

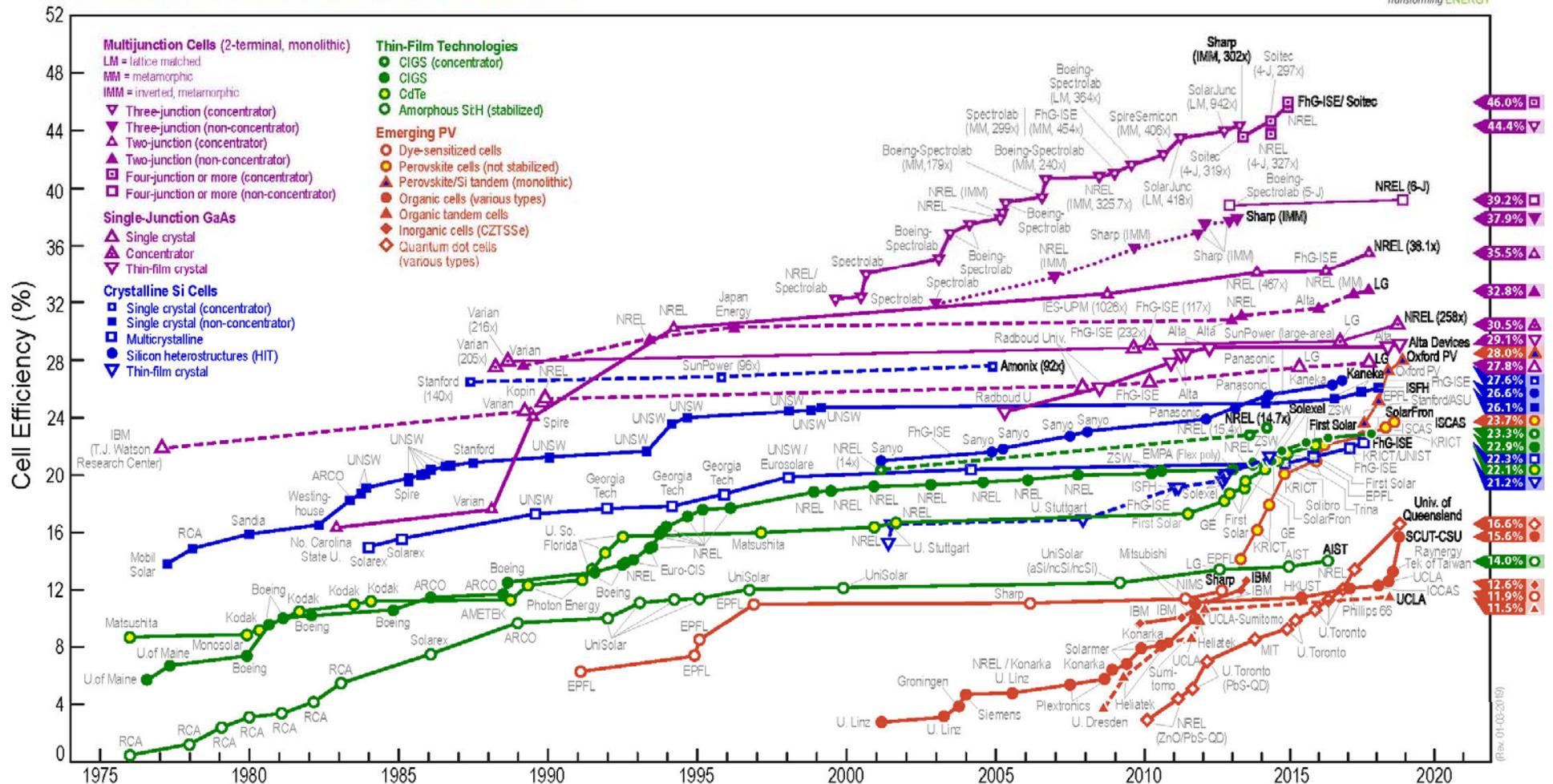
Perovskite Solar Cells



1039 Nanotechnology



Best Research-Cell Efficiencies

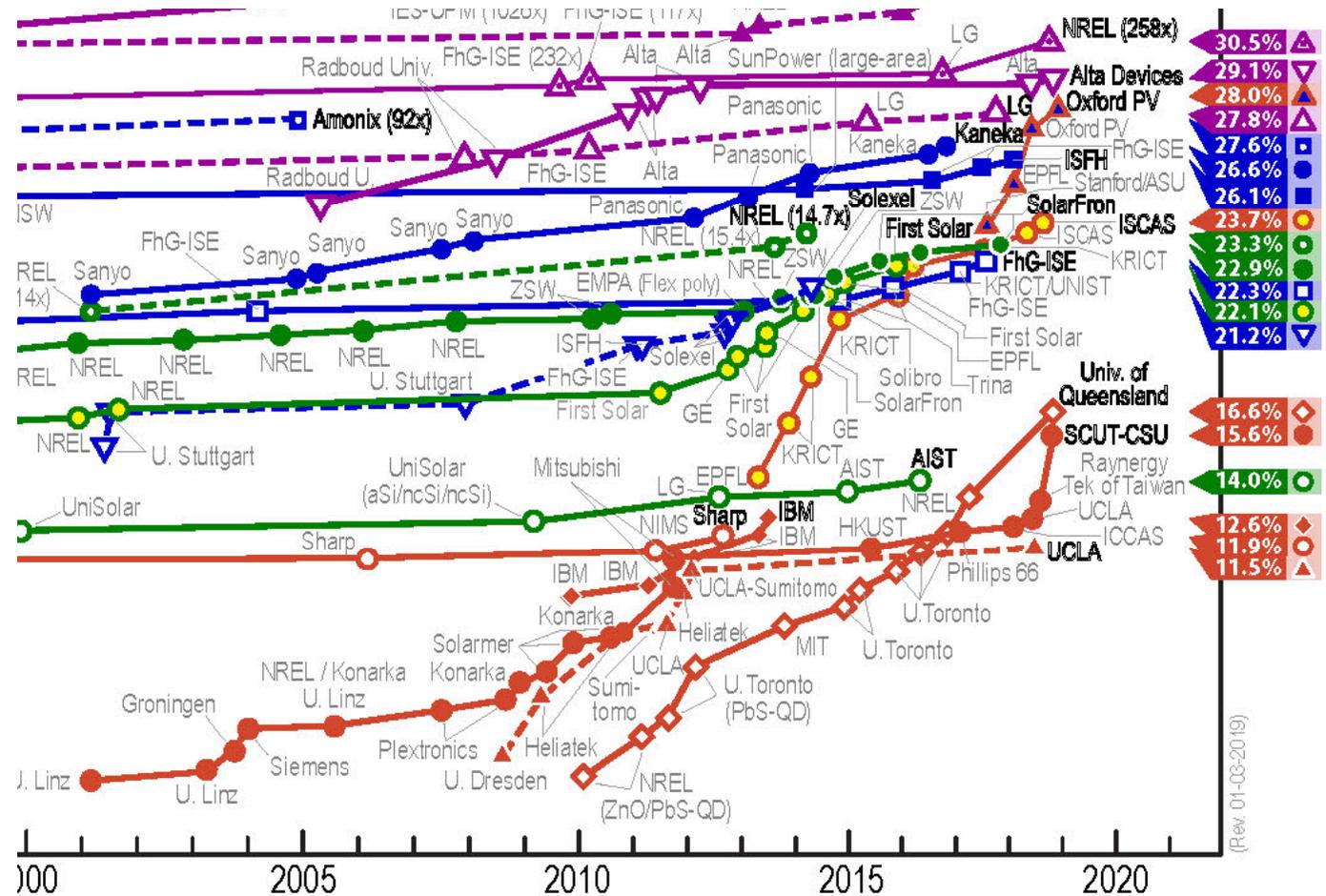


Thin-Film Technologies

- CIGS (concentrator)
- CIGS
- CdTe
- Amorphous Si:H (stabilized)

Emerging PV

- Dye-sensitized cells
- Perovskite cells (not stabilized)
- ▲ Perovskite/Si tandem (monolithic)
- Organic cells (various types)
- ▲ Organic tandem cells
- ◆ Inorganic cells (CZTSSe)
- ◆ Quantum dot cells (various types)





Multijunction Cells (2-terminal, monolithic)

LM = lattice matched

MM = metamorphic

IMM = inverted, metamorphic

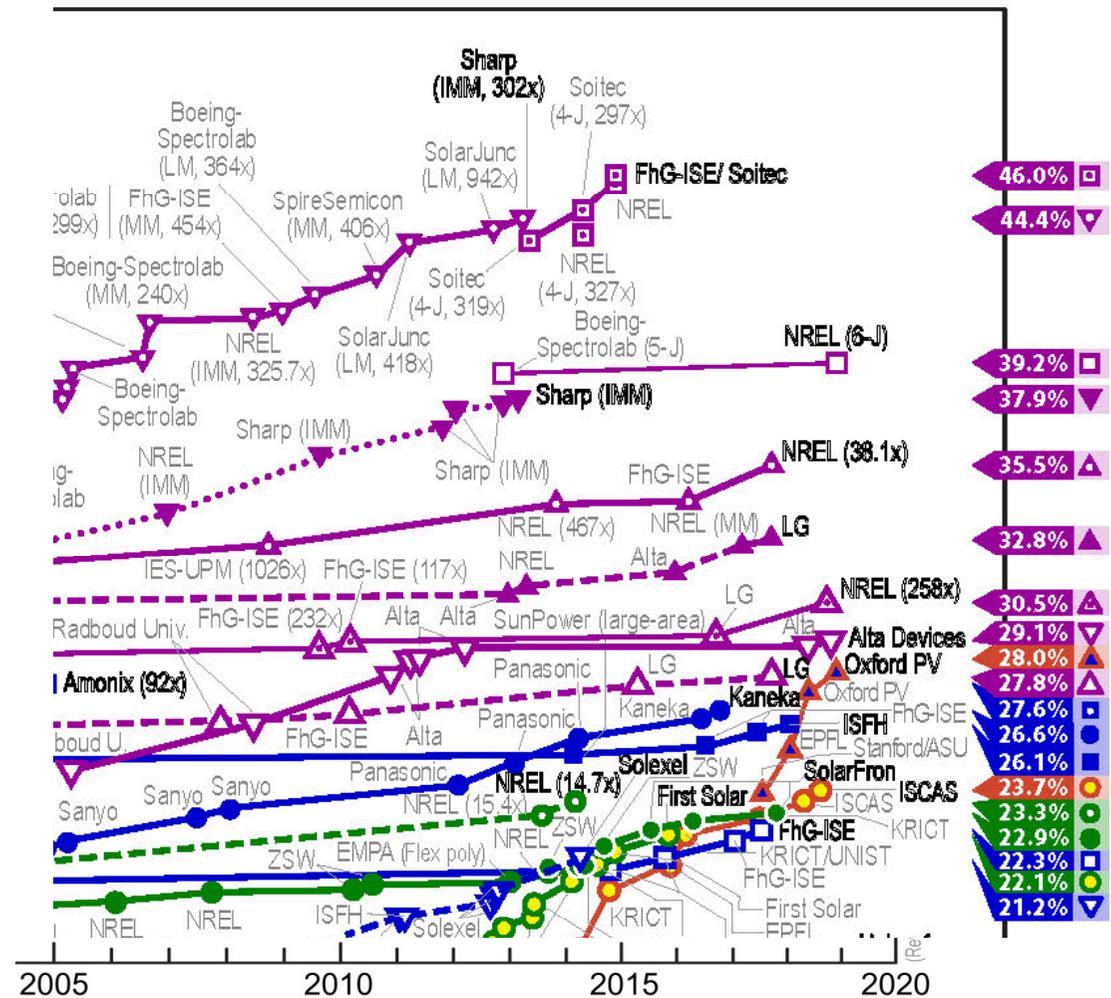
- ▼ Three-junction (concentrator)
- ▼ Three-junction (non-concentrator)
- ▲ Two-junction (concentrator)
- ▲ Two-junction (non-concentrator)
- Four-junction or more (concentrator)
- Four-junction or more (non-concentrator)

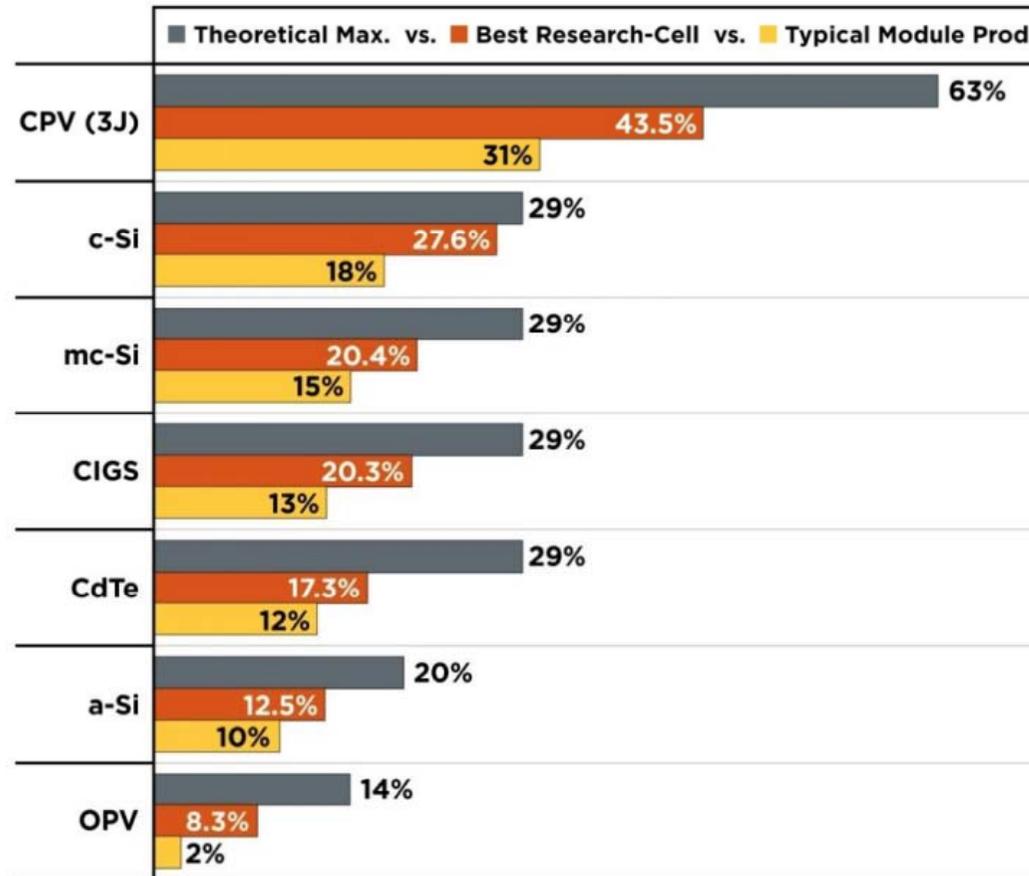
Single-Junction GaAs

- ▲ Single crystal
- ▲ Concentrator
- ▼ Thin-film crystal

Crystalline Si Cells

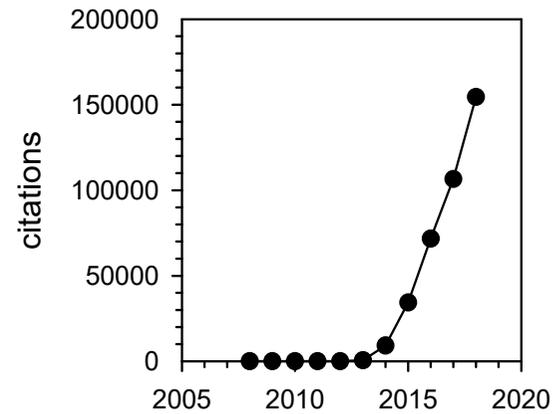
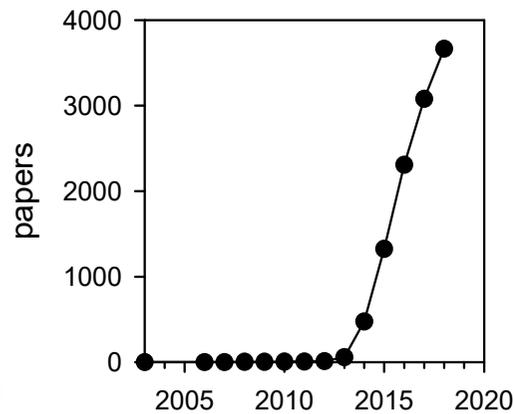
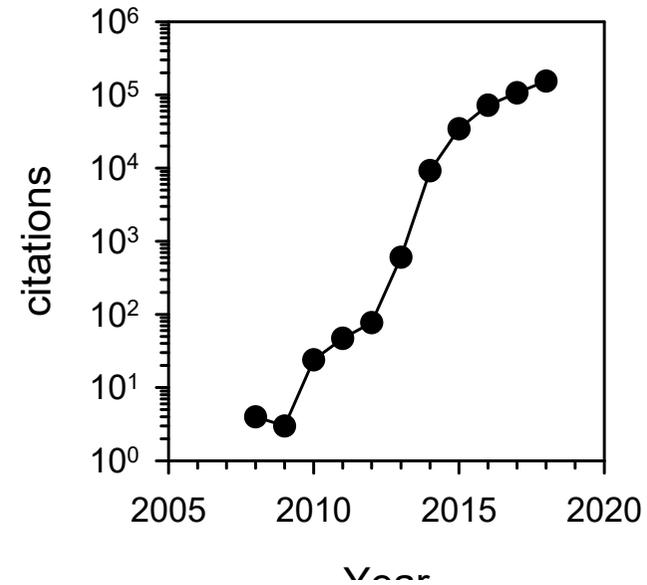
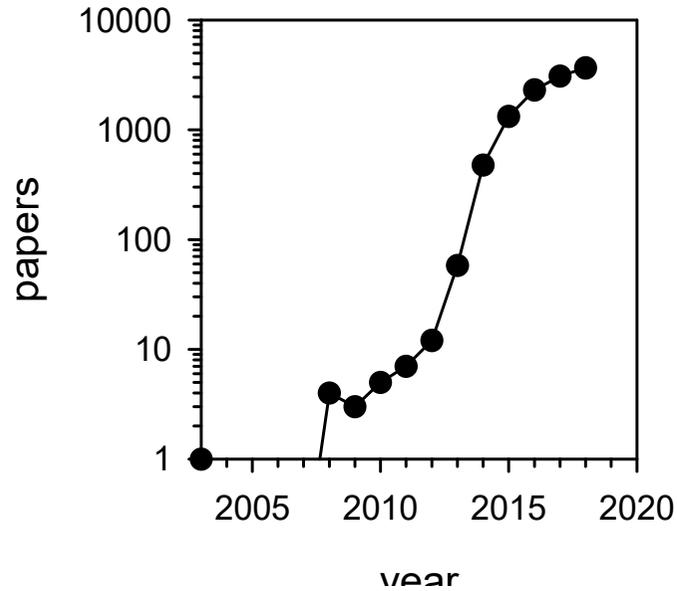
- Single crystal (concentrator)
- Single crystal (non-concentrator)
- Multicrystalline
- ◆ Thick Si film
- Silicon heterostructures (HIT)
- ▼ Thin-film crystal





Source: NREL (2013)

Hybrid halide perovskites: Impact



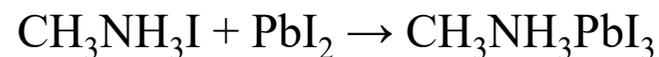
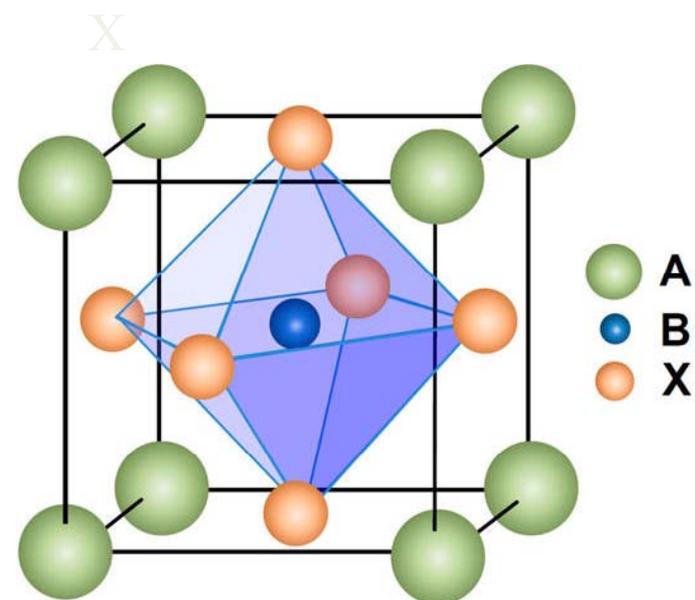
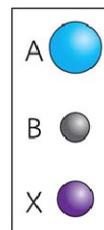
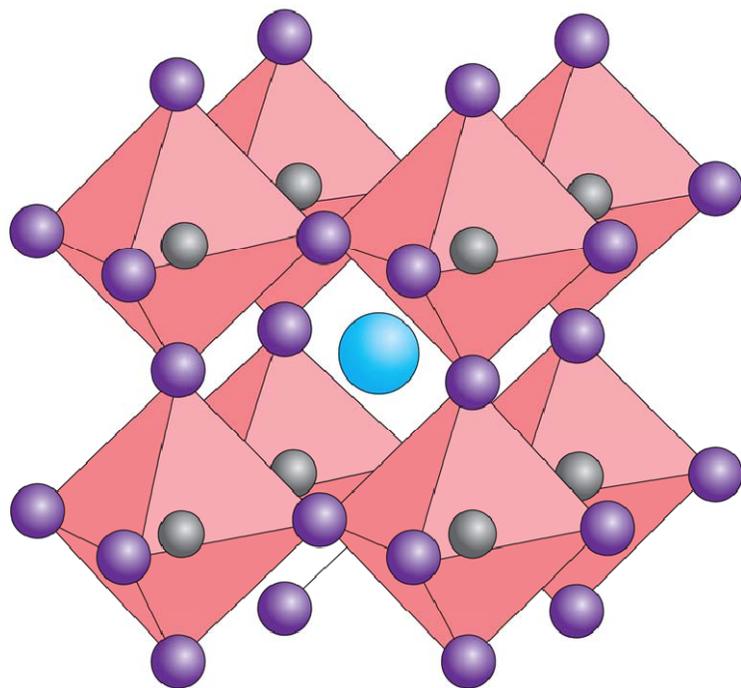
Source: ISI Web of

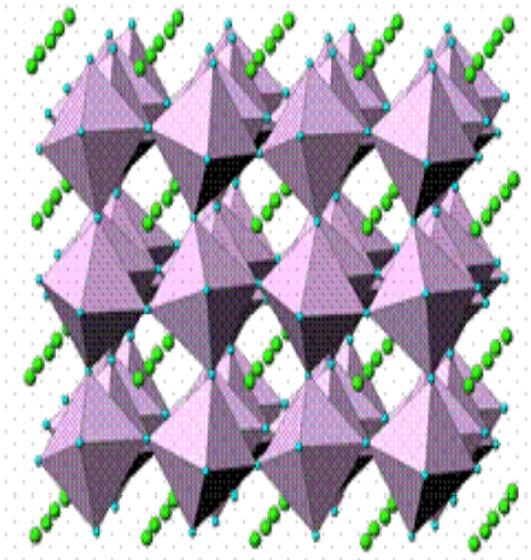
General perovskite structure: ABX_3

A = organic component in cuboctahedral A site ($MeNH_3^+$, $EtNH_3^+$)

B = inorganic components in octahedral B site (Pb_2^+ , Sn_2^+)

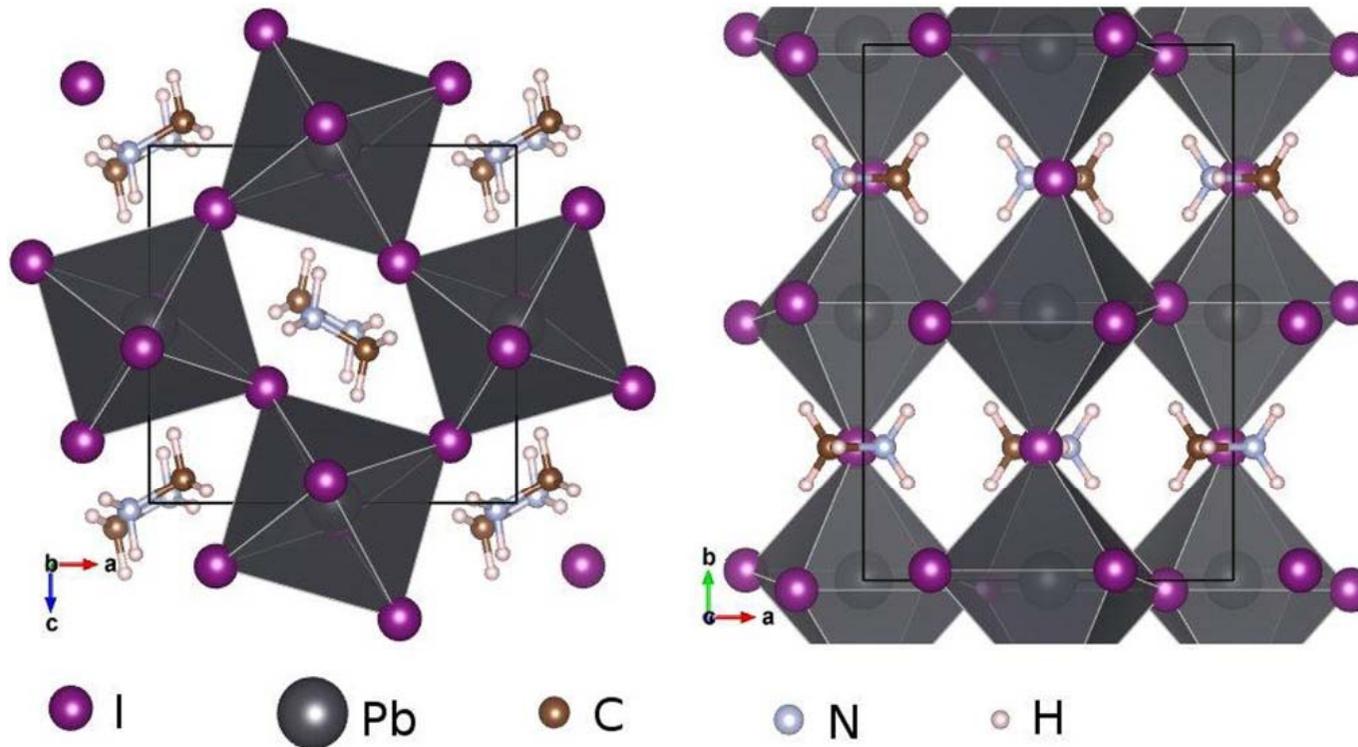
X = halogens (Cl⁻, Br⁻, I⁻)





- Pb^{2+} is connected to 6 anions I^- [PbI_6], which forms an octahedra.
- Each cation CH_3NH_3^+ is located at the center of 4 of these octahedra.
- Conduction band, is derived from the Pb $6p$ orbitals; valence band from I-

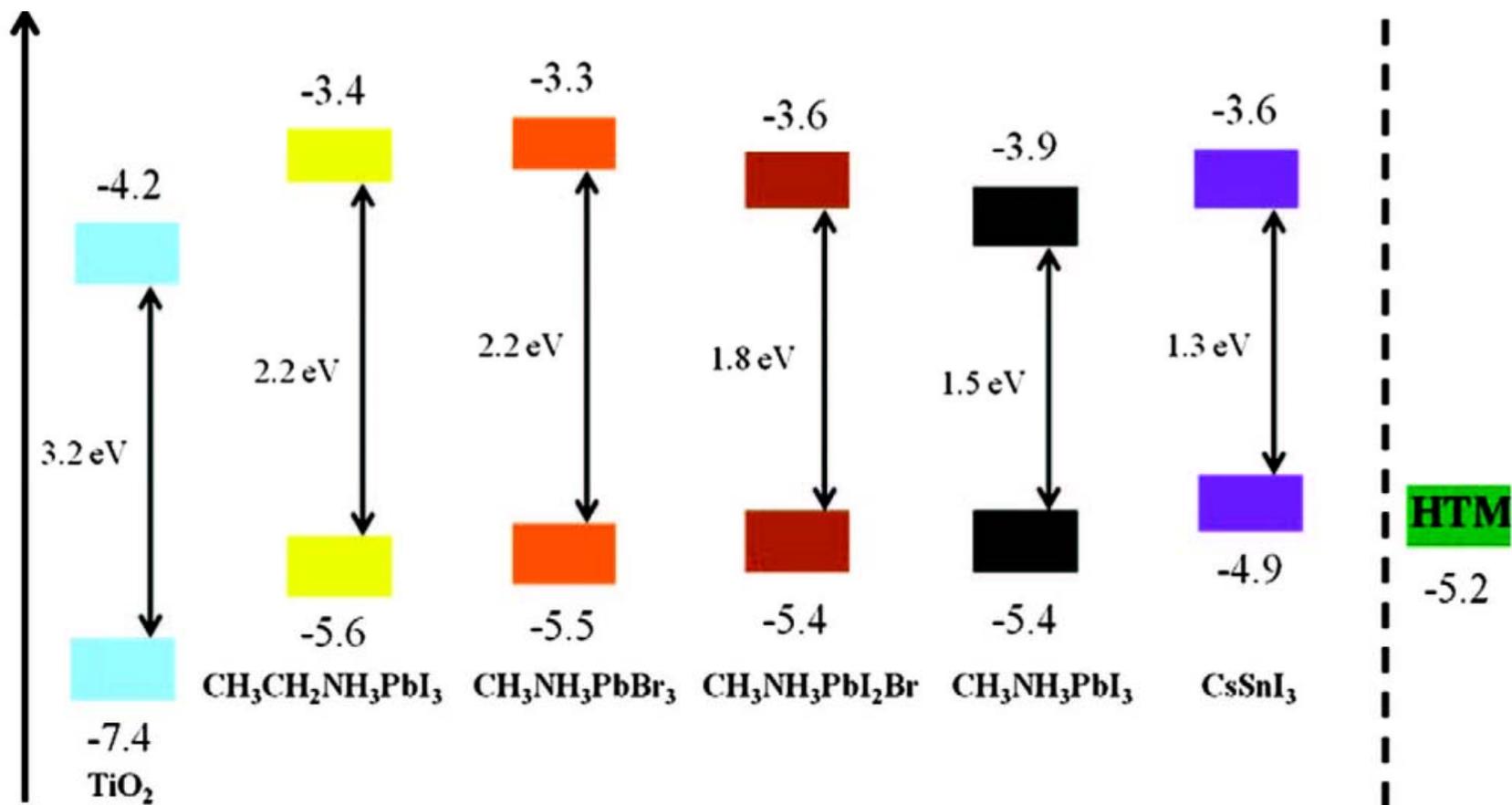
Structure



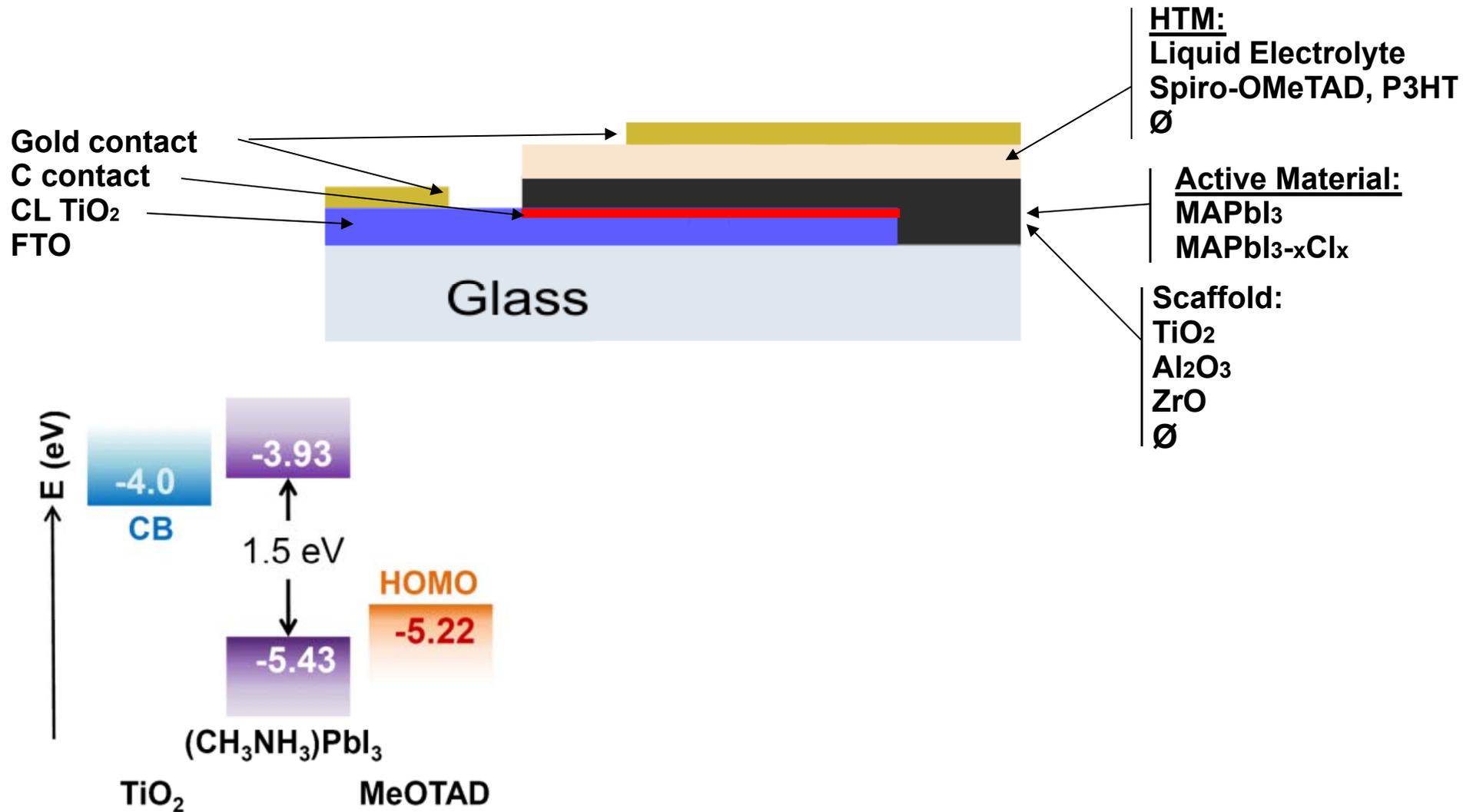
- The crystallographic structure of $\text{CH}_3\text{NH}_3\text{PbI}_3$ depends on temperature:
 - At low temperature: orthorhombic
 - At $T > 161.4$ K: tetragonal
 - At $T > 330.4$ K: cubic
- The rotation of CH_3NH_3^+ is very fast (ps) in the cubic phase unlike in the orthorhombic phase

Hybrid halide perovskites: Versatility

Energy (vs. vacuum, eV)

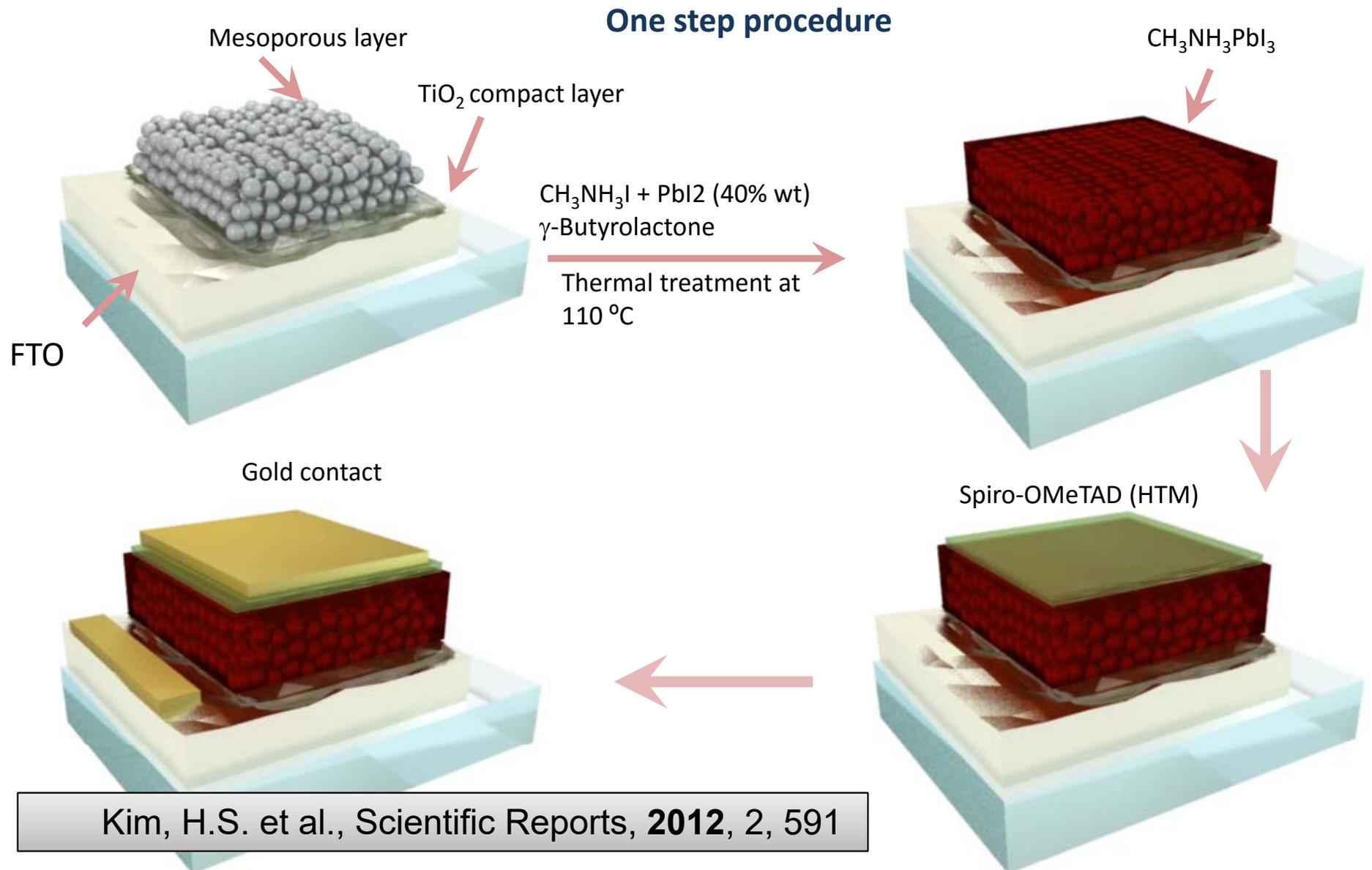


Perovskite solar cells: configuration



Perovskite solar cells: Cell Preparation

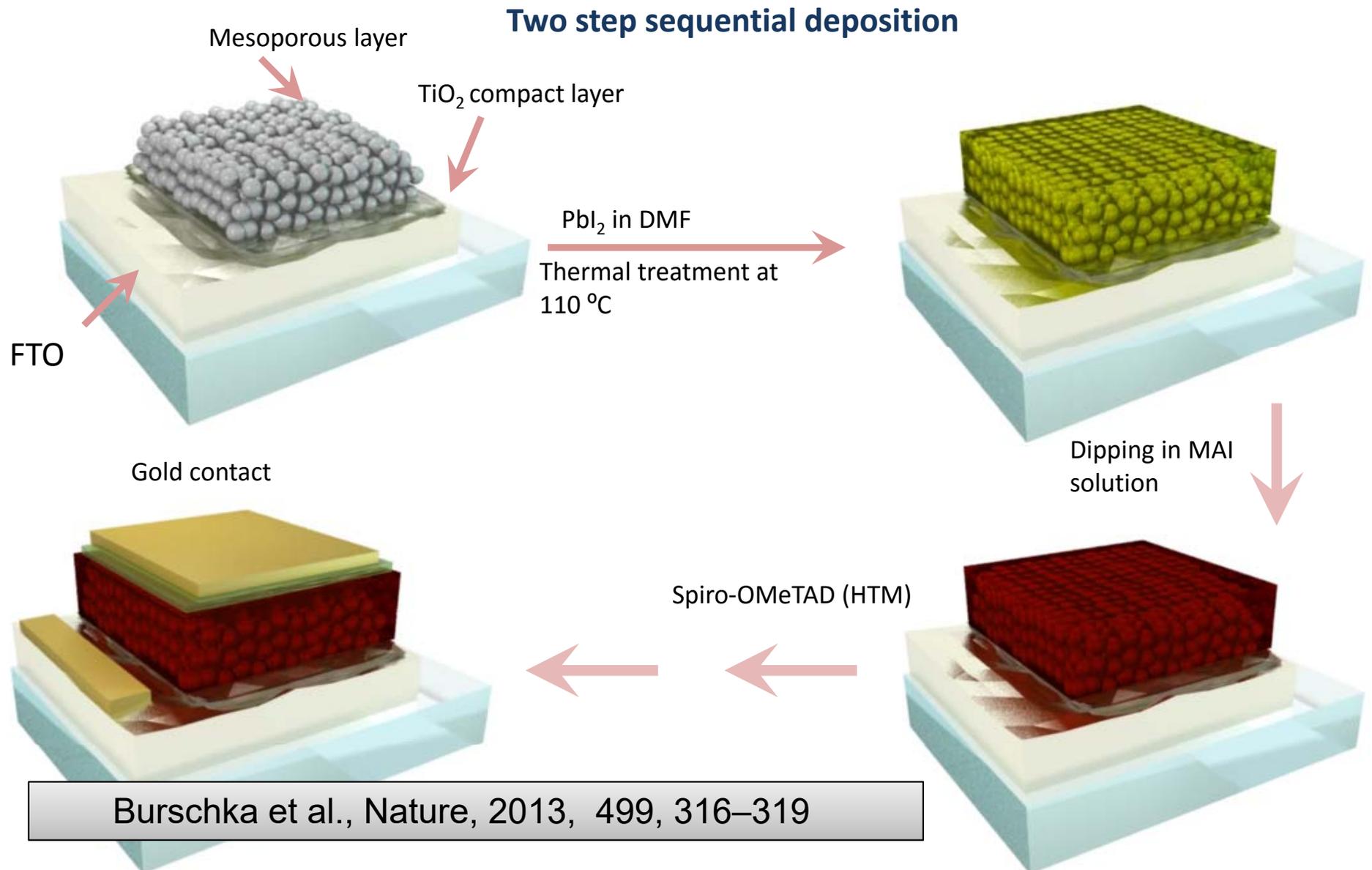
Park Method



Kim, H.S. et al., Scientific Reports, **2012**, 2, 591

Perovskite solar cells: Cell Preparation

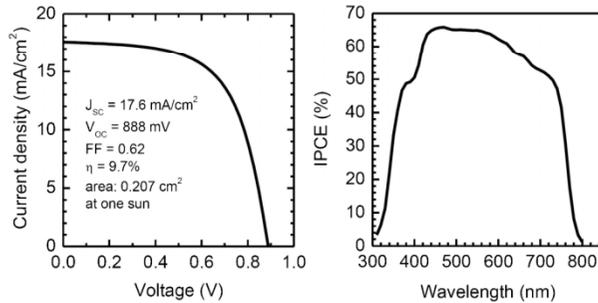
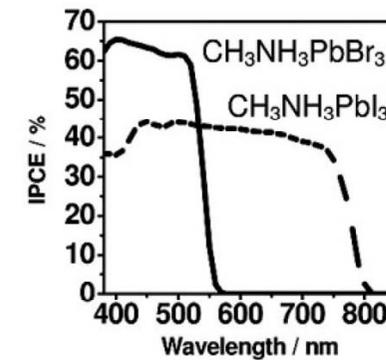
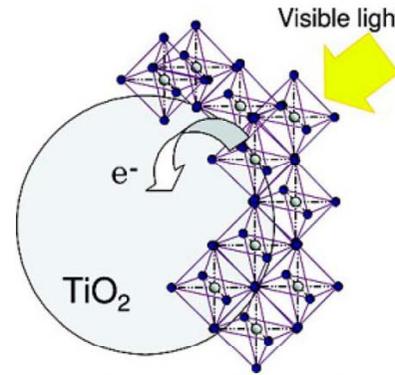
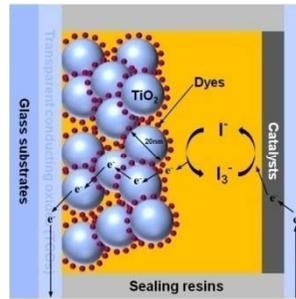
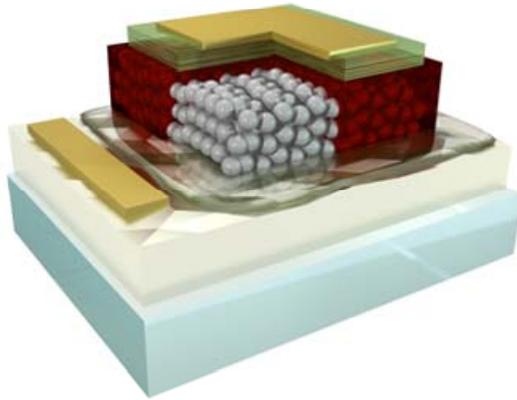
Mitzi-Grätzel Method



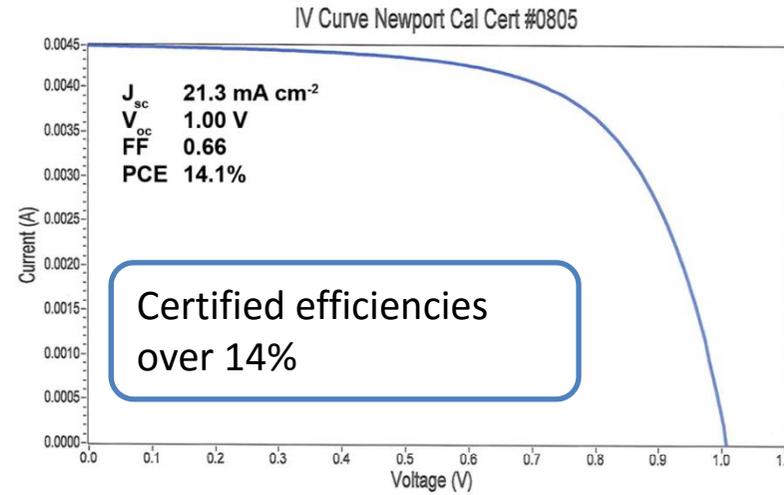
Burschka et al., Nature, 2013, 499, 316–319

Perovskite solar cells: From sensitized to thin film devices

Kojima *et al.*, JACS, 2009, 131, 6050–6051



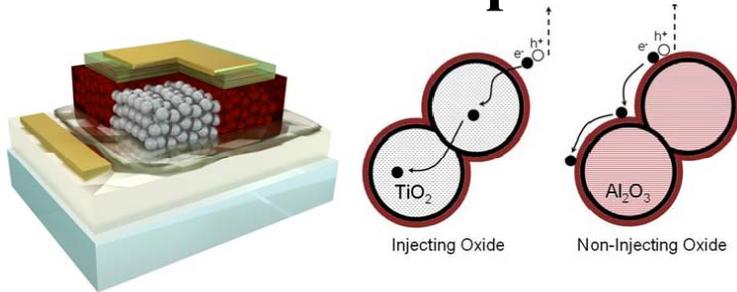
HTM: spiro-OMeTAD
Efficiency: 9%



Kim *et al.*, Scientific Reports, 2012, 2, 591

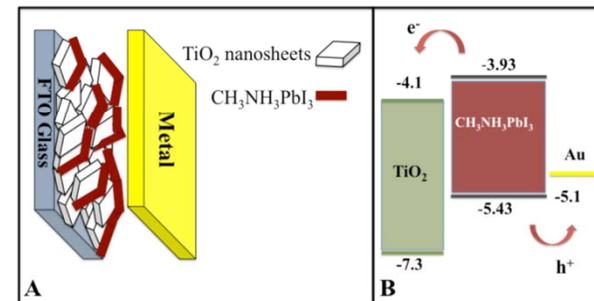
Burschka *et al.*, Nature, 2013, 499, 316–319

No electron transport media



Lee et al., Science, 2012, 338 , 643-647

No Hole Transporting Media



- Etgar, L.; et al., *J. Am. Chem. Soc.* 2012, 134, 17396-17399

- ✓ Devices with MS alumina as an insulating scaffold reports efficiencies higher than 15%.
- ✓ Samples with no hole transporting material reports efficiencies higher than 12%
- ✓ It gives evidence of electron and hole transport in PS layer pointing to a different working mechanism than in sensitized devices.

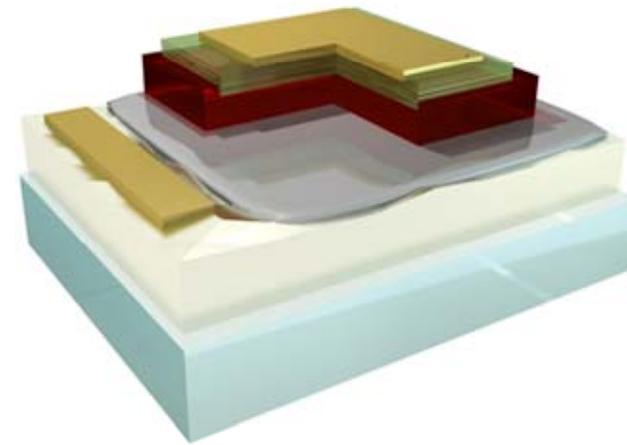
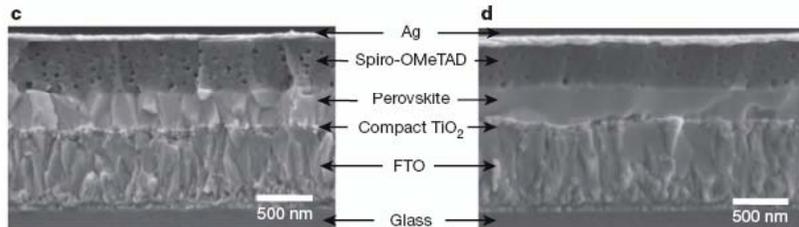
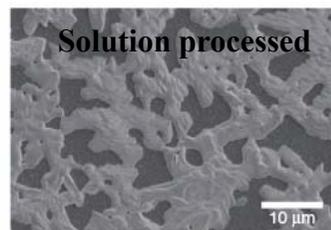
Perovskite solar cells: From sensitized to thin film devices

Thin film solar cell configuration

$\eta = 15.4\%$



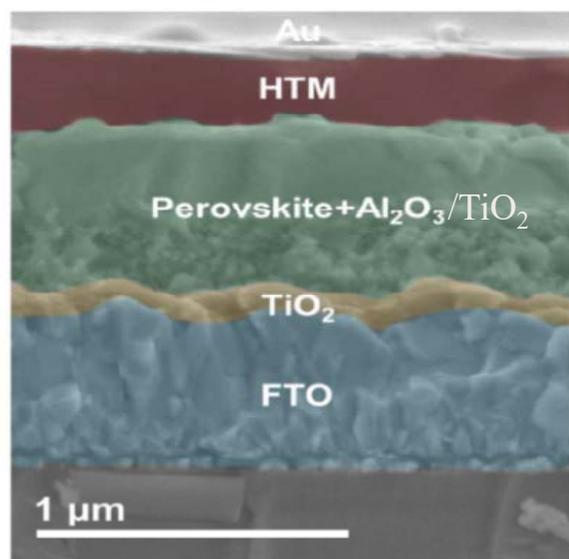
$\eta = 11.4\%$



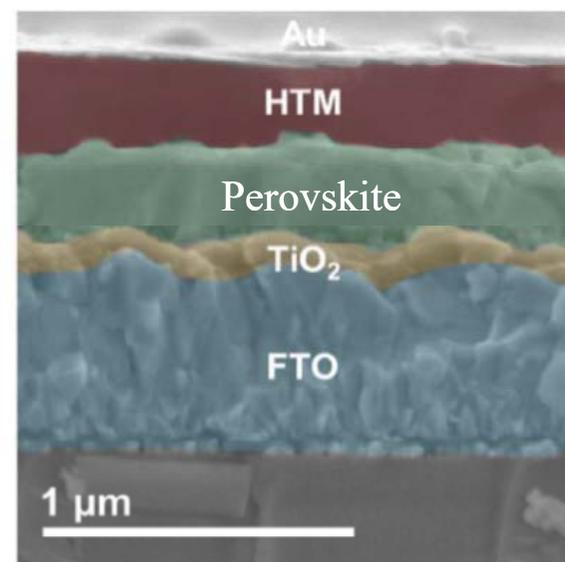
- ✓ Devices with MS alumina as an insulating scaffold reports efficiencies higher than 15% and thin film configuration over 15%
- ✓ It gives evidence of carrier transport and accumulation in PS layer

Liu et al., Nature, 2013,
501(7467),395-8
Eperon et al., Adv. Funct.
Mater., 24, 151–157

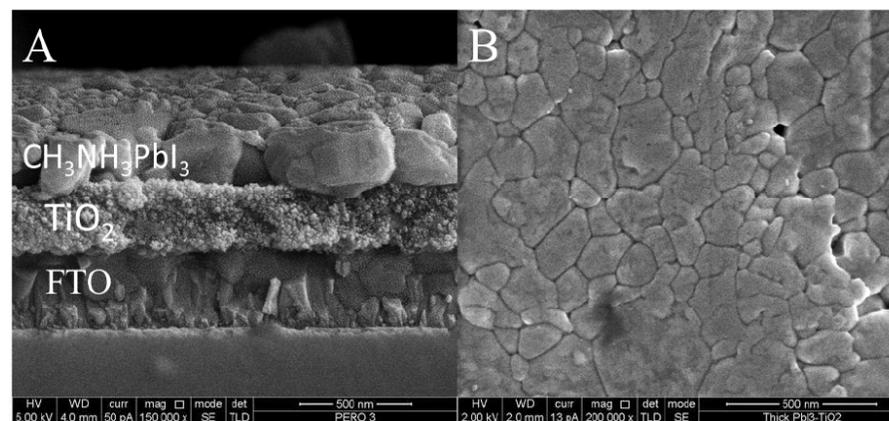
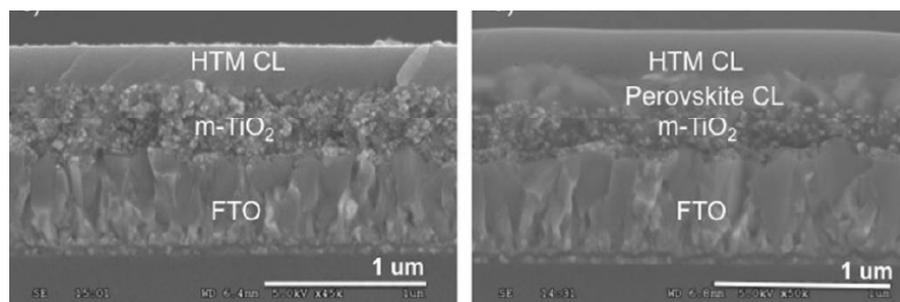
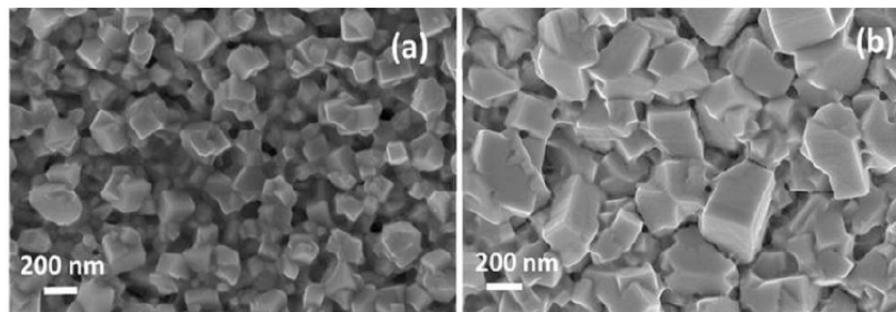
Mesoporous cell



Flat cell

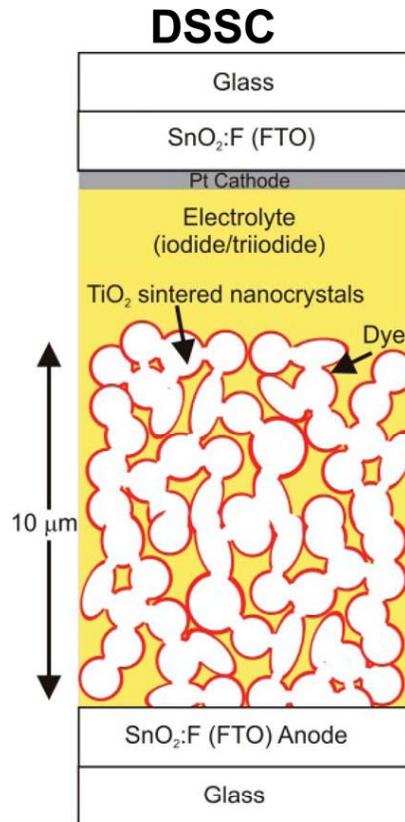


Hybrid halide perovskites: morphologies

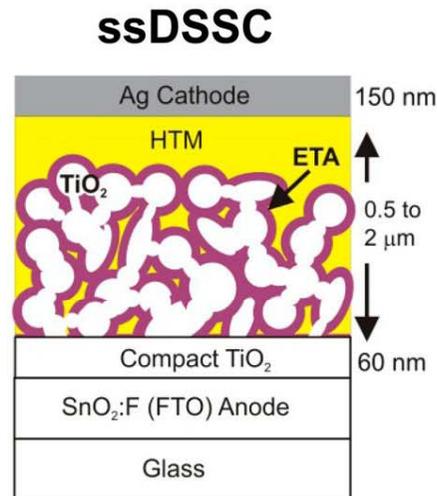


Perovskite solar cells: Historic Evolution

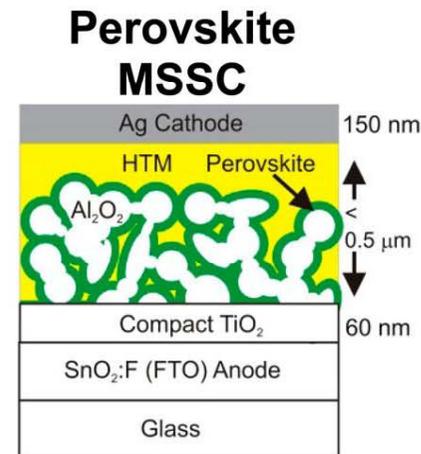
Snaith, H. J. Phys. Chem. Lett. **2013**, 4, 3623–3630



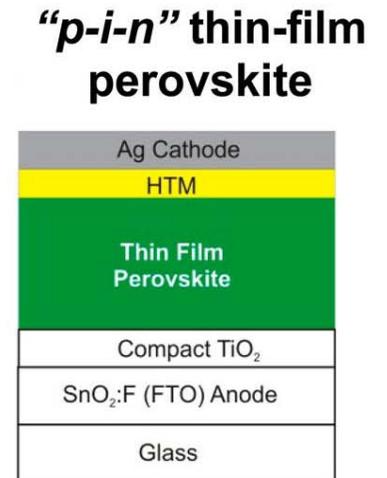
2009
3.8%



2012
9.7%



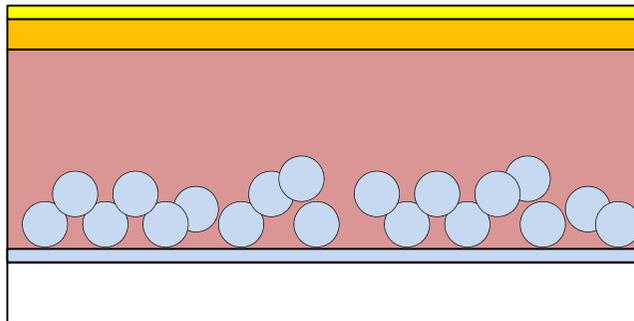
2012
10.9 %



2013
15.4%

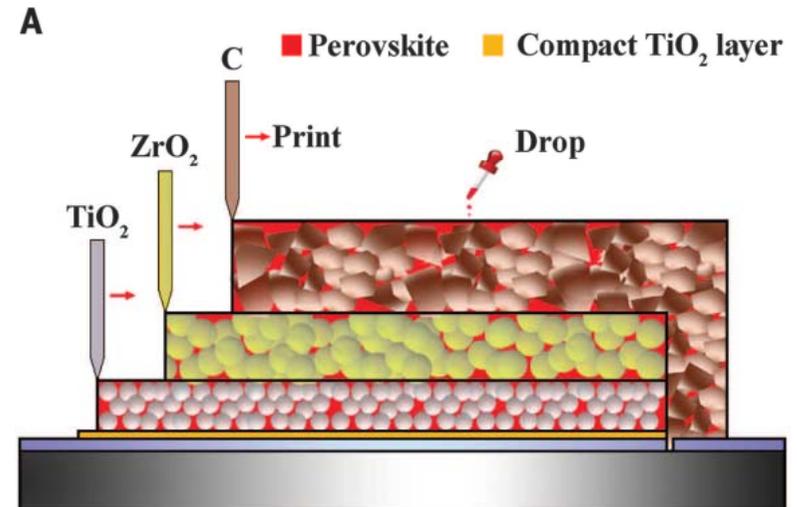
Perovskite solar cells: Historic Evolution

Au
PTAA
Perovskita
NP-TiO₂
Compact TiO₂
FTO



May 2014 (16.2%)

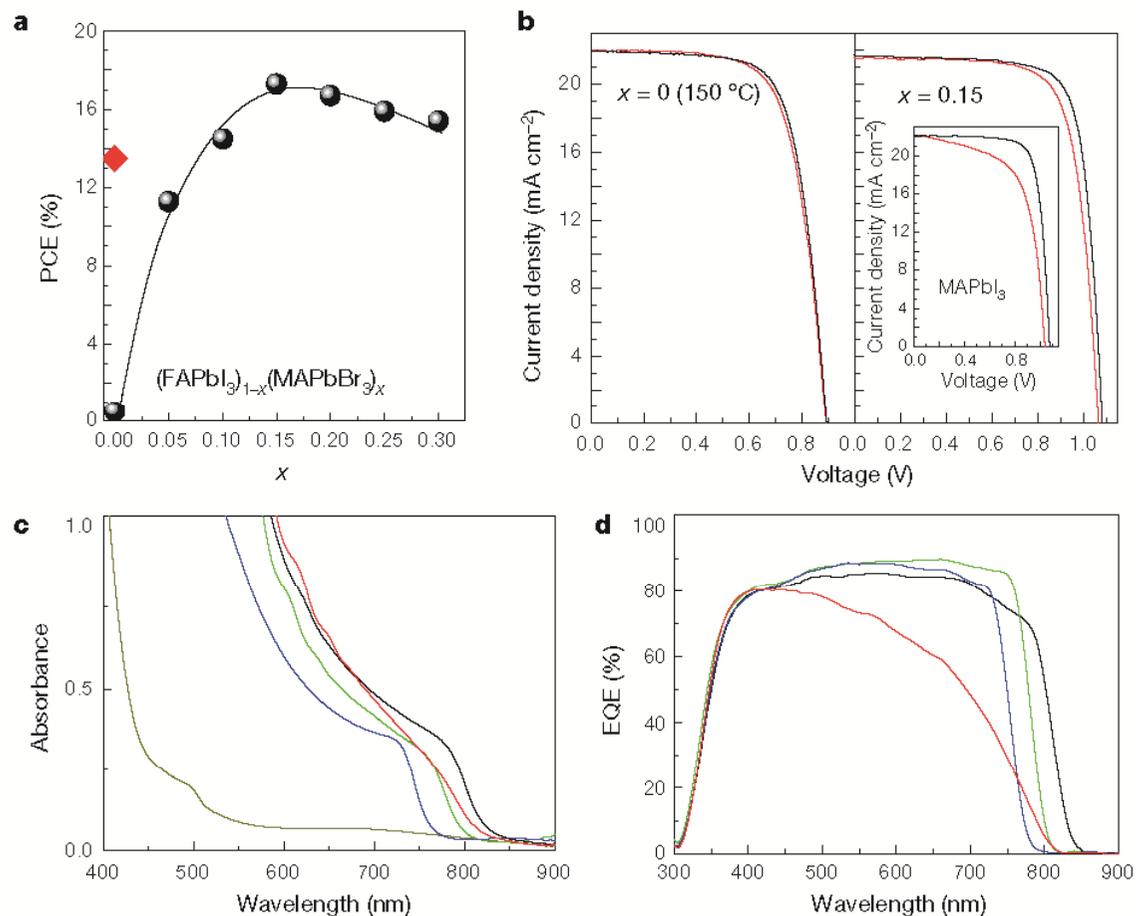
Seok, Nat. Materials. 2014



HTM free 2014 (12.8%)

Han, Science. 2014, 345, 295–298

Perovskite solar cells: Historic Evolution



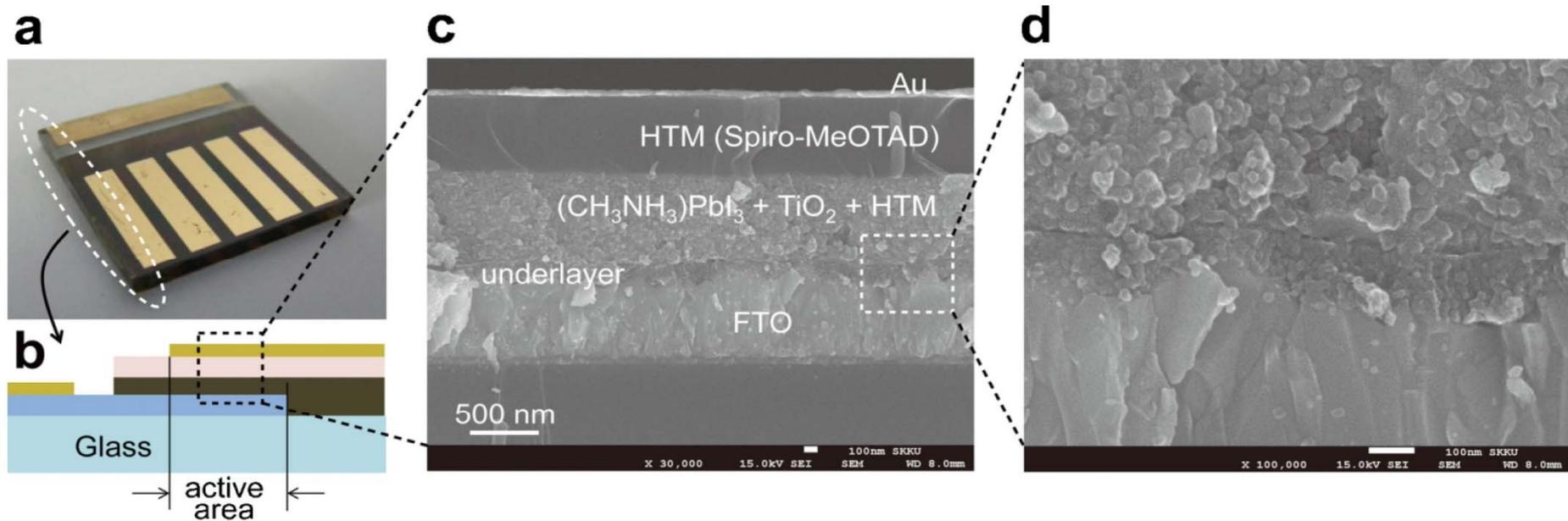
May 2014 (17.8%)

Dec 2014 (20.1%)

Sang Il Seok Nature, 2015, 517, 476–480

Perovskite solar cells: Historic Evolution

Perovskita solar cell:



Eficiències 2013: 15.1% Flat band (Henri Snaith, Oxford University)
15.2% DSC structure (Michael Grätzel, EPFL)

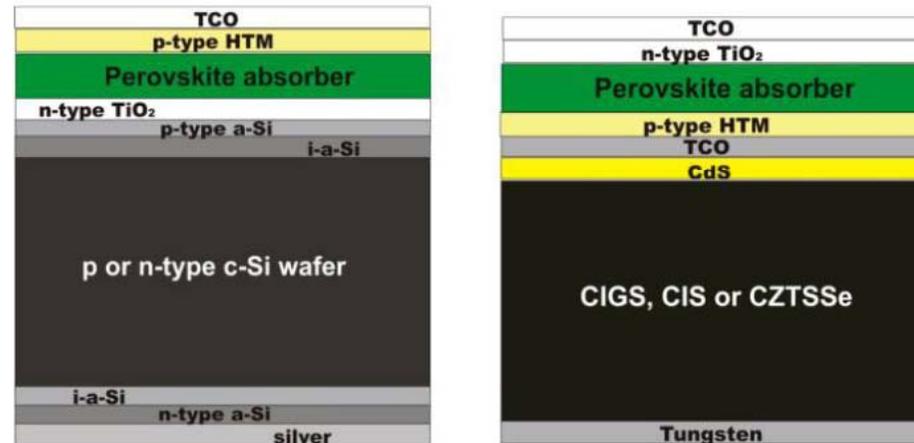
Eficiències 2015: 18 % Flat band (Henri Snaith, Oxford University)
20.7% DSC structure (Park, KRICT, Michael Grätzel, EPFL)

Eficiència 2017: 21-22% DSC structure (Michael Grätzel, EPFL, Sang Il Seok, Korea)

Eficiència 2019: 23.7% DSC structure (Sang Il Seok, Korea)

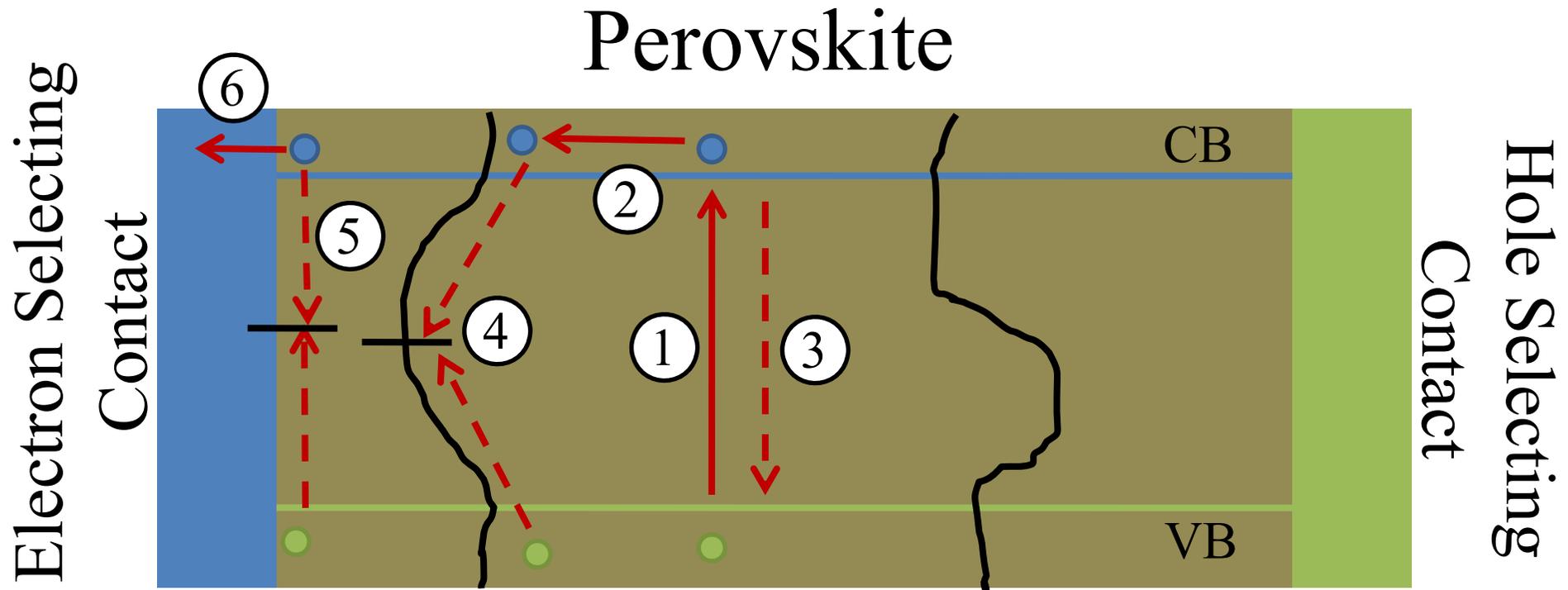
Perovskite solar cells: Challenges

- Hybrid multijunction solar cells



Snaith, H. J. Phys. Chem. Lett. **2013**, 4, 3623–3630

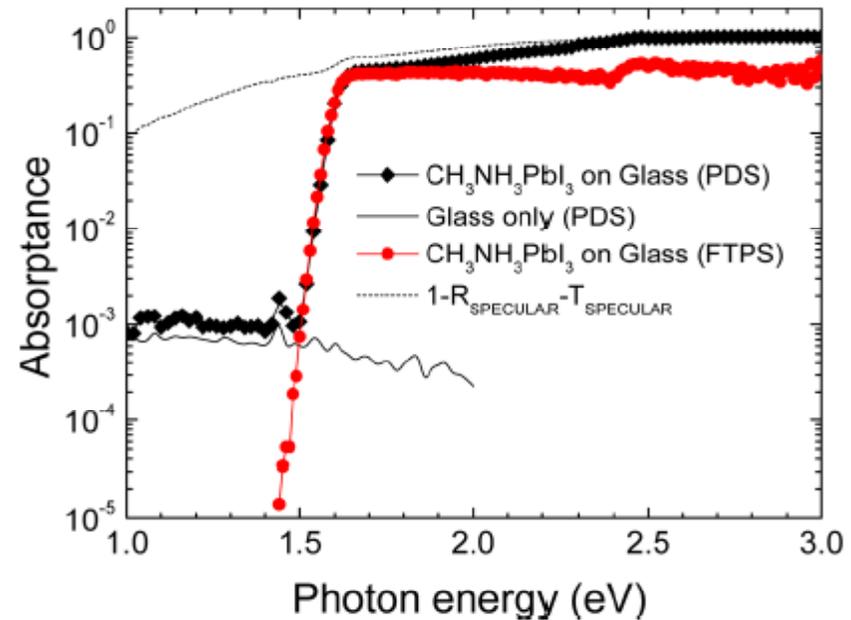
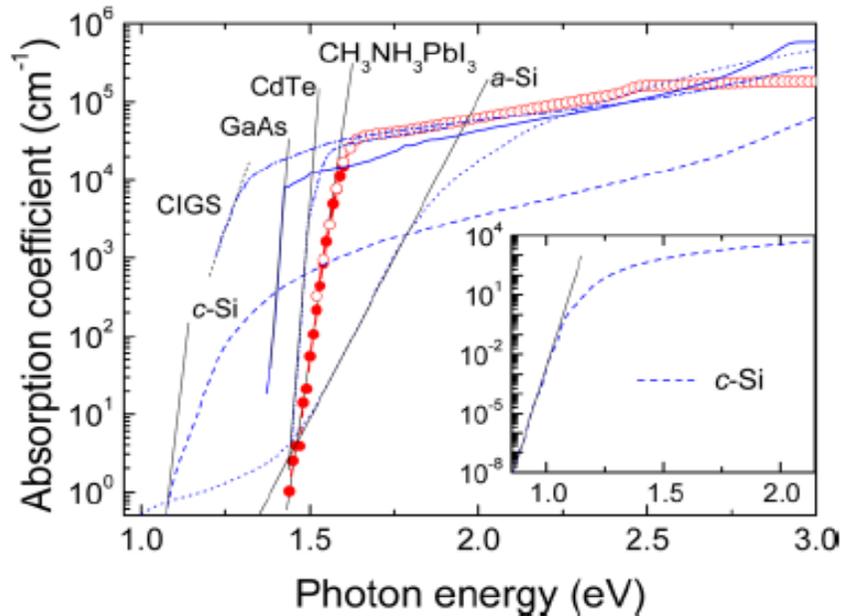
- **Stability**
- **Use of less toxic materials**



- | | |
|----------------------|---------------------------|
| ① Photogeneration | ④ Grain boundary rec. |
| ② Transport | ⑤ Interface recombination |
| ③ Bulk recombination | ⑥ Charge transfer |

Optical properties

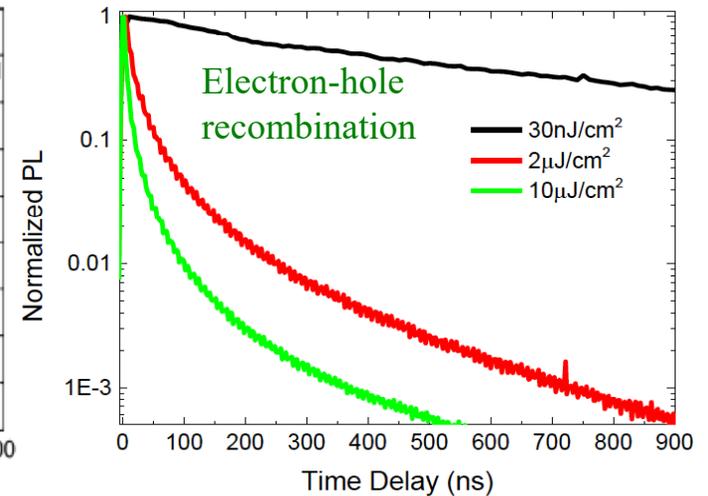
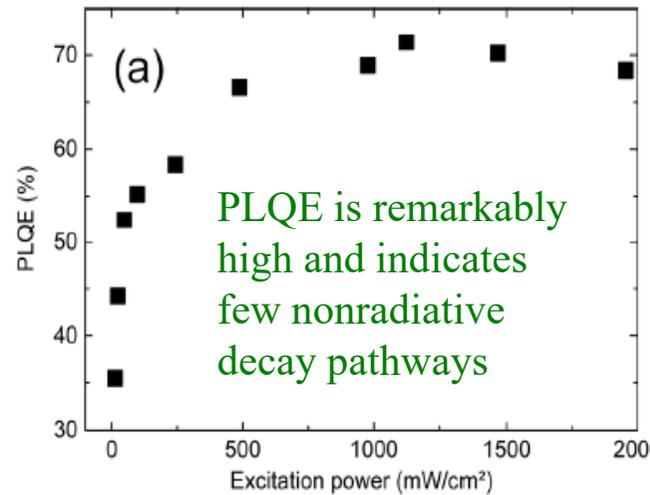
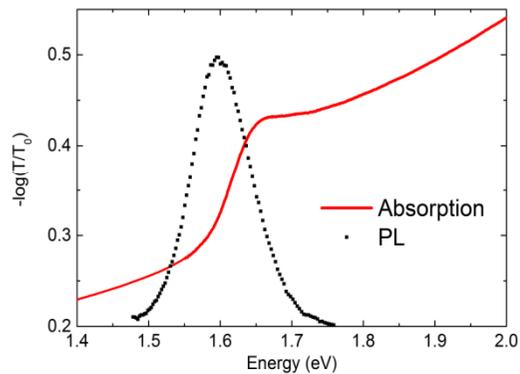
ABSORPTION BAND-EDGE



- 1) Sharp band-edge (1.57 eV) > most other comparable semiconductors.
- 2) For $E < E_g$ Urbach tail is observed (slope ≈ 15 meV: very low degree of structural disorder ... high crystallinity in the film). Materials with the smallest Urbach energy lead to the lowest $E_G/q - V_{OC}$ values.
- 3) Purely Urbach-exponential trend over more than four decades, suggests no optically detectable deep states.

Optical properties

PL-QE and lasing



*Low PLQE at low power due to the presence of defects (long PL decay times).

*Radiative recombination becomes dominant over non radiative at high fluences after defects are filled (short PL decay times).