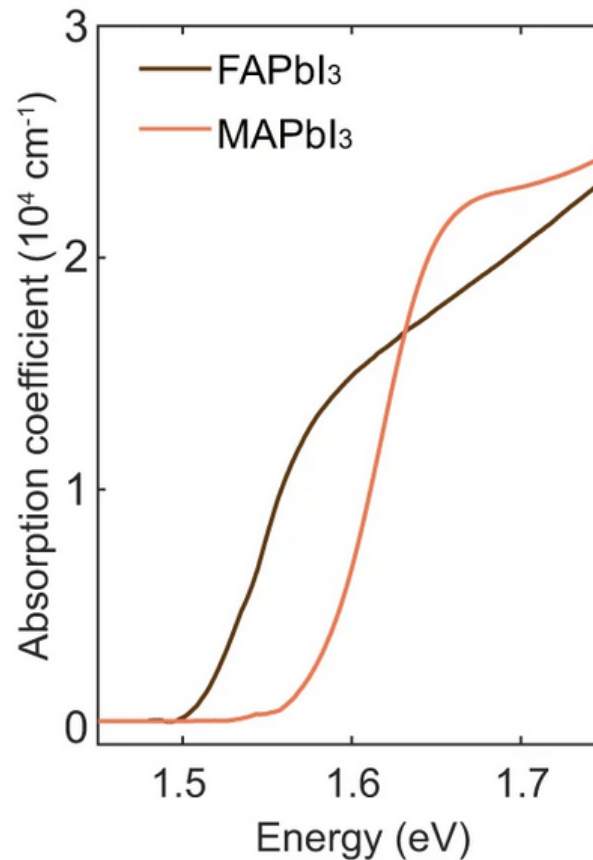


Feng, J., Wang, X., Li, J. et al. Resonant perovskite solar cells with extended band edge. Nat Commun 14, 5392 (2023). DOI:10.1038/s41467-023-41149-1

Bandgap engineering of $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ perovskites



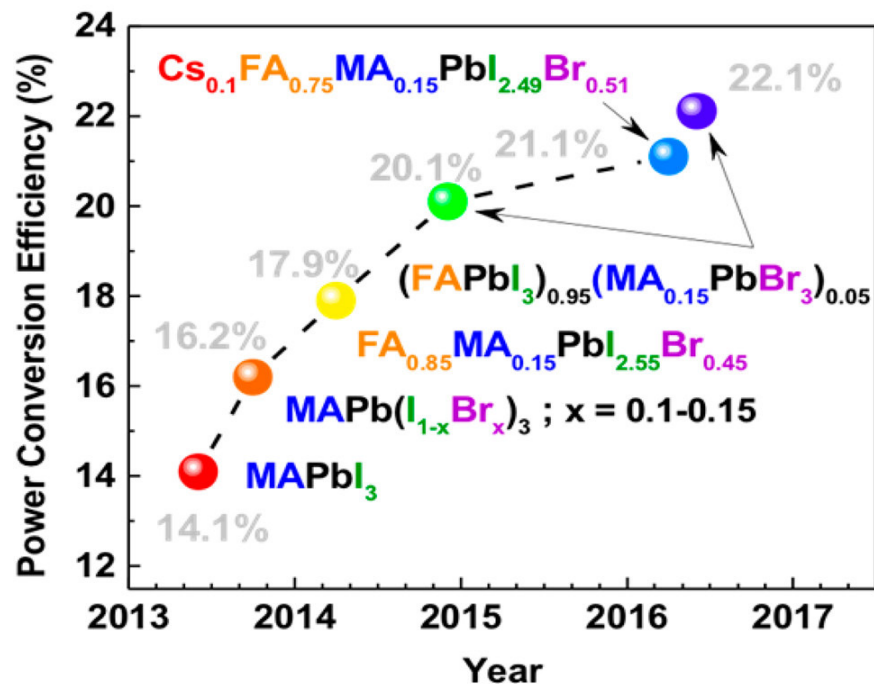
J. H. Noh, S. H. Im, J. H. Heo, T. N. Mandal and S. I. Seok, *Nano Lett.*, 2013, 13, 1764–1769.



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

Composition engineering

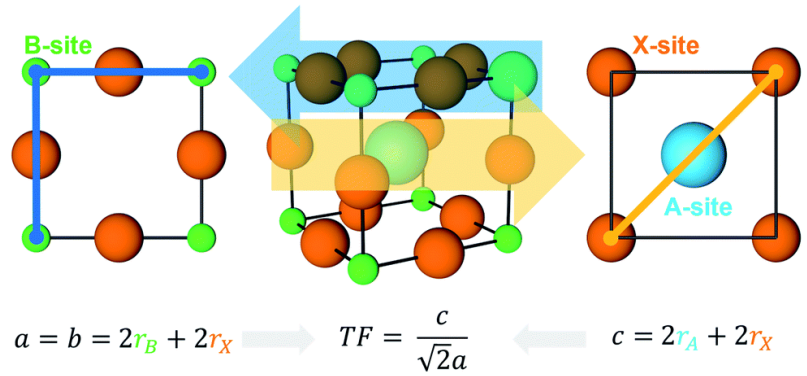
- Best research perovskite solar cells efficiencies certified by NREL. For each of certified efficiencies, the chemical compositions of mixed perovskites are specified.



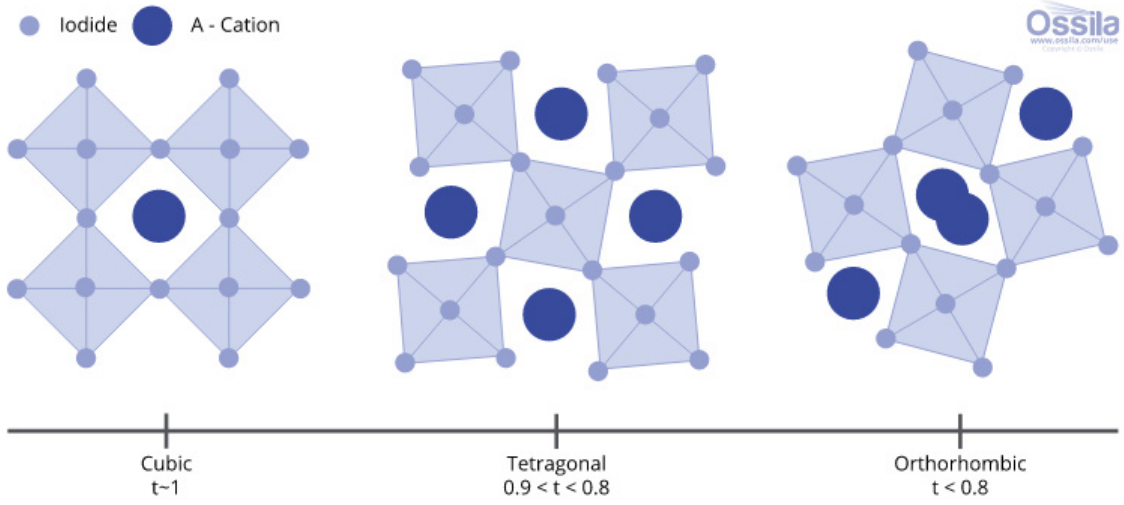
- The role of the additional cations as well as the mixed halides is yet to be fully understood
- Hypothesis: complementary size cations may help stabilizing the perovskite phase by tuning tolerance factor
- Similar size cation/anion, acts as defect passivator.

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.



Examples will be given in the excersises

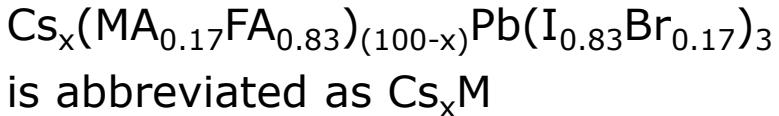
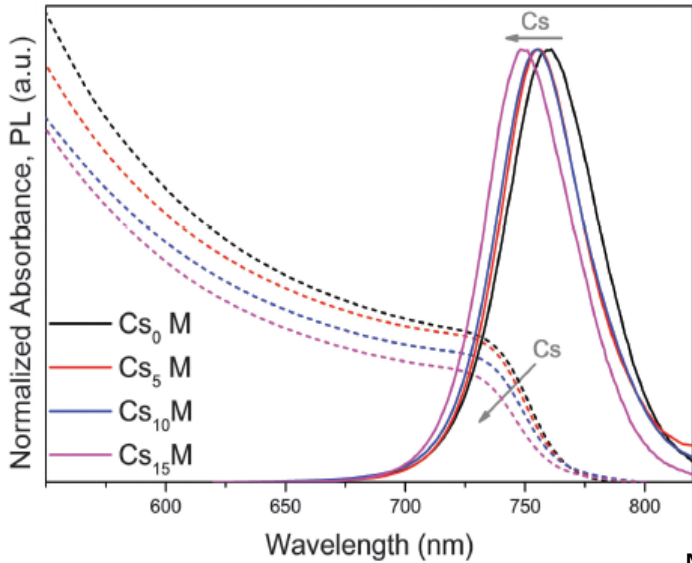
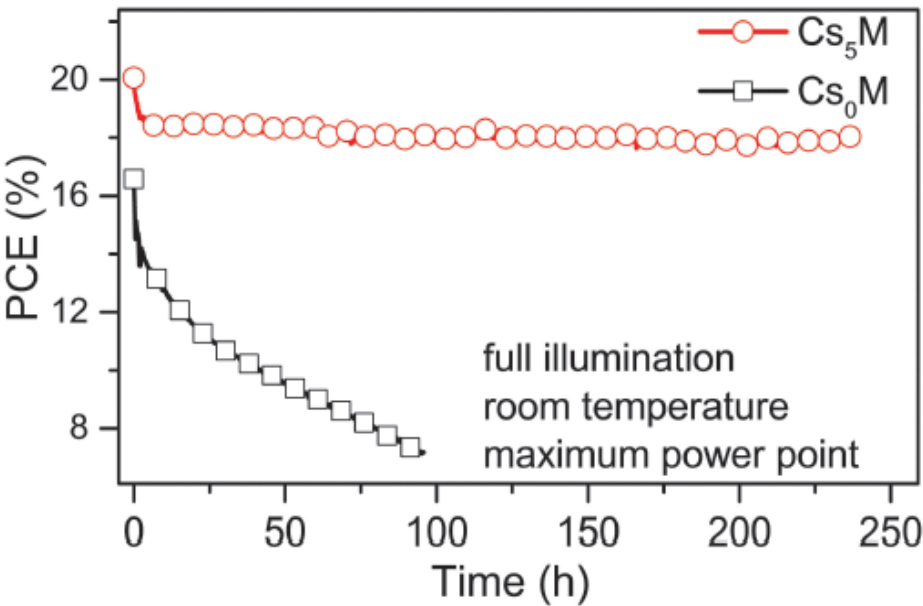
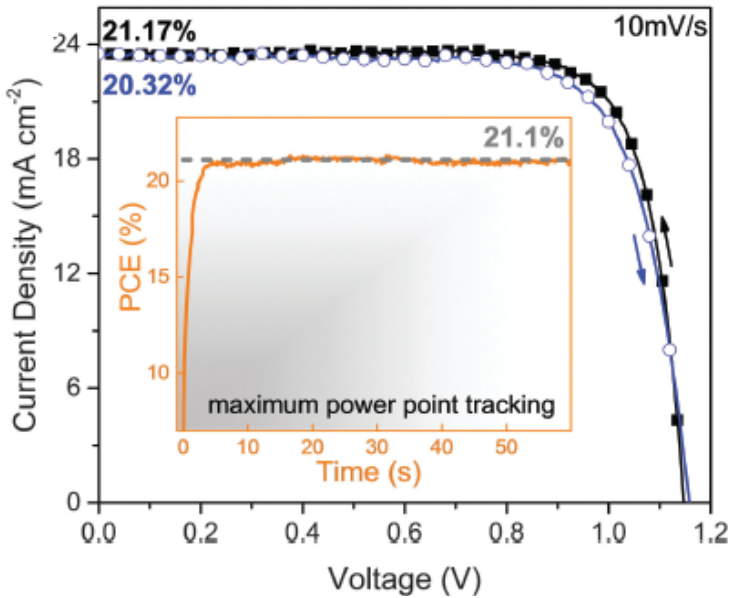


Composition engineering

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)

Cesium-containing triple cation perovskite solar cells



- improved stability
- reproducible fabrication
- enhanced lifetime

Defects in Perovskites

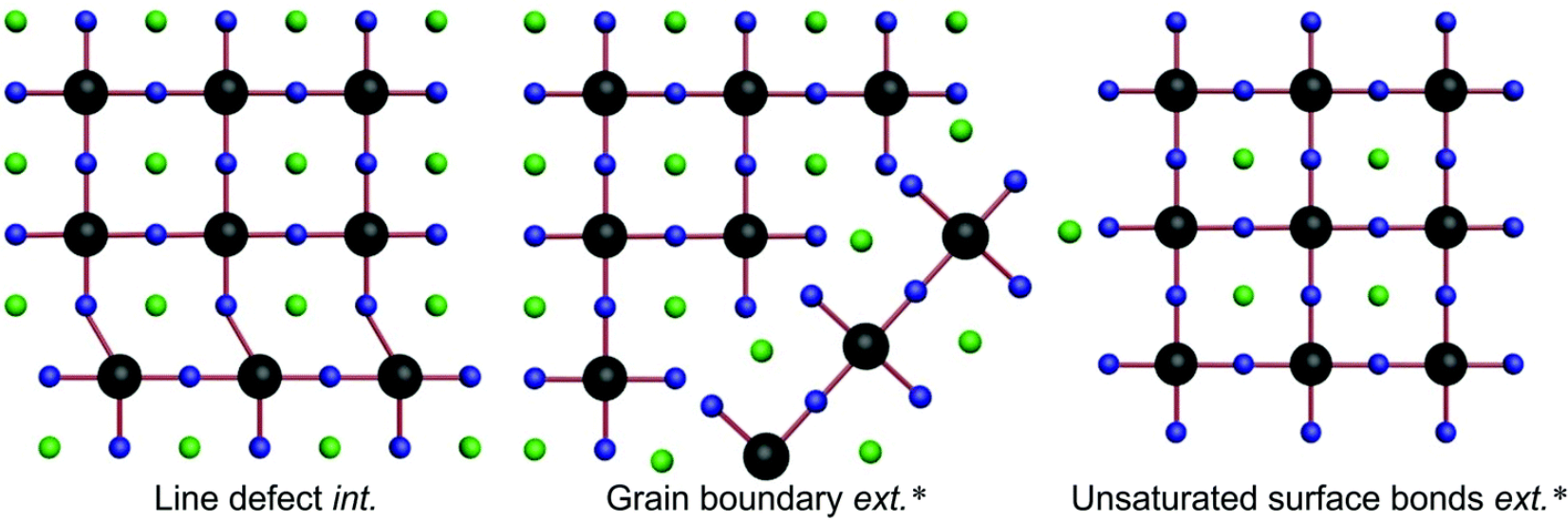
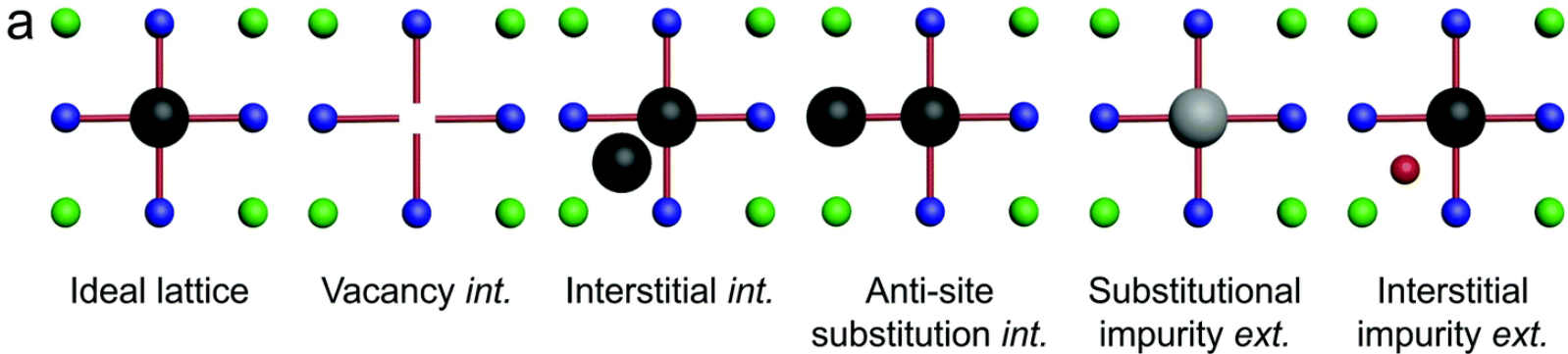
- ❑ Zero-dimensional (0D)
 - ❑ Vacancies, interstitials
 - ❑ Foreign atoms

- ❑ One-dimensional (1D)
 - ❑ Dislocations

- ❑ Two-dimensional (2D)
 - ❑ Grain boundaries
 - ❑ Also creates pathways for oxygen penetration!
 - ❑ Surfaces with dangling bonds

- ❑ Three-dimensional (3D)
 - ❑ Agglomerates
 - ❑ Pin holes

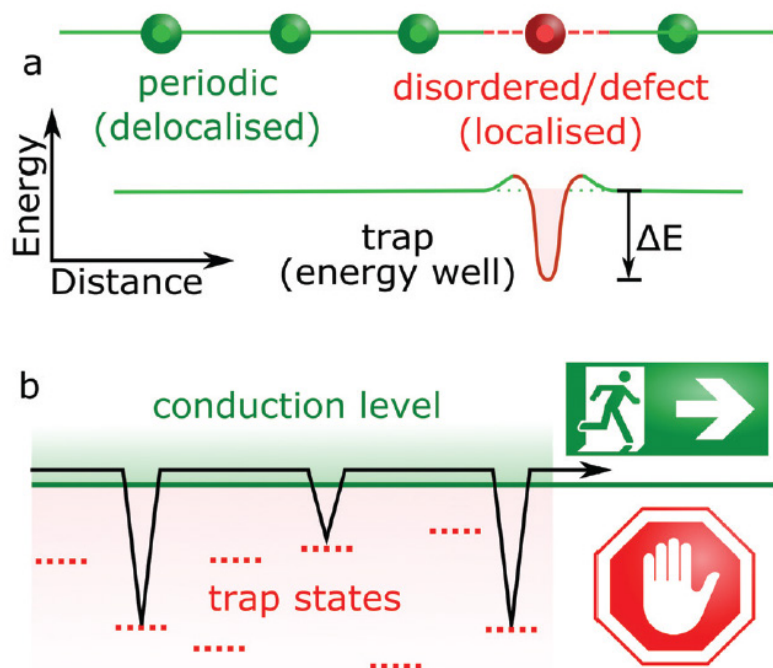
Defects in Perovskites



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

Defects in Perovskites

- Structural non-periodicity introduces disorder into the lattice bonding and orbital configuration, impacting the properties of free carriers moving through these orbitals

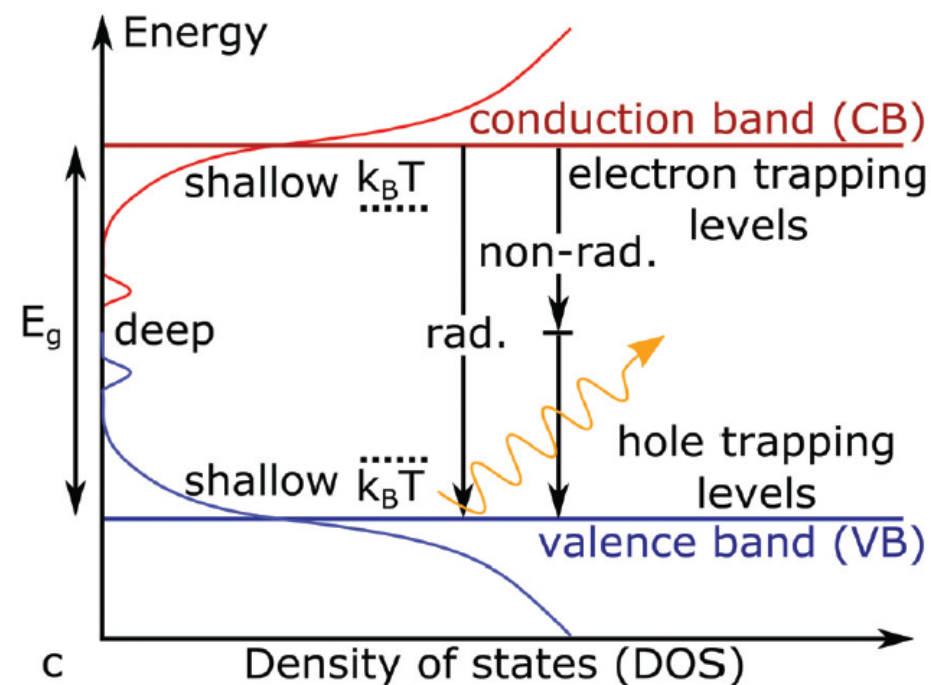


- The crystalline imperfections form localized electronic states at energy levels different to the carrier transport bands, providing means for (photo-) generated free carriers to energetically fall into and get trapped
- Once the free charge is captured and localised at a defect site, its fate will depend on the nature of the trap and can widely vary.

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

Defects in Perovskites

- Structural non-periodicity introduces disorder into the lattice bonding and orbital configuration, impacting the properties of free carriers moving through these orbitals

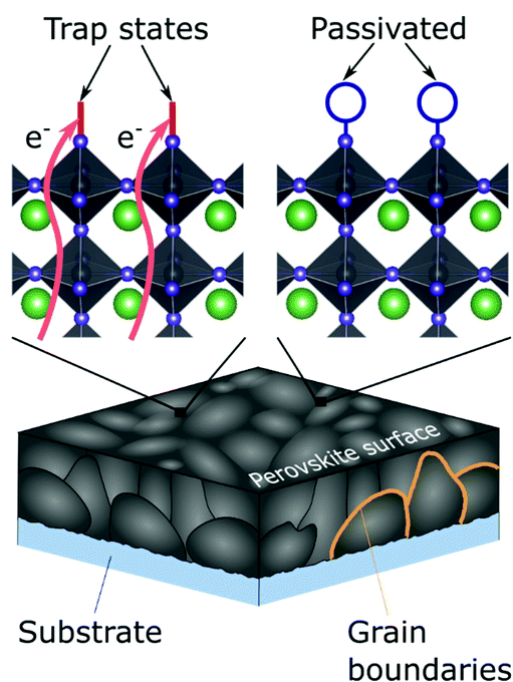


Jin et al., *Mater. Horiz.*, 2020, 7, 397-410;
DOI: 10.1039/C9MH00500E

- When captured on shallow traps at non-zero temperatures a charge can be thermally excited back to the transport band
- Deep traps hinder detrapping and can facilitate non-radiative recombination pathways
- Not all defects introduce carrier trapping; if a defect energy level resides above or below the conduction and valence band edges, the defect state is typically considered harmless.
- 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.

Defects in Perovskites

- ❑ The density of traps per unit volume and their relative energy in the electronic band structure strongly influence device performance
- ❑ The 'soft' crystal lattice, and subsequent low defect formation energies, are expected to introduce relatively large concentrations of defects in perovskites. However, the defect energy levels in LHPs favour the formation of relatively shallow and even benign states, making perovskites relatively tolerant to imperfections.

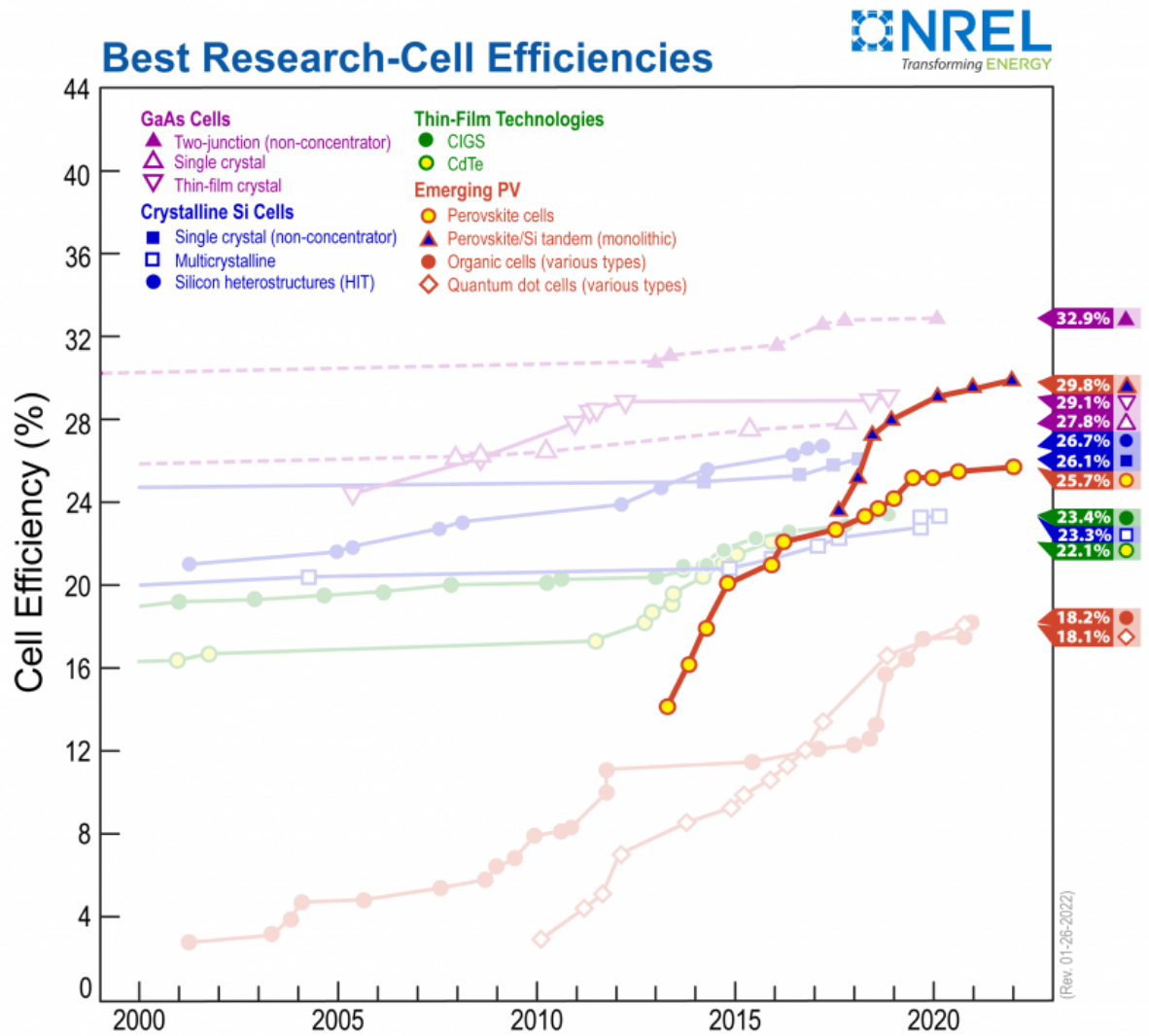


- ❑ Many strategies are developed to eliminate defects by post-processing
- ❑ Most successful strategies involve defect passivation

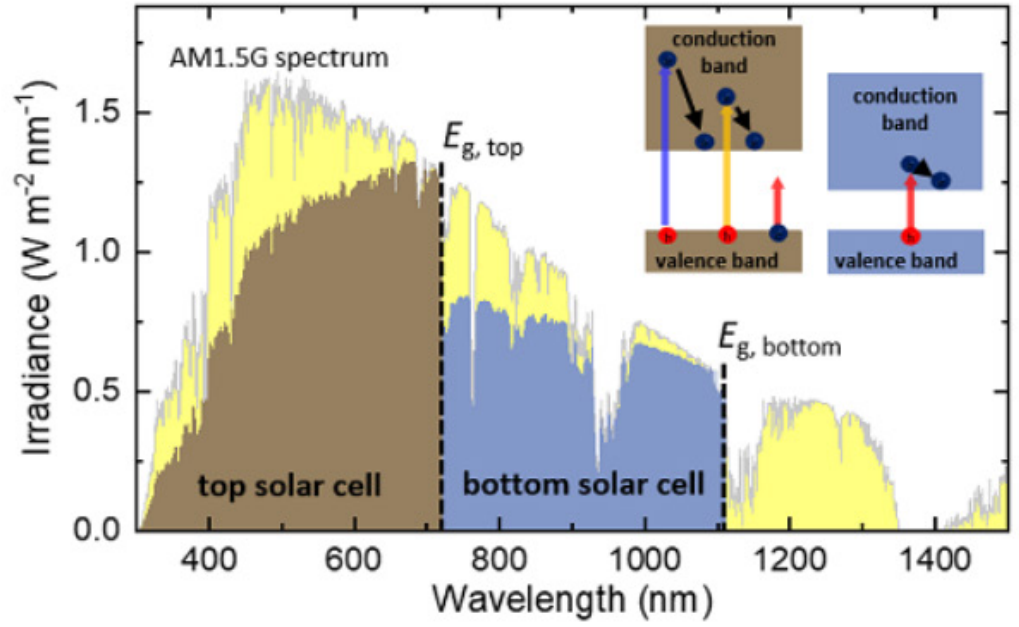
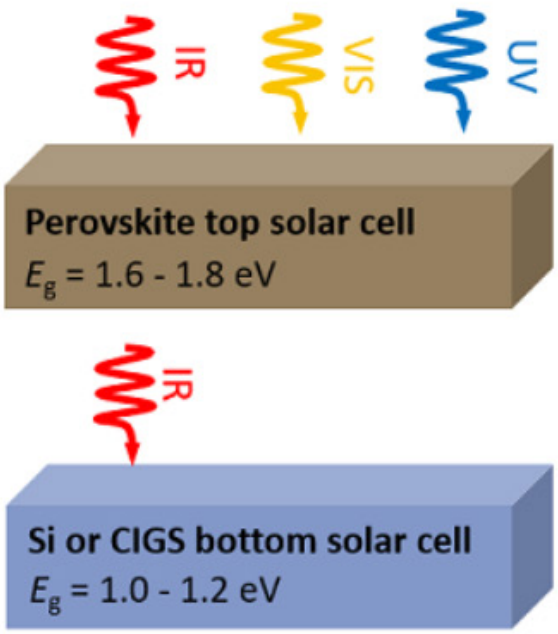
See exercise

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

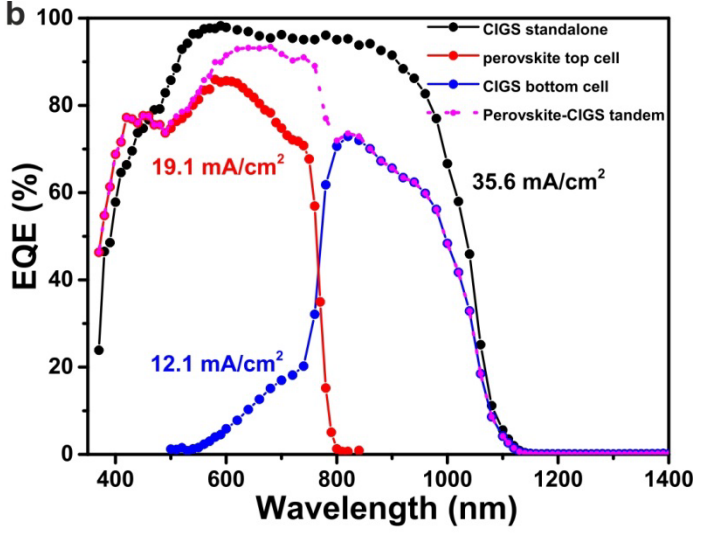
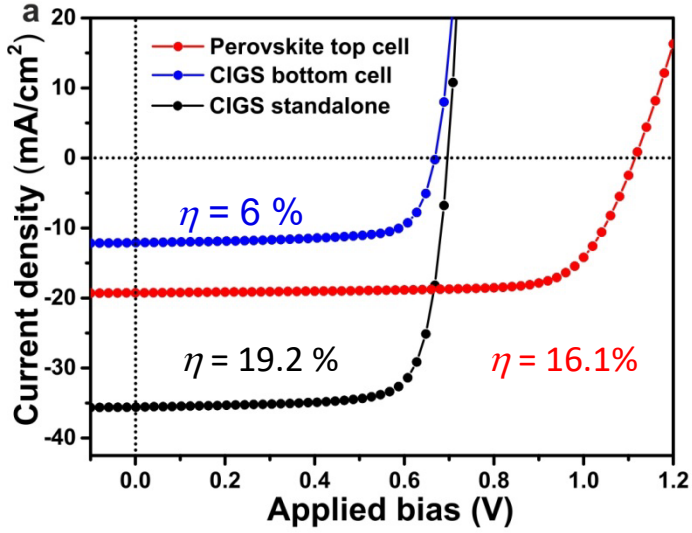
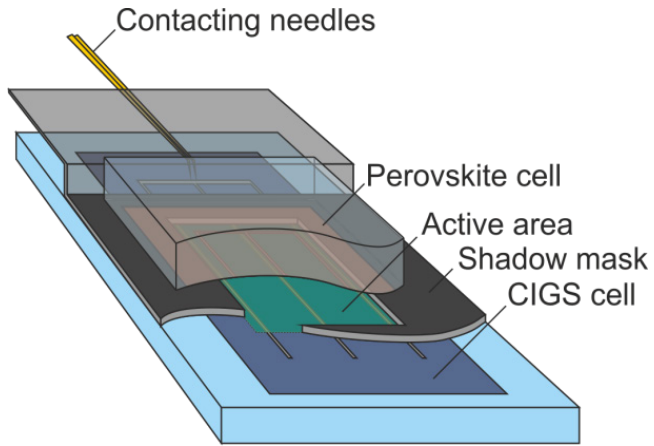
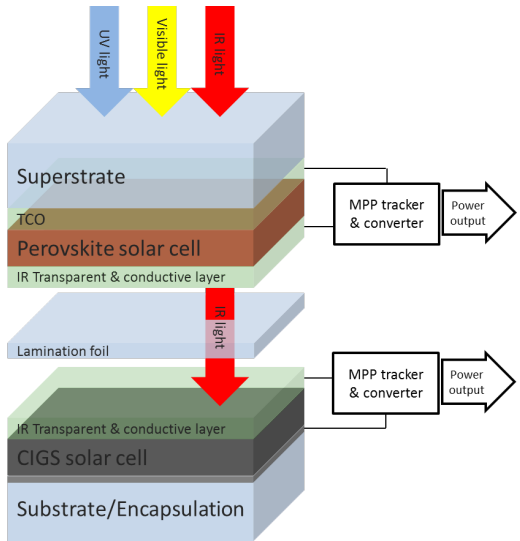
Tandem cells or another reason for band gap engineering



Tandem cells or another reason for band gap engineering

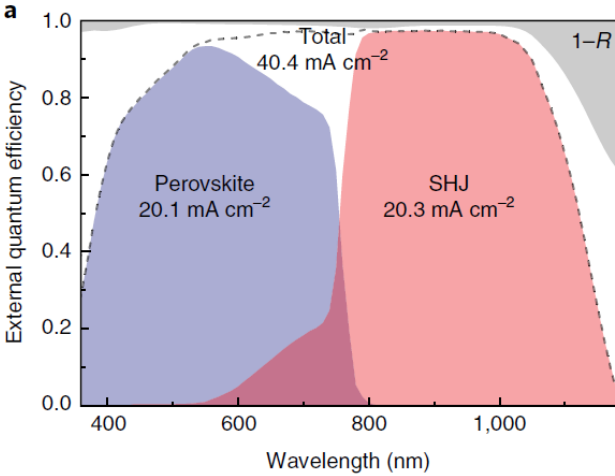
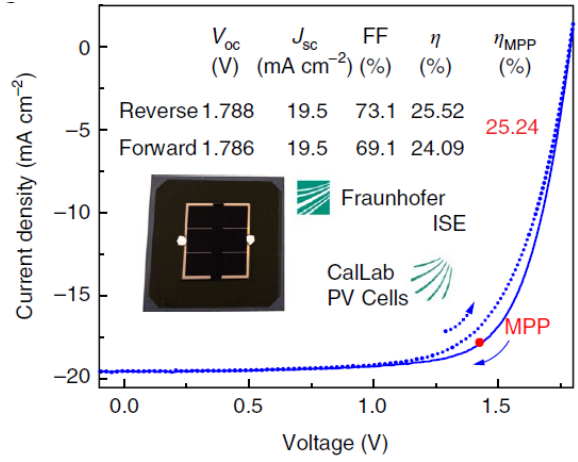
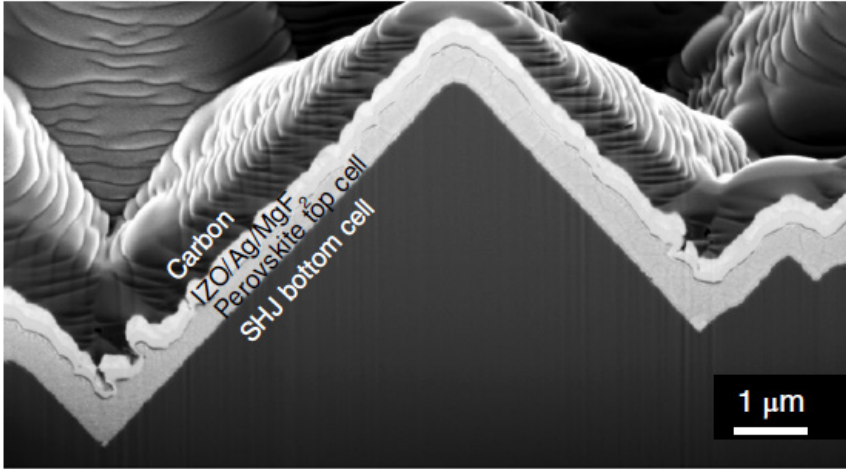
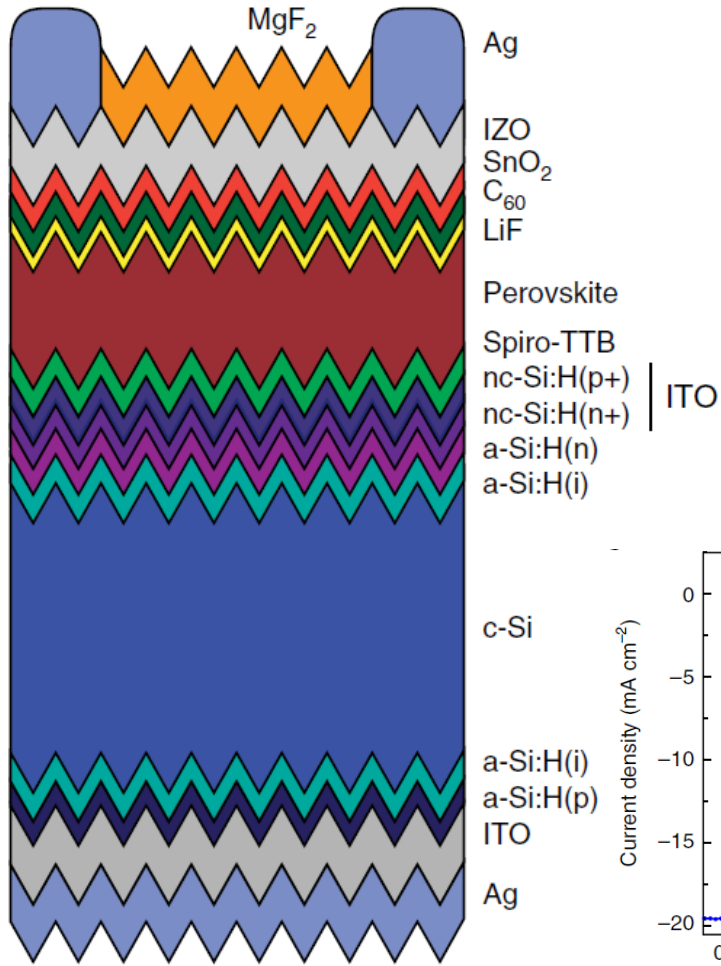


22.1% 4-terminal perovskite/CIGS tandem cells



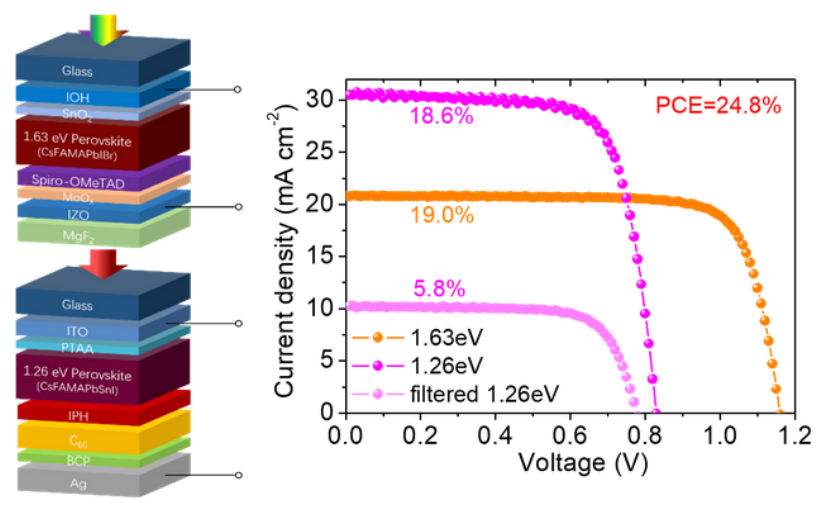
F. Fu, S. Buecheler, A.N. Tiwari et al., *Nature Energy*, 2, 16190 (2016)

25.2% 4-terminal perovskite/Si tandem solar cells

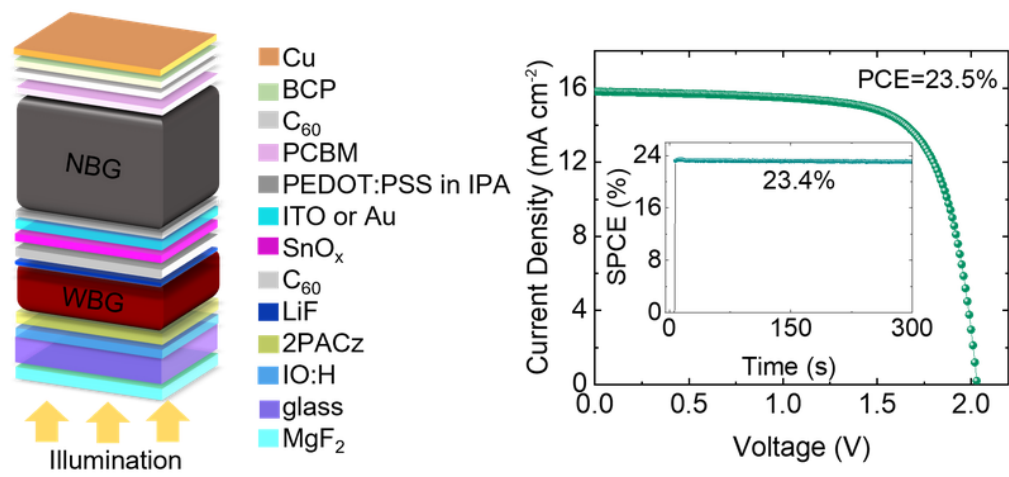


All perovskite tandem solar cells

Four-terminal all-perovskite tandems



Two-terminal all-perovskite tandems



More challenges

- ❑ Stability
 - ❑ Performance and life span can be negatively affected by exposure to moisture, oxygen, light, heat and mechanical stress

- ❑ Lead:
 - ❑ Lead, which is a common ingredient in PSCs, is a heavy metal that is toxic and poses major health and environmental risks

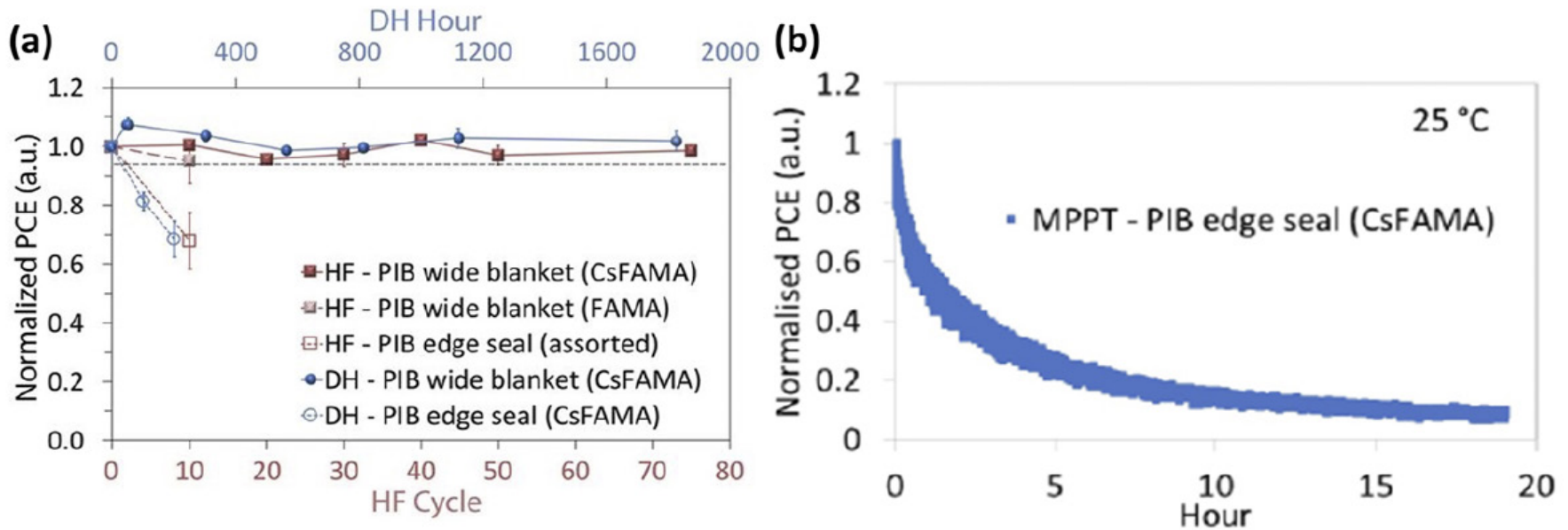
- ❑ Scalability
 - ❑ PSCs are primarily made using solution-based techniques like spin coating

Stability of Perovskite solar cells

- ❑ The poor stability of perovskite solar cells is the main factor for their industrialization – they need to compete with Si-technology. The high industry **standard lifespan (25-30 years)** for modules is typically backed up with 25-year production warranties, guaranteeing at least 80% efficiency during that period.
- ❑ Perovskites are intrinsically **unstable** when exposed to **light, heat, or applied voltage**. The mechanisms are not fully understood
- ❑ Their lifespan significantly decrease when exposed to **moisture and oxygen**. Different encapsulation strategies are currently developed.
- ❑ Standard **accelerated lifetime tests** developed for “other” PV-technologies seem **not very meaningful** for Perovskites.

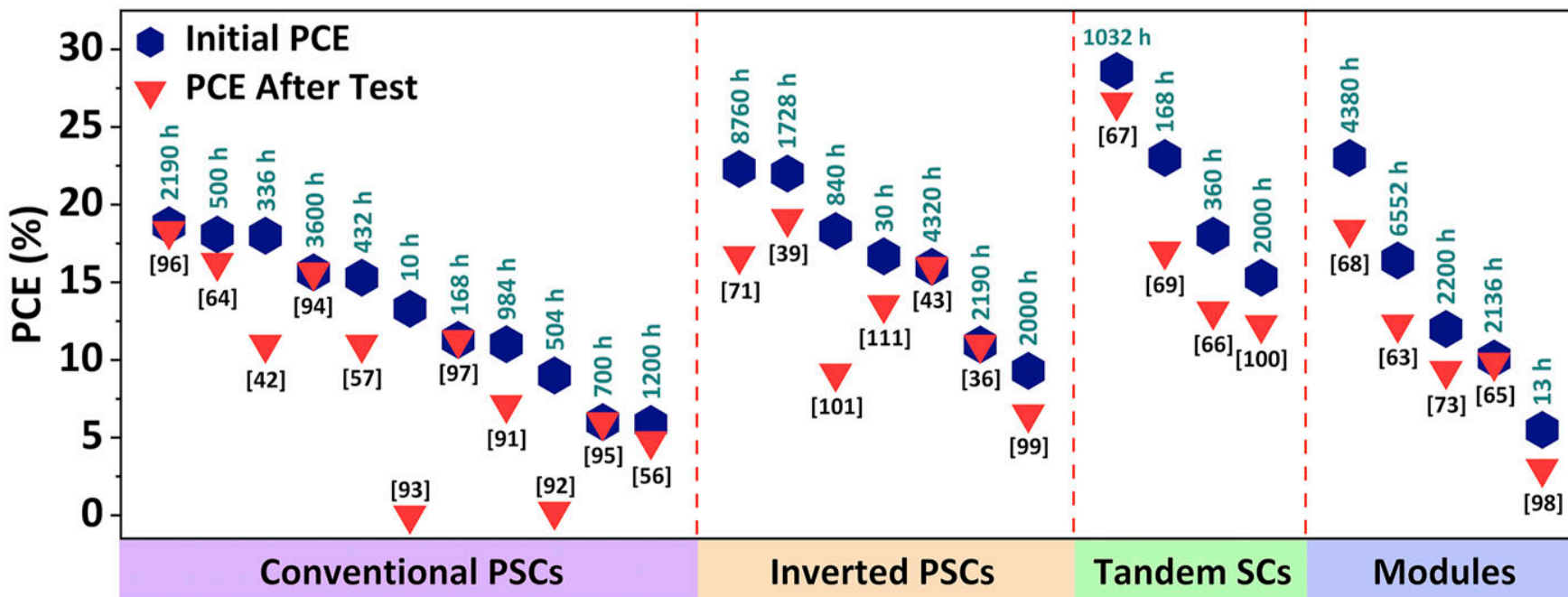
Stability tests:

- 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.

Stability issues of perovskite solar cells – intrinsic factors

- ❑ Thermal instability:
 - ❑ Especially MA based cells decompose, some undergo phase transitions, composition engineering helps.
 - ❑ Perovskite ion and electrode metal diffusion is accelerated at high T

- ❑ Reverse bias instability:
 - ❑ Different mechanisms, such as biased induced migration of halides into ETL, accumulation of ionic charges at contacts leading to reverse breakdown, and oxidation of iodide by influx of holes, and metal ion migration inducing the formation of shunts

- ❑ Illumination
 - ❑ Photoinduced halide segregation (reversible)
 - ❑ Irreversible materials decomposition, e.g. (MAPI) leads to the formation of PbI_2 , methylamine, HI, and I_2 gases



or oxidation of iodide by excess photogenerated holes

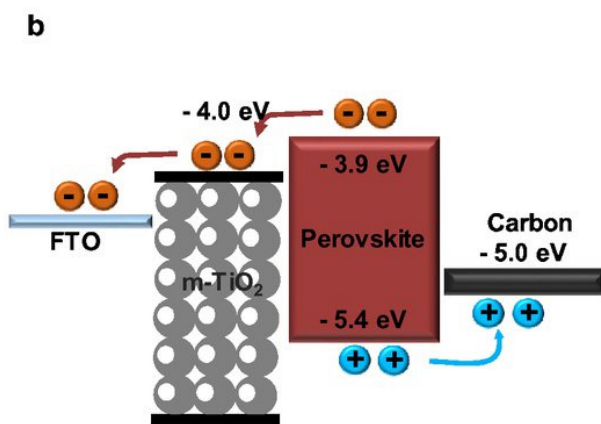
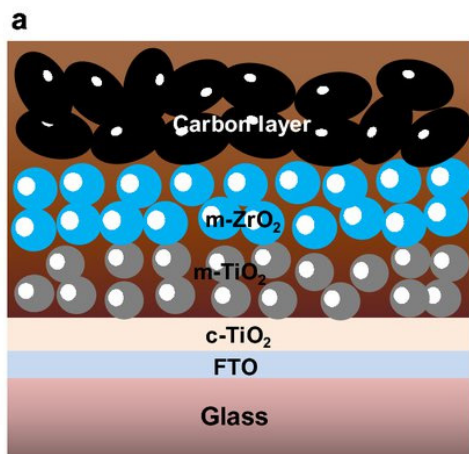
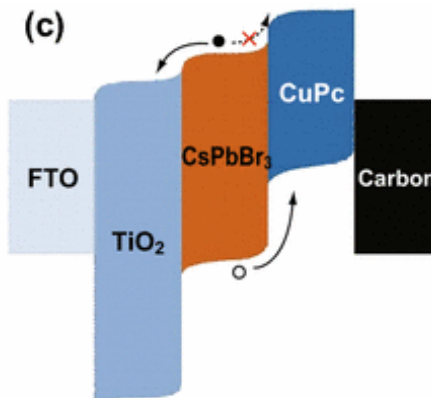
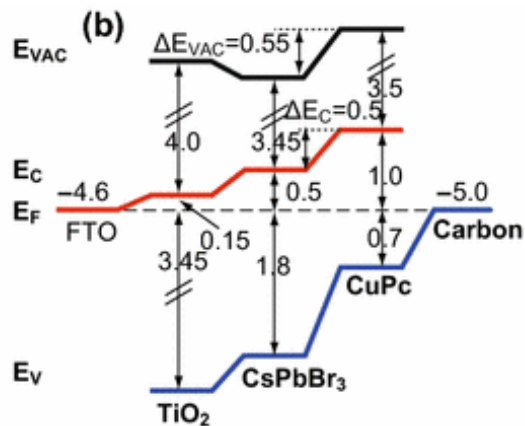
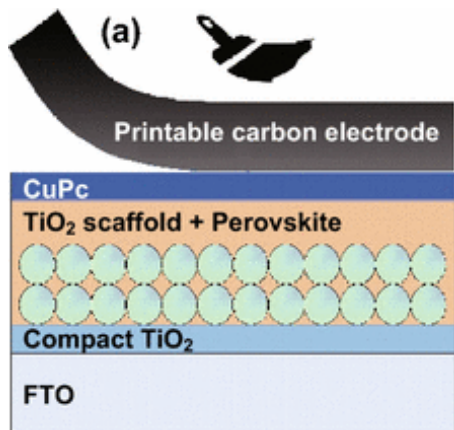
T. Huang et al., J. Phys. Chem. C, <https://doi.org/10.1021/acs.jpcc.1c05841>

❑ Interface stability, grain boundary passivation. M. Khenkin et al., 2020, Nature Energy, VOL 5, 35–49

Ambient stability of perovskite solar cells

- ❑ Perovskite degradation due to deprotonation of organic cation and the loss of volatile HI (moisture and polar solvents)
- ❑ Degradation upon exposure to moisture involves the formation of hydrated phases at first, followed by perovskite degradation due to deprotonation of organic cation, and loss of volatile organic amines
- ❑ Under illumination, oxygen serves as electron scavenger and superoxide ion is generated. This process leaves the excess of photogenerated holes in the perovskite, which leads to iodide oxidation, and consequently ion migration and/or photoinduced segregation of the perovskite. The photo-oxidation process is accelerated by the presence of moisture, as well as by elevated temperature.

Carbon based perovskite solar cells

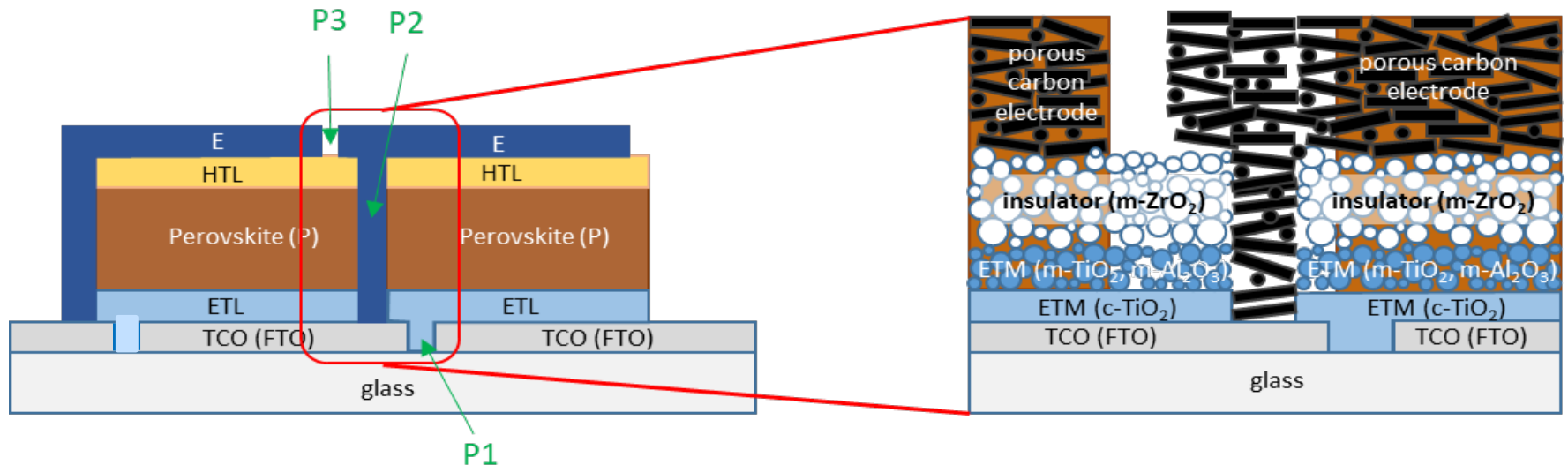


- Good air stability
- High low light intensity efficiency
- Completely printable
- But: low efficiency ~ 13.83 %

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

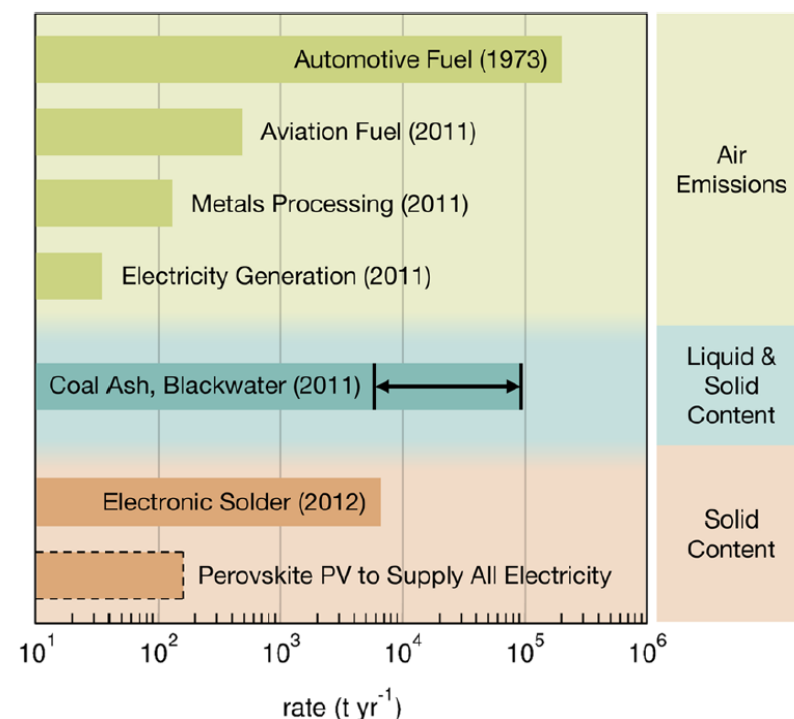
Uniqueness of the mesoscopic PSC architecture

- ❑ 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



Environmental issues

- ❑ 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.
- ❑ Health issues with lead are known since Roman times



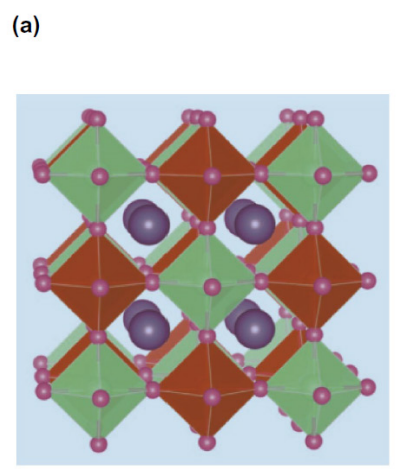
D. Fabini et al., J. Phys. Chem. Lett. 2015, 6, 3546–3548

B. Hailegnaw et al., J. Phys. Chem. Lett. 2015, 6, 1543–1547

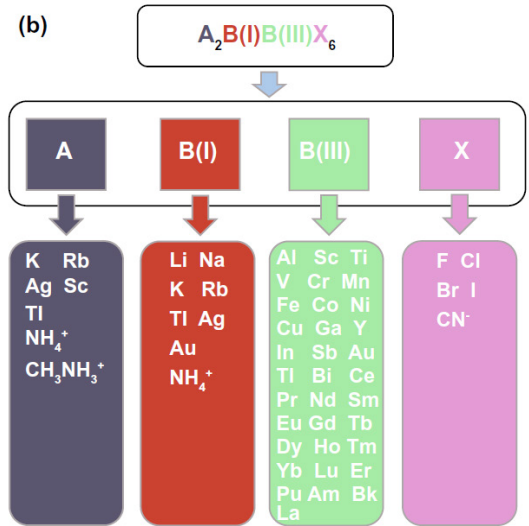
A. Babayigit, A. Ethirajan, M. Muller, B. Conings, Nature Materials 2016, 15, 247.

Possible remedies

FASnI ₃ (CDTA)	ITO/PEDOT:PSS/FASnI ₃ /C ₆₀ /BCP/Ag	21.83	0.64	0.74	10.32	Solution process
FASnI ₃ (THDH)	ITO/PEDOT:PSS/FASnI ₃ /PCBM/BCP/Ag	22.12	0.54	0.71	8.48	Spin coating
CsSnI ₃ (SnCl ₂)	ITO/CsSnI ₃ /PC ₆₁ BM/C ₆₀ /Ag	9.89	0.50	0.68	3.56	Spin coating
CsSnBr ₂ (HPA)	FTO/c-TiO ₂ /m-TiO ₂ /Al ₂ O ₃ /CsSnBr ₂ /Carbon	17.40	0.31	0.57	3.20	Spin coating
FA _{0.8} Cs _{0.2} SnI ₃	ITO/PEDOT:PSS/FA _{0.8} Cs _{0.2} SnI ₃ /PCBM/Bis-C ₆₀ /Ag	16.05	0.24	0.36	1.38	Spin coating
CsSnI ₃ (SnI ₂)	ITO/CuI/CsSnI ₃ /C ₆₀ /BCP/Al	8.50	0.47	0.54	2.13	Solution process
FA _{0.75} MA _{0.25} SnI ₃ (SnF ₂)	ITO/PEDOT:PSS/FA _{0.75} MA _{0.25} SnI ₃ /C ₆₀ /BCP/Ag	21.20	0.61	0.63	8.12	Spin coating
FA _{0.75} MA _{0.25} SnI _{2.75} Br _{0.25} (SnF ₂ + MACl)	ITO/PEDOT:PSS/FA _{0.75} MA _{0.25} SnI _{2.75} Br _{0.25} /C ₆₀ /BCP/Ag	22.30	0.52	0.70	8.07	Secondary crystallization growth process
CsSnBr ₃ (SnF ₂)	FTO/c-TiO ₂ /m-TiO ₂ /CsSnBr ₃ /Spiro-OMeTAD/Au	9.00	0.41	0.58	2.10	Spin coating
CsSnBr ₃ (SnF ₂)	ITO/MoO ₃ /CsSnBr ₃ /C ₆₀ /BCP/Ag	2.40	0.40	0.55	0.55	Vapor deposition
FASnI ₂ Br	ITO/PEDOT:PSS/FASnI ₂ Br/C ₆₀ /Ca/Al	6.82	0.47	0.54	1.72	Low-temperature processed
(BEA)FA ₂ Sn ₃ I ₁₀	ITO/PEDOT:PSS/(BEA)FA ₂ Sn ₃ I ₁₀ /PCBM/Ag	18.85	0.62	0.55	6.43	liquid phase crystallization method
(FA _{0.9} EA _{0.1}) _{0.98} EDA _{0.01} SnI ₃	FTO/PEDOT:PSS/GeI ₂ doped Sn-perovskite/C ₆₀ /BCP/Ag/Au	20.32	0.84	0.78	13.24	Spin coating



3D A₂B(I)B(III)X₆ Halide Double Perovskites



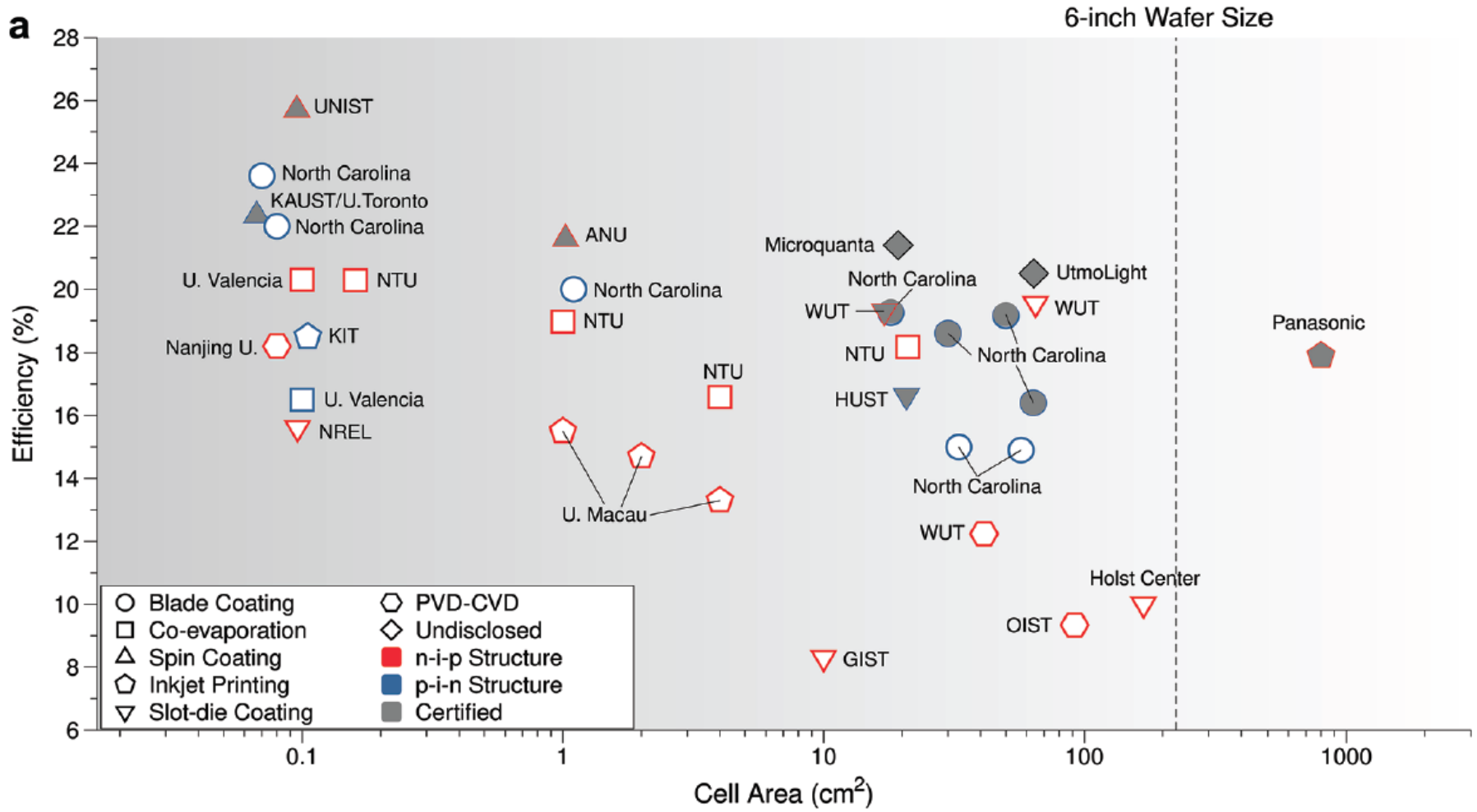
❑ But: Sn is also toxic.

-> Explore «double perovskites»

Cs₃Bi₂I₉ (PCE of a few %)

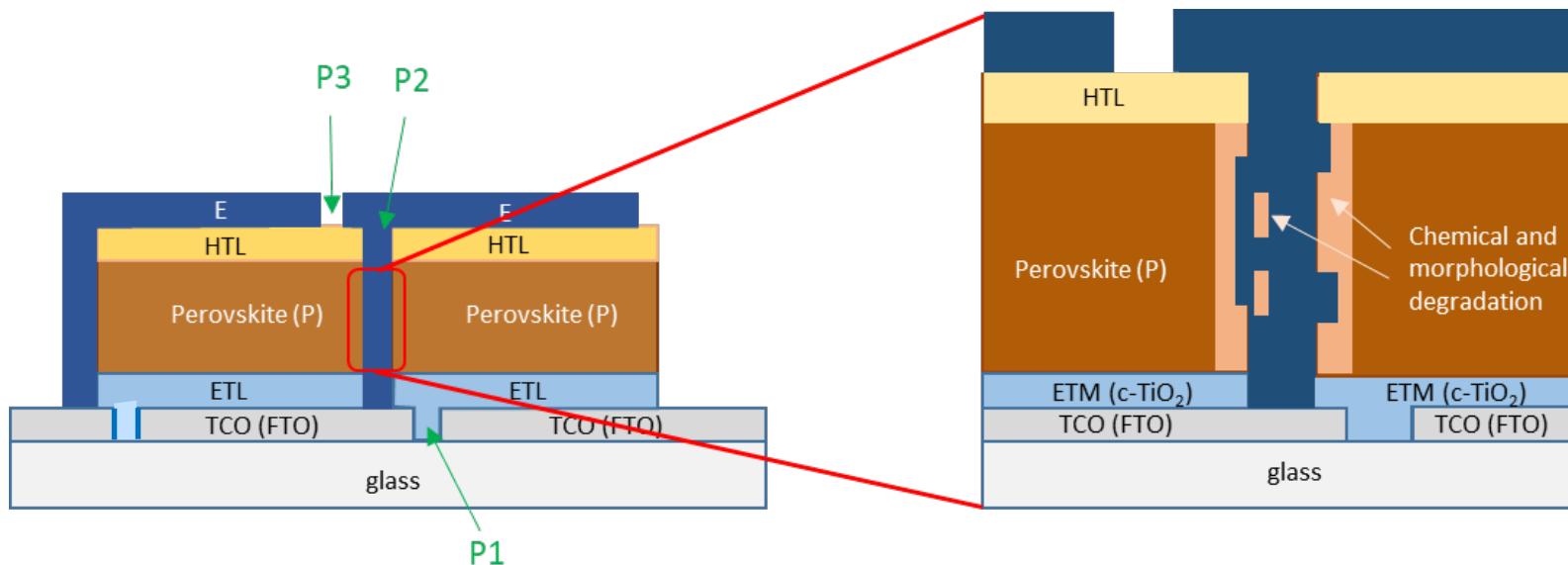
M. Wang et al., Nano-Micro Lett. (2021) 13,
 B. W. Park et al, 2015, Adv. Mater, 27, 43
 J. Li et al., Nano Energy 2021, 80, 105526

Towards industrialization – from lab scale to modules



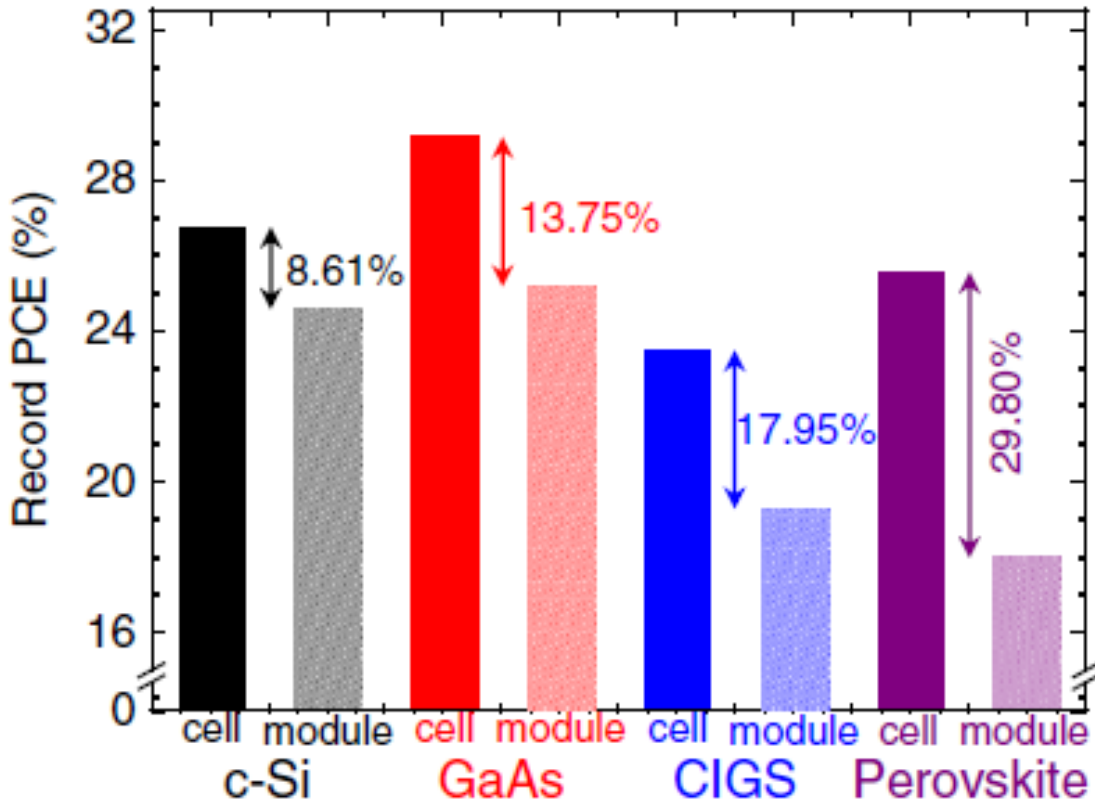
The challenge of series interconnect

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



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

Efficiency loss in modules



Towards industrialization – different strategies



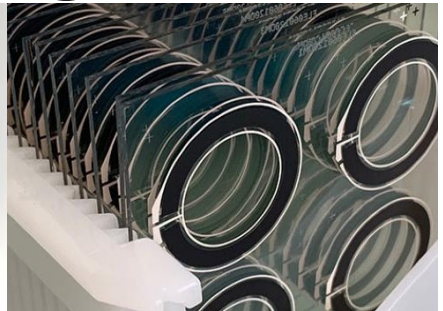
Oxford PV **perovskite Si tandem solar cell** achieves 28% efficiency



Saule Technologies: **fully printed (Inkjet)**



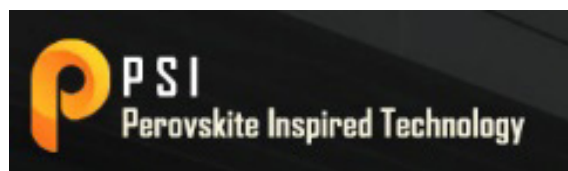
fully printed carbon based hole conductor free, custom design, indoor applications



Companies working on Perovskite modules (no claim of completeness)



Australia, former GreatCell



Indian startup incubated at the Tides Business Incubation Center within IIT Roorkee



RenShine Solar is a Chinese developer of perovskite solar cells



Voltec Solar is a France-based producer of photovoltaic panels



China-based perovskite solar module manufacturer

Companies working on Perovskite modules (no claim of completeness)



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



LONGi Green Energy Technology Co., Ltd. (China) is a solar technology that develops solutions for large-scale power plants

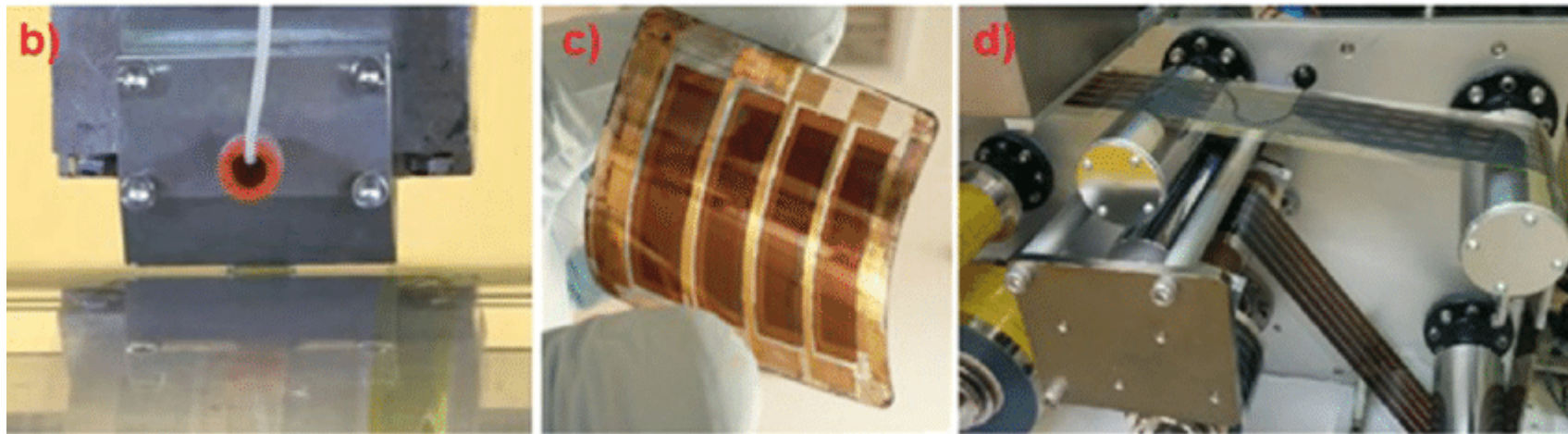
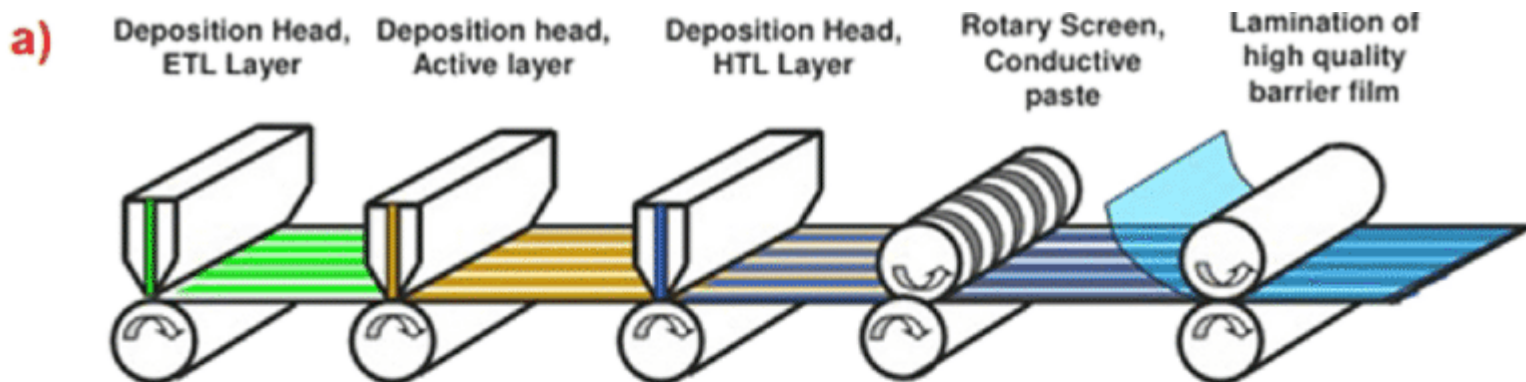


Grape Solar (US) is a retail solar brand with over a decade of experience providing grid-tied, grid-interactive and off-grid solar systems to businesses and individuals



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

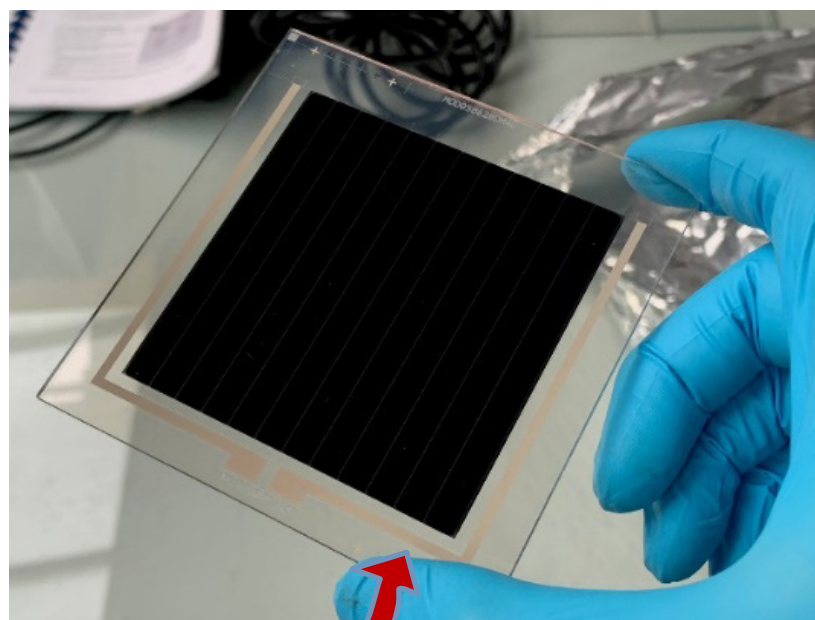
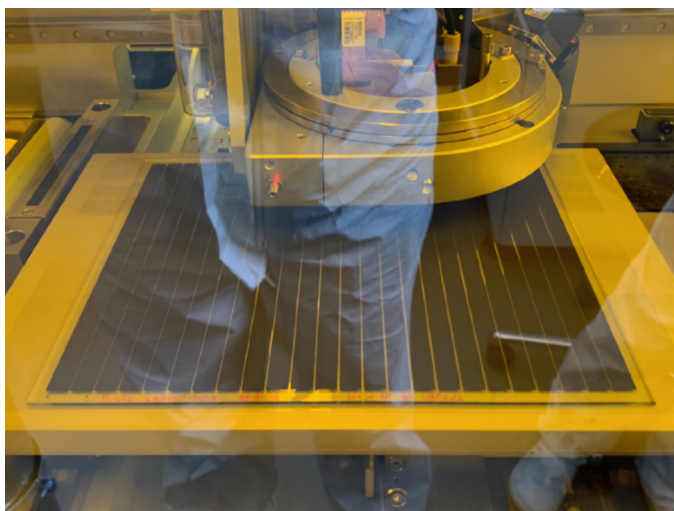
Fully printed Perovskite solar cells



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)

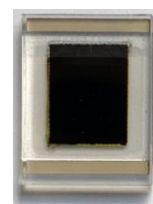
Uniqueness of the mesoscopic PSC architecture

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



A. Verma et al, J.Mater.Chem.C,
2020,8,6124

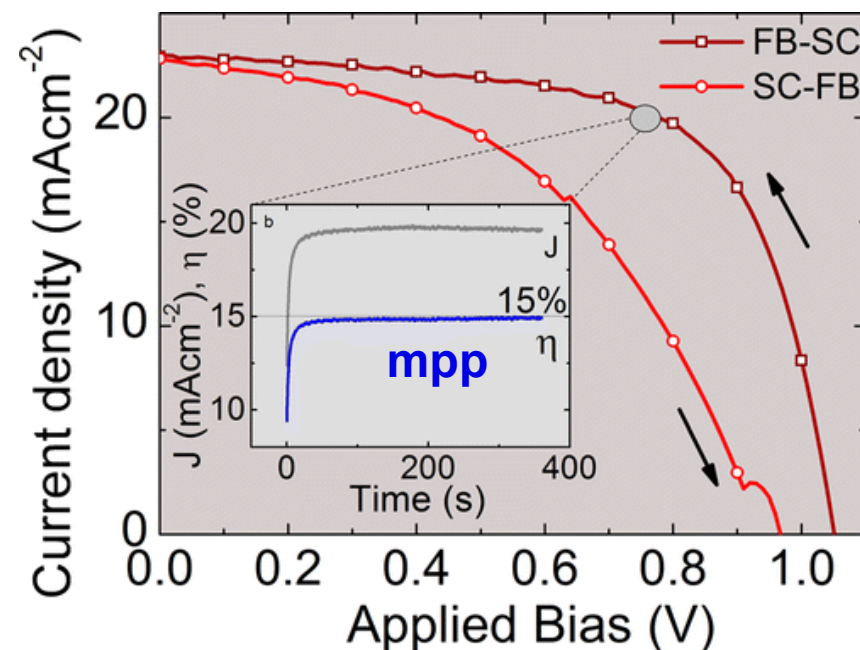
A. Verma et al, Materials Advances, 2020,
DOI: 10.1039/d0ma00077a



Both have a PCE of 13 %

How to measure the perovskite solar cells

- ❑ Mask your solar cells properly
- ❑ Calibrate your light source
- ❑ The best way to evaluate the perovskite solar cell is to present the **steady state maximum power output over time**



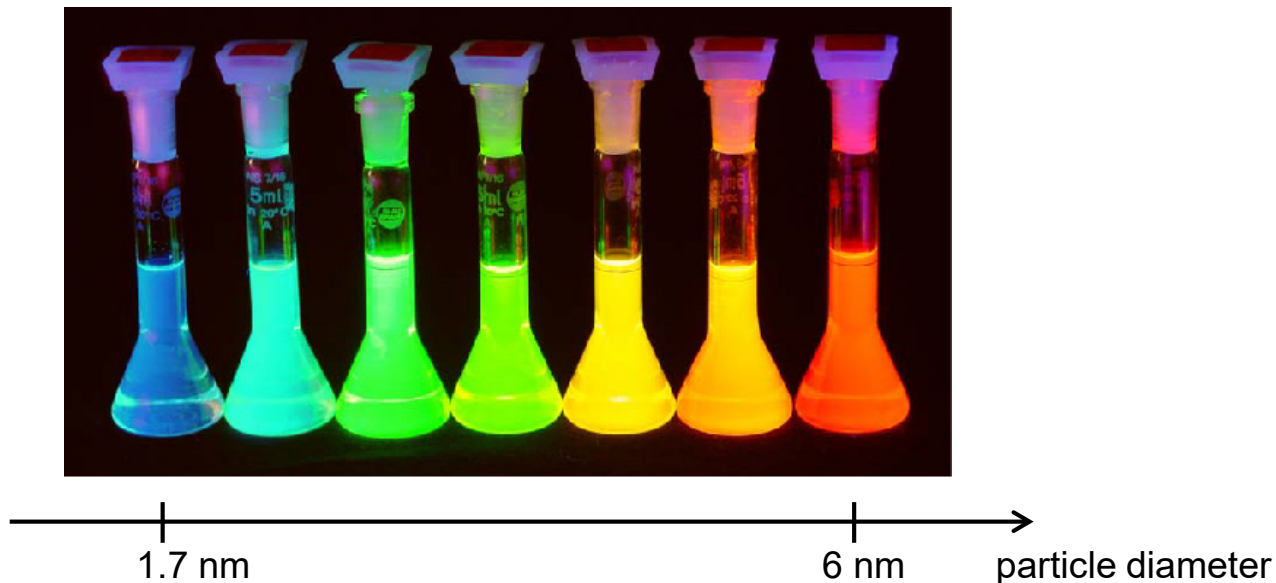
Certify the cell by accredited standard labs or company

- ❑ National Renewable Energy Laboratory (NREL, USA)
- ❑ National Institute of Advanced Industrial Science and Technology (AIST, Japan)
- ❑ Fraunhofer Institute for Solar Energy Systems (ISE, Germany)
- ❑ Newport, USA

Learning outcome

- ❑ What are Perovskite solar cells?
 - *Based on the perovskite structure, most researched is MAPbI_3*
- ❑ Architectures? How are they made?
 - *Mesoscopic and planar; solution processing or evaporation*
- ❑ Why are they so good?
 - *High absorption, low exciton binding energy, long charge carrier diffusion*
- ❑ Strategies for efficiency improvement
 - *Controlled crystallization, composition engineering, defect passivation*
- ❑ Tandem solar cells
 - *As top cell in combination with Si, CIGS or all perovskite*
- ❑ Challenges towards industrialization
 - *Stability: many degradation mechanisms, sealing important, no good alternative to lead, efficiency loss upon up-scaling, worth mentioning: the holeconductor free, carbon carbon based, mesoscopic solar cell*

3.3B Hybrid solar cells - Quantum dot

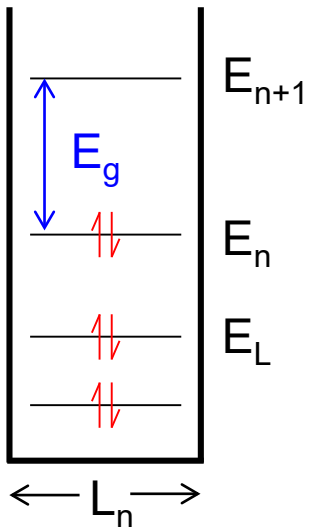


Nanoproperties: change in properties of due to its physical size. The image shows CdSe-CdS core-shell nanoparticles with various diameters.

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

Quantum Confinement Effect

Particle in a box model



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

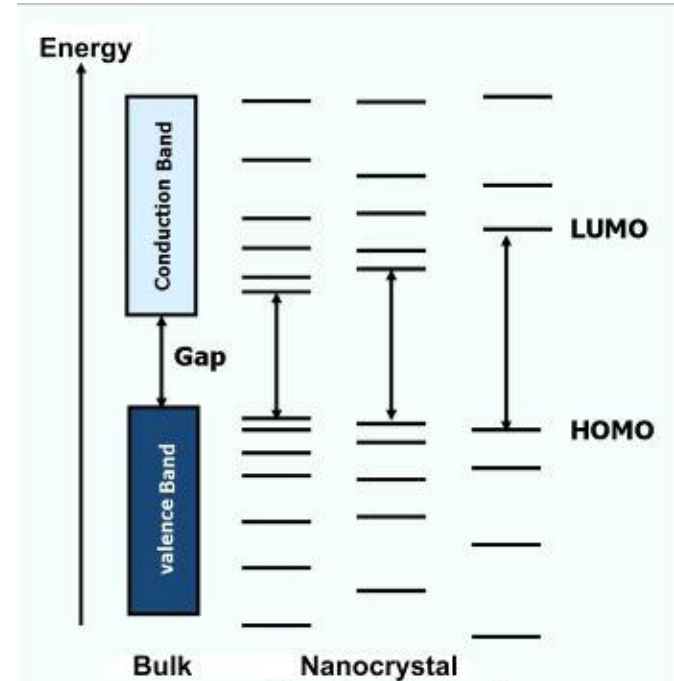
where, $L_n \approx n \cdot L_0$
(for large enough box length)

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

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

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

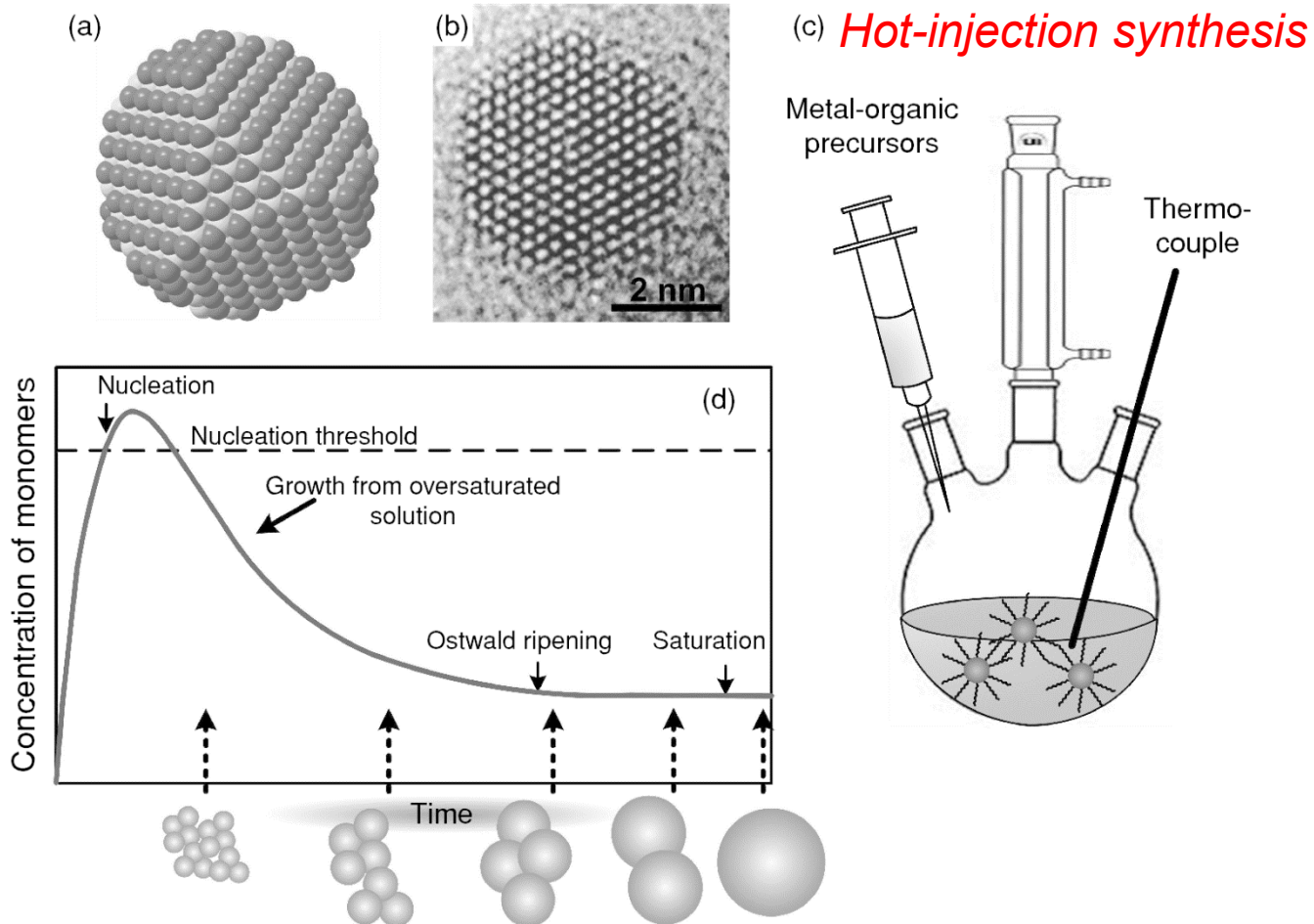
$$E_g = \frac{h^2}{8m_e (L_0)^2} \left(\frac{2}{n} + \frac{1}{n^2} \right)$$



$$n_1 > n_2 > n_3$$

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

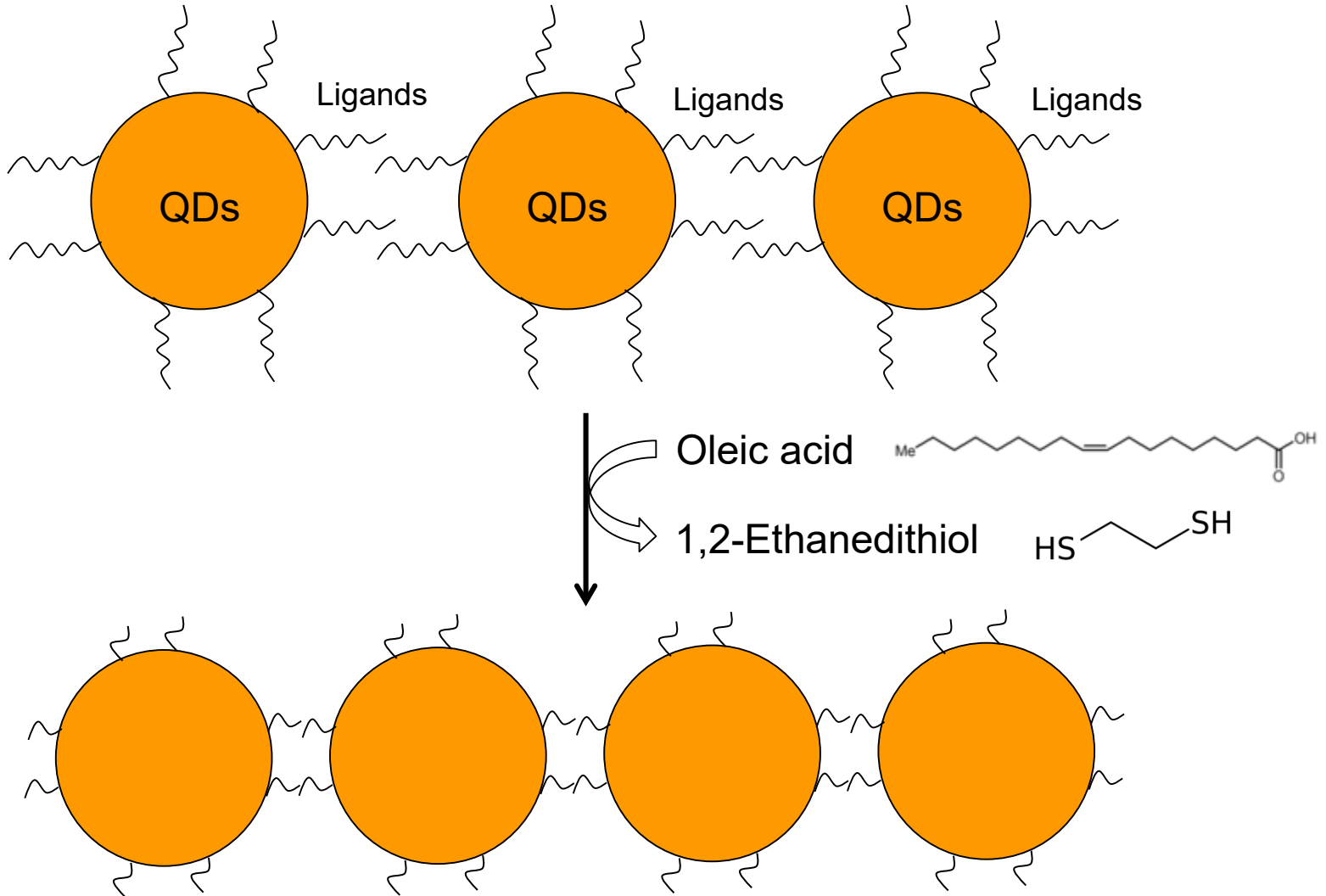
Thermodynamics and Kinetics in QDs Synthesis



Bodnarchuk, M., & Kovalenko, M. (2013). *Colloidal Quantum Dot Optoelectronics*

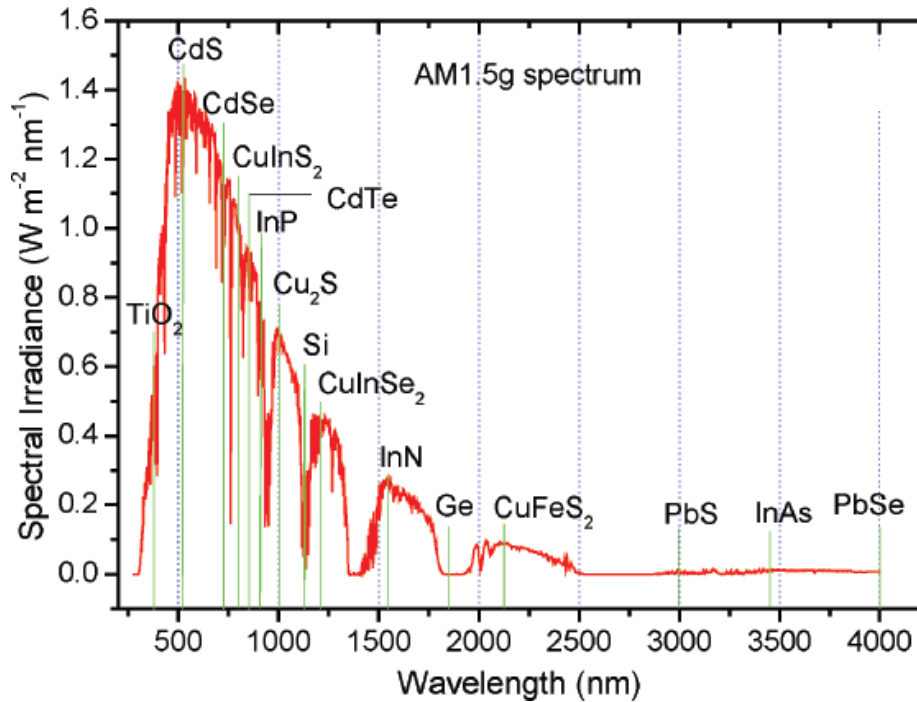
3.3B Hybrid solar cells – Quantum Dots and Photovoltaics (pp. 1-29). Cambridge University Press.

Ligand Exchange

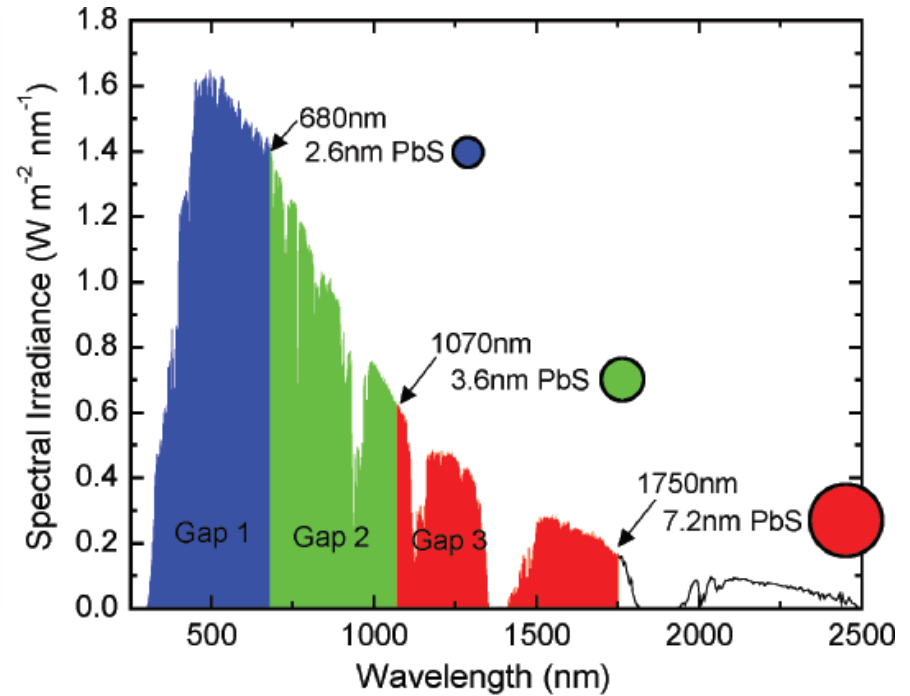


Band gap tunability in QDs

Changing the material of nanocrystals

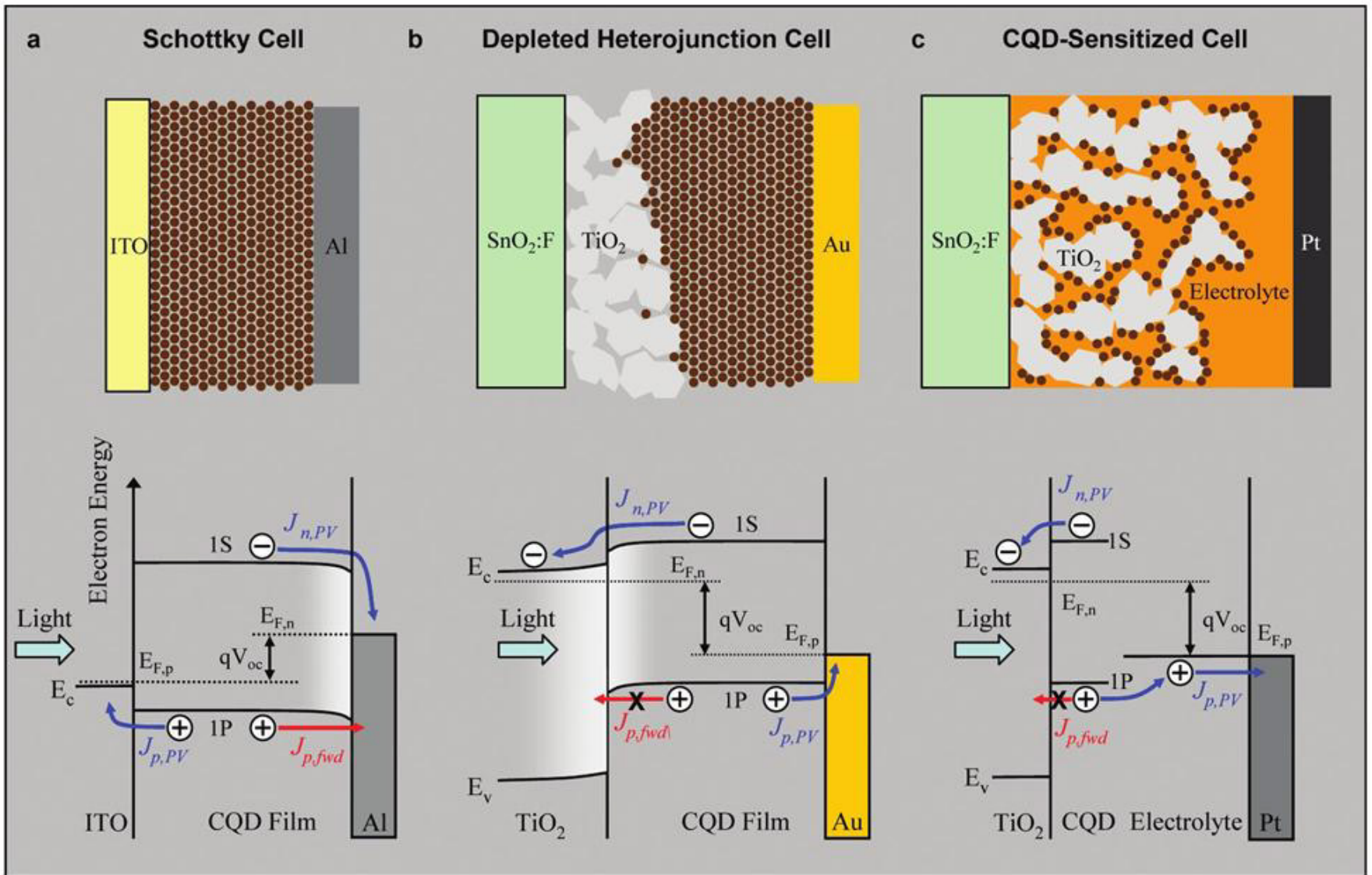


Changing the radius of nanocrystals - quantum confinement effect

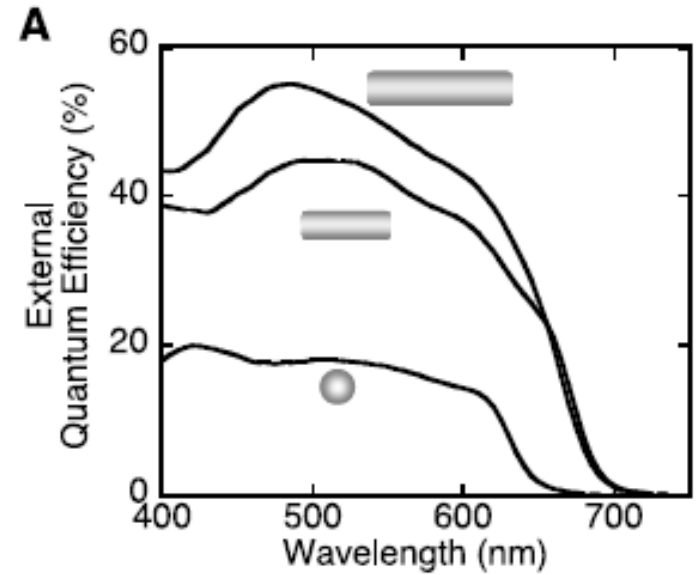
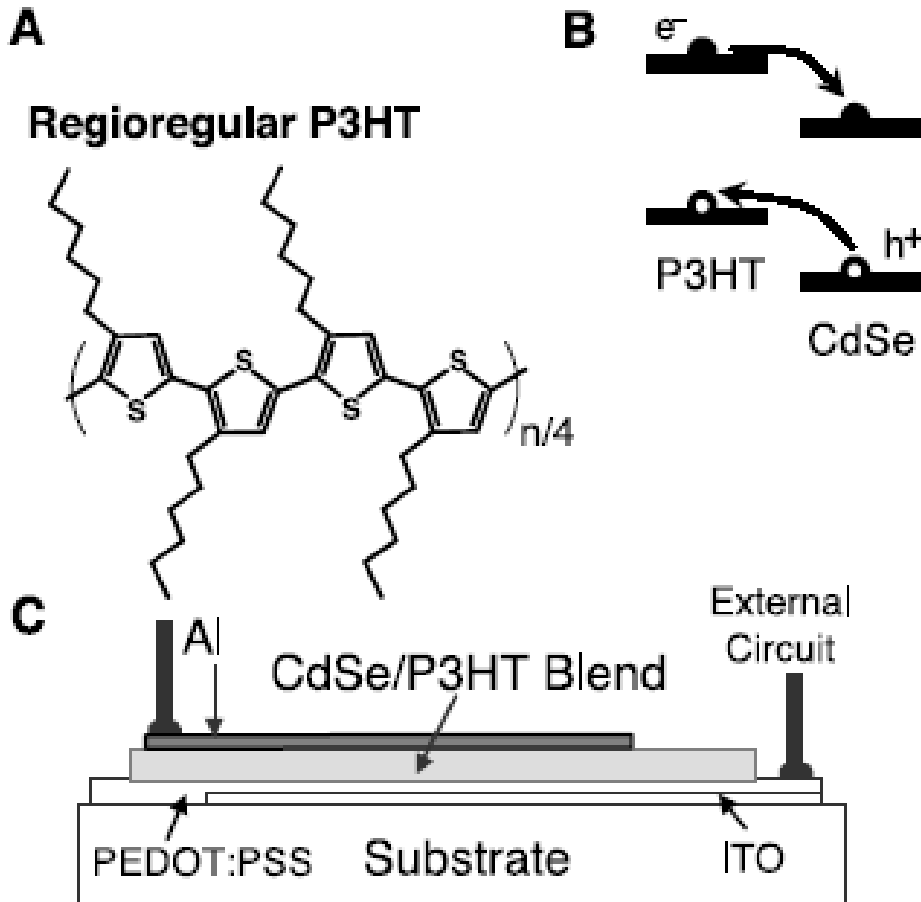


→ J. Tang, E.H. Sargent, *Adv. Mater.* **13**, 12 (2011)

Design of „real“ QD solar cells



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

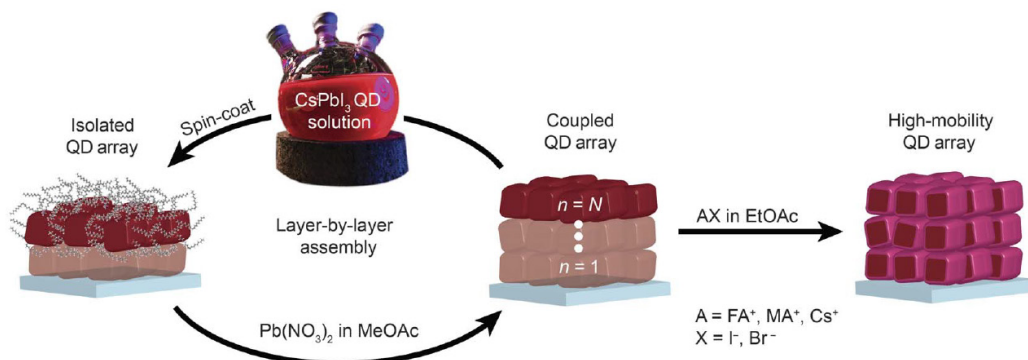
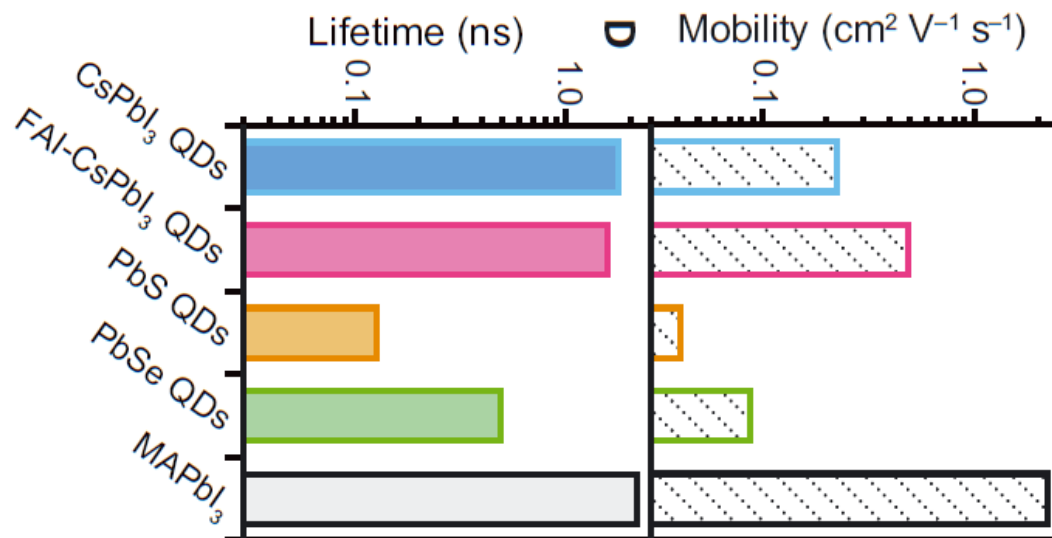
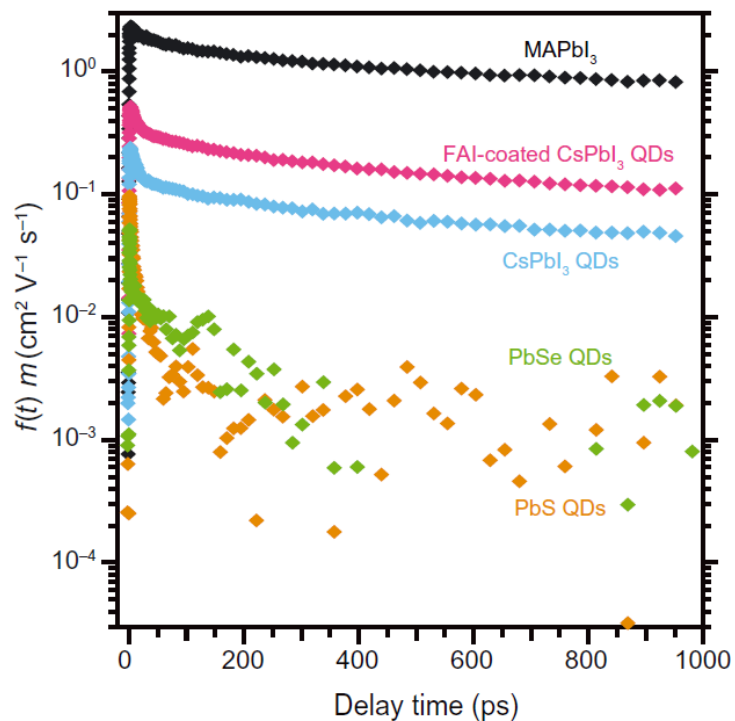


Table 1. Effect of AX salts on PV parameters extracted from *J-V* scans.

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.....