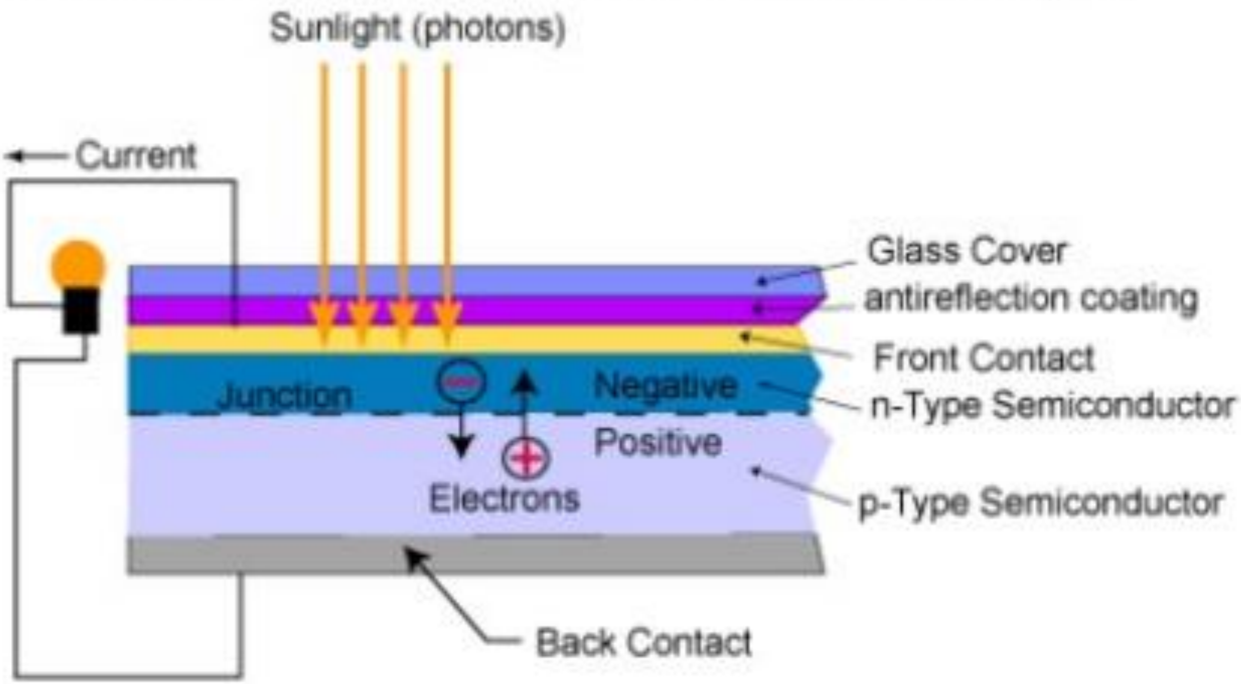
Basic Structure of a Photovoltaic Solar Cell

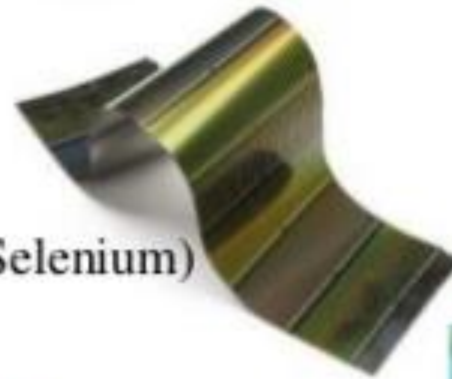
- A photovoltaic solar cell is made of three main part:
  - **Light Absorber**; converting incident photons to electron and holes
  - **Carrier Collector/s**; capturing the carriers (electron and holes)
  - **Metal Contacts**: transferring the carriers to the circuit
- The heart of a solar cell is the absorber layer



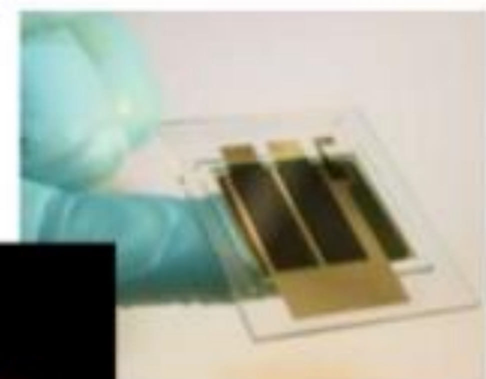
Basic schematic of a photovoltaic solar cell

Three Generations of Solar Cells

- Wafer based: Highest efficiency
  - Monocrystalline silicon 25%
  - Polycrystalline silicon 20%
  - Multi-junction cell (different band-gap materials) 40%
- Thin Films:
  - Amorphous thin film silicon 13%
  - CdTe (Cadmium Telluride) 17%
  - CIGS (Copper Indium Gallium Selenium) 20%

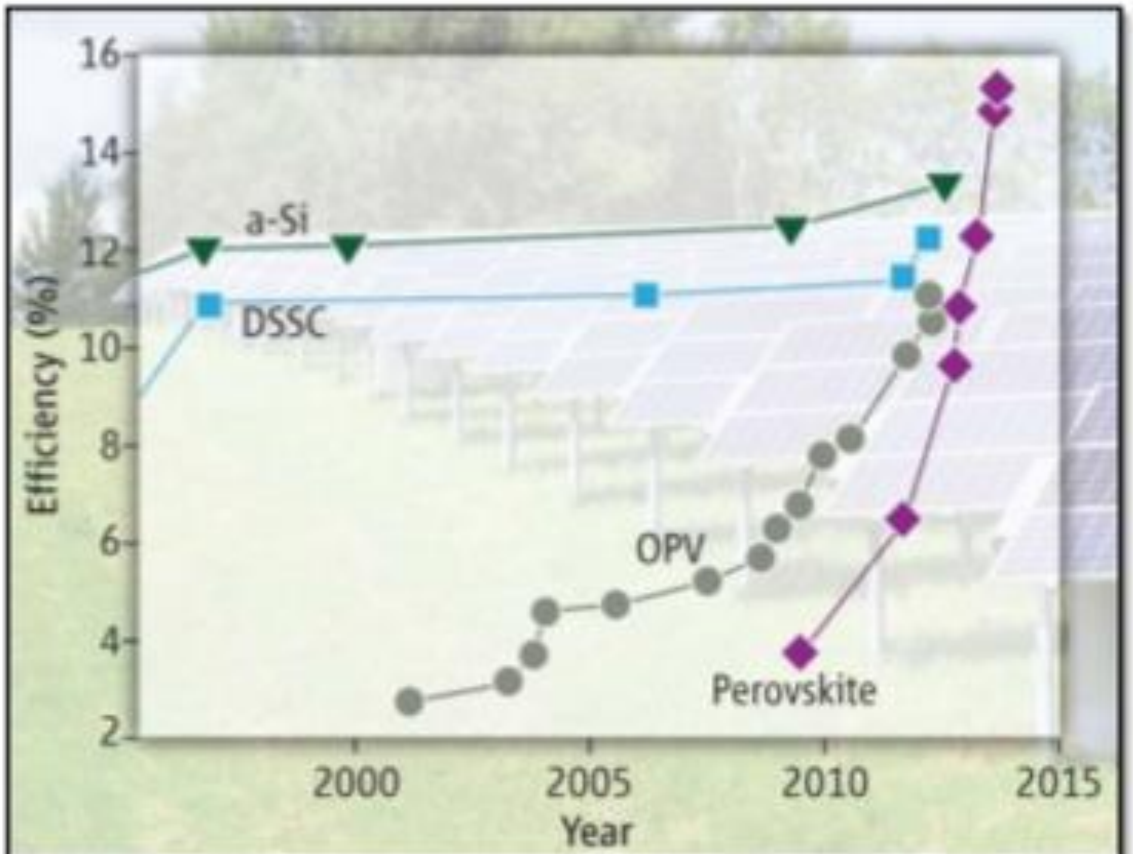


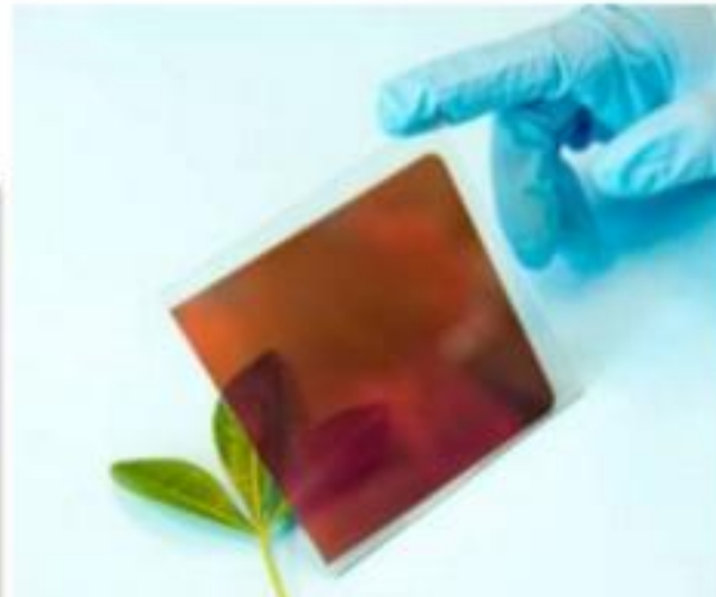
- Low Cost and high Efficient:
  - DSSC (Dye-sensitized solar cells)
  - QDSSC (Quantum Dot-sensitized solar cells)
  - OPV (Organic photovoltics)
  - QDs-Polymer Hybrid solar cells
  - **Perovskite Solar Cells**



Emergence of Perovskite Solar Cells

- Efficiency jump in photovoltaics research
- From 3.8 % in 2009 to 15.9 % in 2014





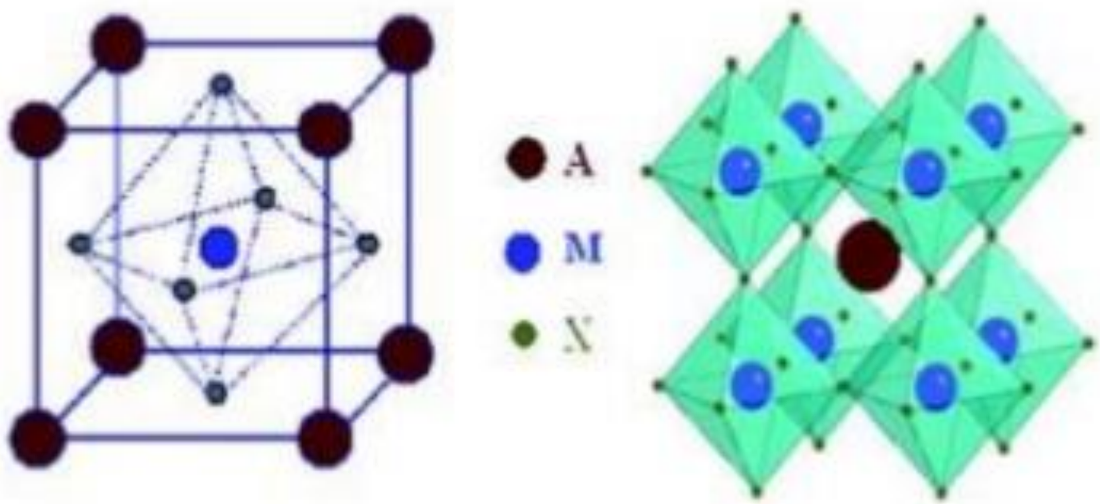
15% perovskite solar cell made in University of Oxford

Superiorities of Perovskite Solar Cells

1. High efficiency; with an efficiency of 15.9% after only several years work.
2. Facile low temperature solution-based fabrication method;
3. High absorption coefficient.
4. Higher stability in air.
5. High diffusion length, high charge-carrier mobilities.
   - it means that the light-generated electrons and holes can move large enough distances to be extracted as current, instead of losing their energy as heat within the cell
6. very high values of open-circuit voltages (V_{OC}) typically obtained.

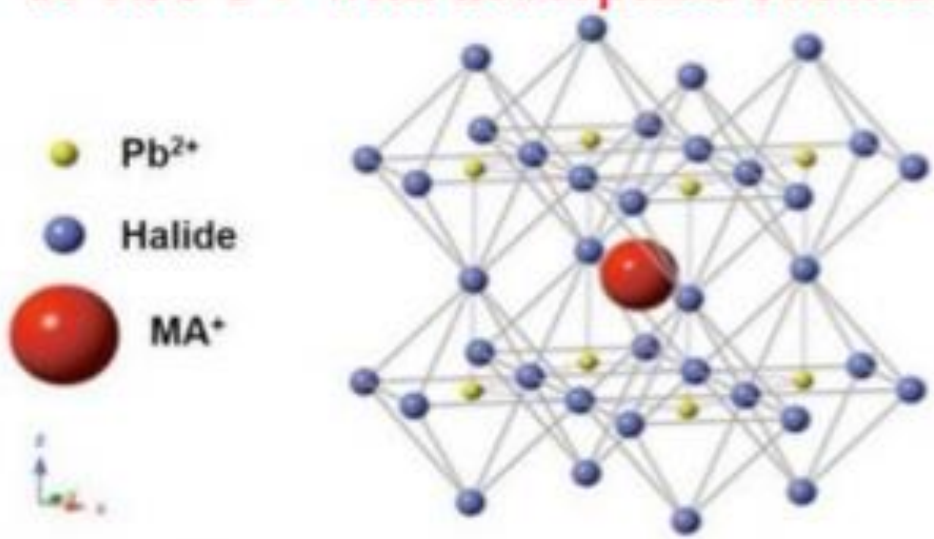
Perovskite Crystal Structure

- Usually have stoichiometry of AMX_3
- X is an oxide or halide anion such as Cl, Br and I.
- M refers to a metal cation with a coordination number of 6.
- The MX_6 octahedra share corners and A is usually a large cation that fills the cuboctahedral holes with coordination number of 12.
- A can be Ca, K, Na, Pb, Sr, other rare metals.



Organic–inorganic Hybrid Perovskites

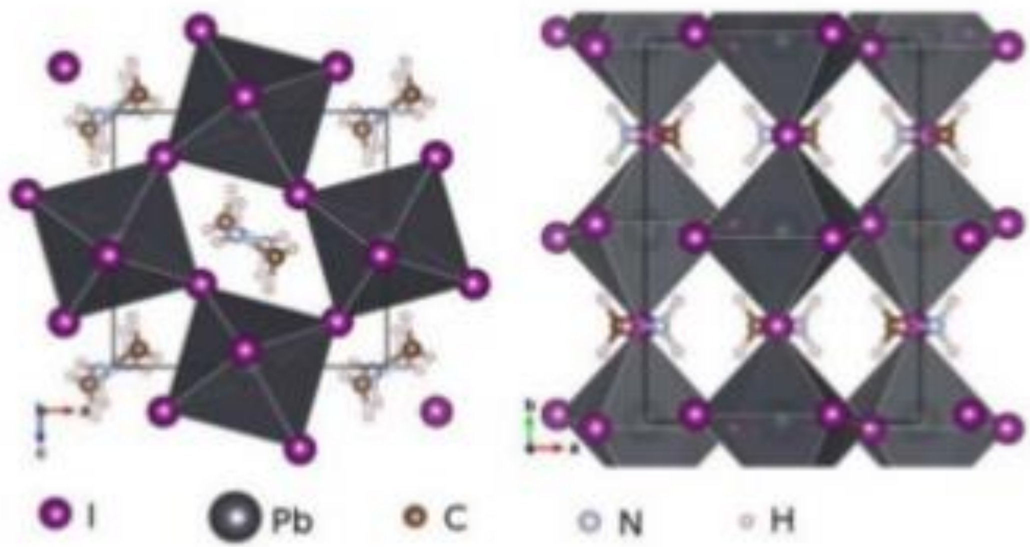
- First three-dimensional organic–inorganic hybrid perovskite, discovered by replacing caesium in $CsPbX_3$ (X = Cl, Br or I) with methylammonium cations (MA = $CH_3NH_3^+$) by Dieter Weber, in 1978.
- $CH_3NH_3PbI_3$ is most common used materials for making high efficiency perovskite solar cells.
- $CH_3NH_3PbI_3$ is a semiconducting pigment with a direct bandgap of 1.55 eV with absorption coefficient as high as 10^4–10^5 cm^{-1}



Methylammonium (MA)

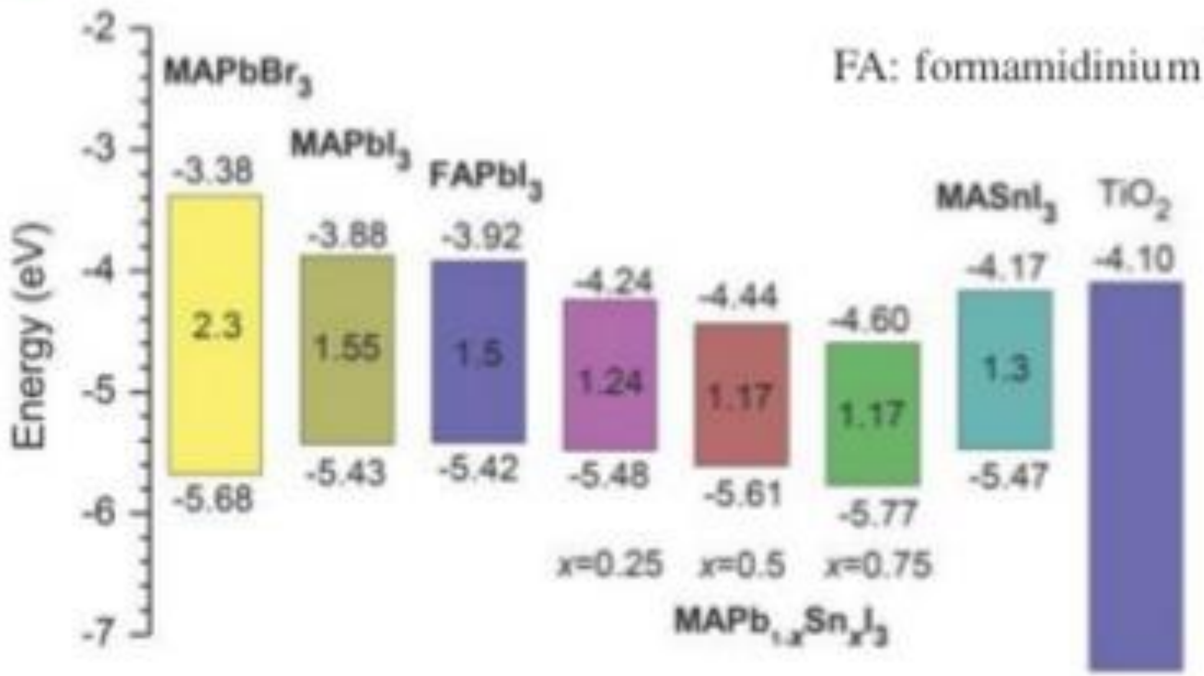
Organic–inorganic Hybrid Perovskites cont.

- The unit cell parameter *a* increases from 5.68 to 5.92 and to 6.27 Å as the size of halide increases from X = Cl to Br and to I, respectively.
- The large size and aspherical shape of MA cause distortion in network and drives several phase transitions by decreasing T.
- For T <160 K orthorhombic, 162.2 K<T< 327.4 K tetragonal and T > 327.4 K cubic.



Band Gap Tuning

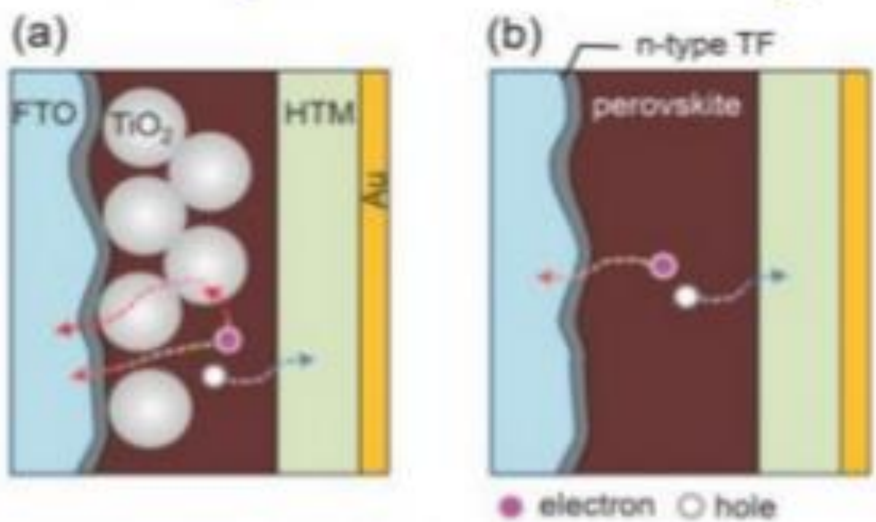
- Bandgap tuning is required to extend the absorption to longer wavelengths without sacrificing the absorption coefficient.
- Changing in any of A, M and X in AMX_3 changes the bandgap
- The bandgap also can be tuned in between 1.55 eV and 1.17 eV by varying the ratio of lead to tin



FA: formamidinium $HC(NH_2)_2^+$

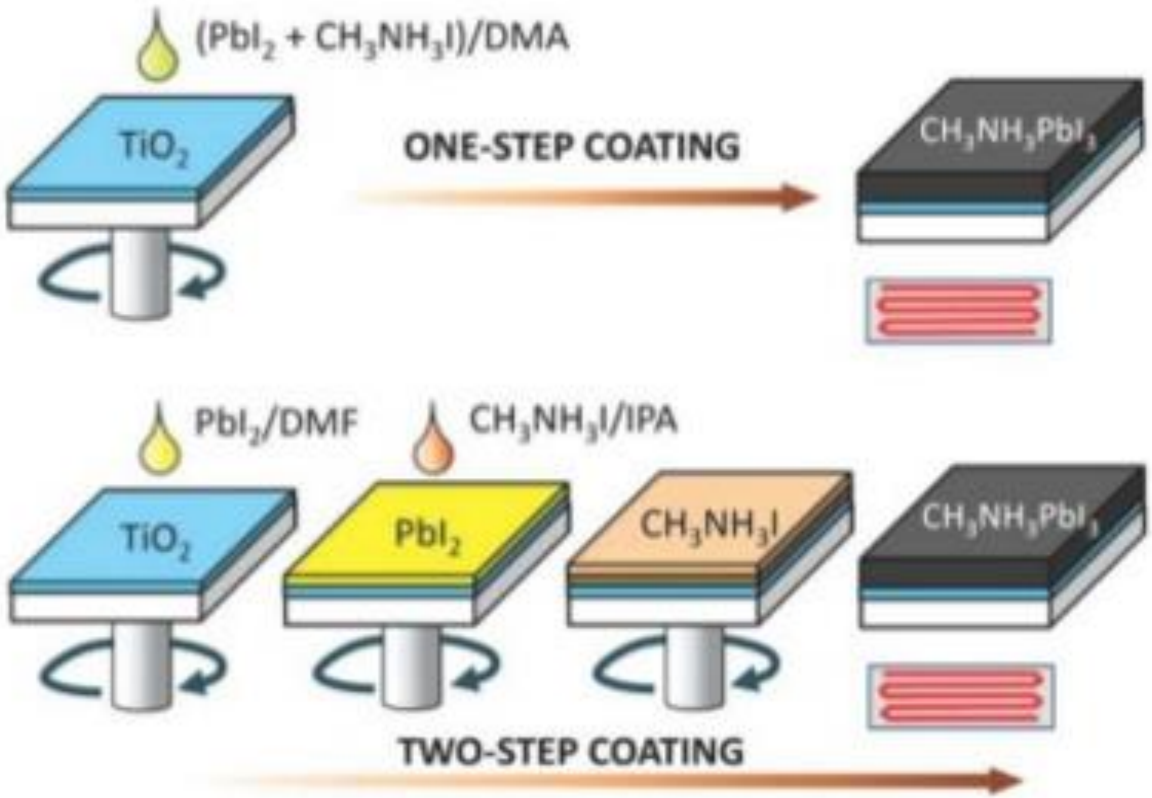
Device structure

- The device structure, related materials, and interfacial modification are key factors in performance of solar cells.
- Two typical structures can be constructed: a) mesoscopic nanostructure and b) planar structure.
- Mesoporous TiO_2 layer usually is used to collect the electrons
- Organic Hole transporting material (HTM) collects the holes
- Planar structure has simpler structure and higher efficiency



Preparation Method

- There are two common methods:
  1) one step coating: spin-coating a mixed CH_3NH_3I and PbI_2solution
  2) two-step coating: spin-coating CH_3NH_3I after coating with PbI_2



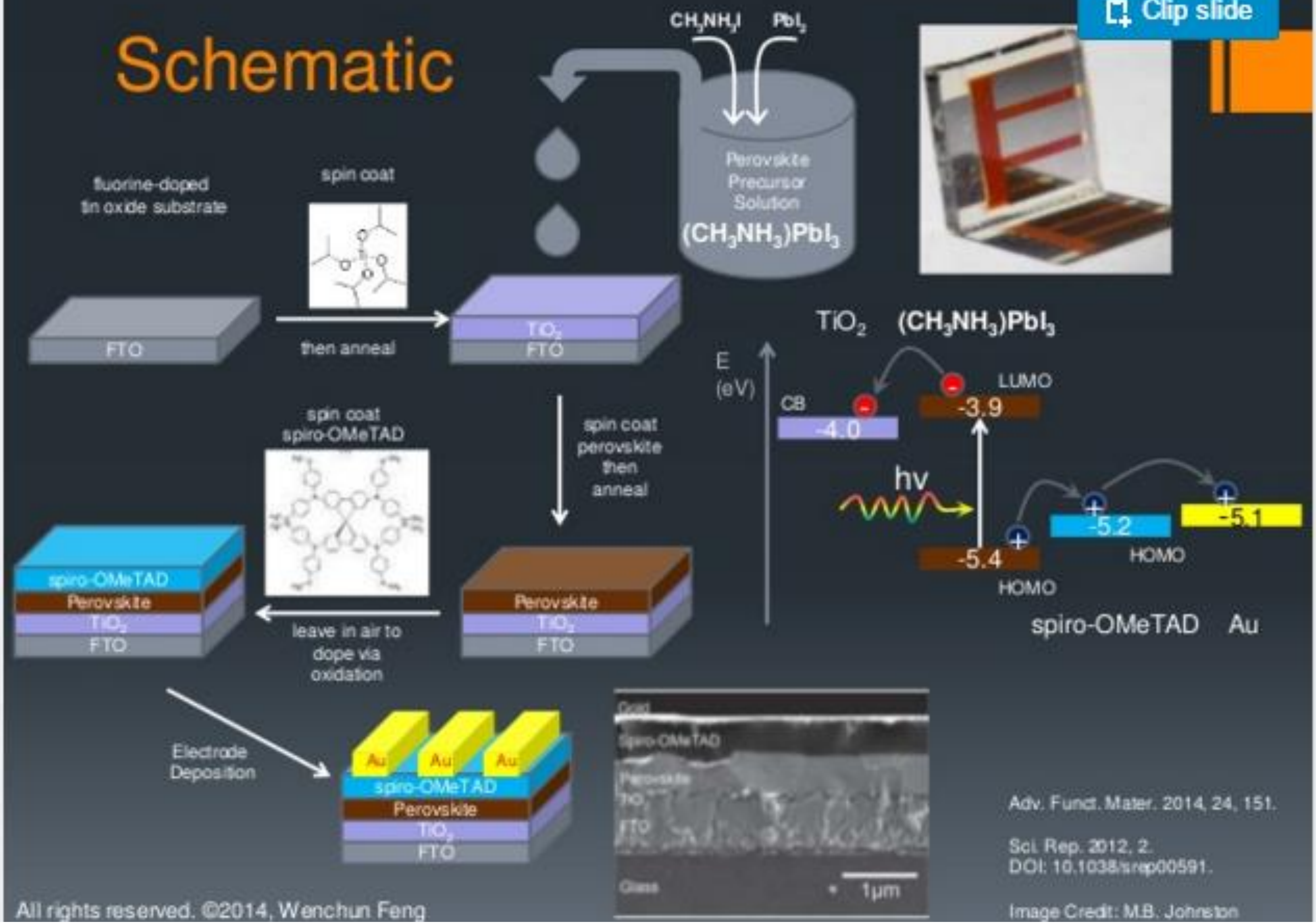
Preparation Method cont.

- All deposition process happens at a low temperature (below 150 °C), which is suitable for the fabrication of flexible solar cells based on PET substrates.
- The concentration of the CH_3NH_3I solution affects the crystal size from about 90 nm to about 700 nm.
- Photovoltaic performance was strongly influenced by the CH_3NH_3I concentration, i.e., the crystal size of $CH_3NH_3PbI_3$
- $CH_3NH_3PbI_3$ degrades in humid conditions and forms PbI_2 at higher temperatures due to the loss of CH_3NH_3I
- Lead (Pb) compounds are very toxic and harmful to the environment.
- Video instruction of fabricating perovskite soalr cells:
  - https://www.youtube.com/watch?v=RqW9HrasNPA

Future Challenges of Perovskite Solar Cells

- Improving efficiency to exceed thin film CdTe solar cells
  - By understanding their material properties and optimal cell designs
- Increasing air and temperature stability
- Replacing toxic Pb with a greener element
- Is AMX_3 (perovskite structure) the best stoichiometry? Have we tried other structures?

Schematic

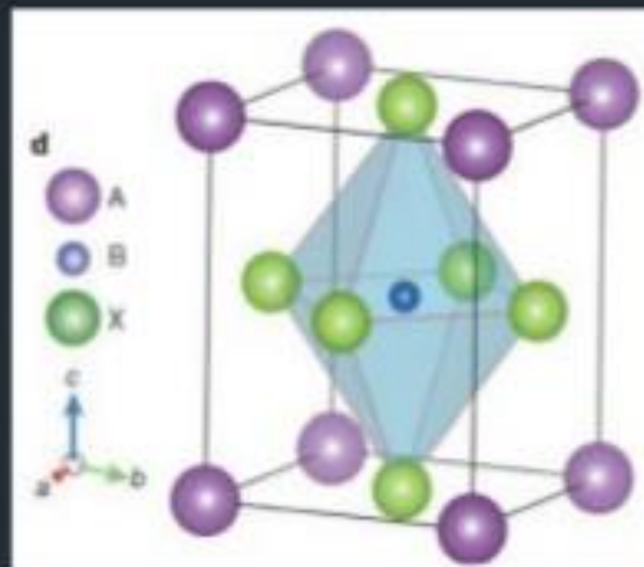


Adv. Funct. Mater. 2014, 24, 151.

Sci. Rep. 2012, 2. DOI: 10.1038/srep00591.

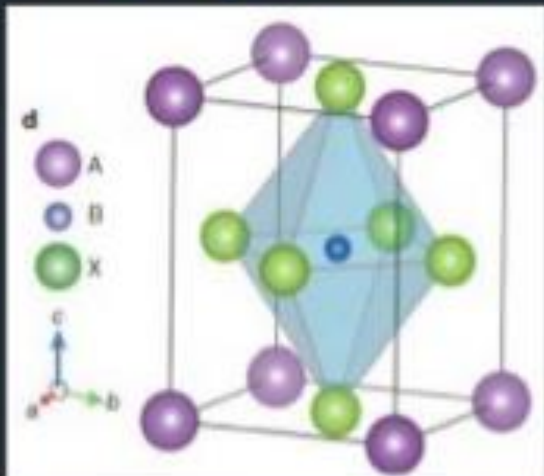
Image Credit: M.B. Johnston

What is Perovskite?



- A perovskite structure is any material with the same type of crystal structure as calcium titanium oxide ($CaTiO_3$), known as the perovskite structure **ABX3**.
- First discovered by Gustav Rose in 1839 and named after Russian mineralogist L. A. Perovski.

CH_3NH_3PbX
methylammonium lead halide



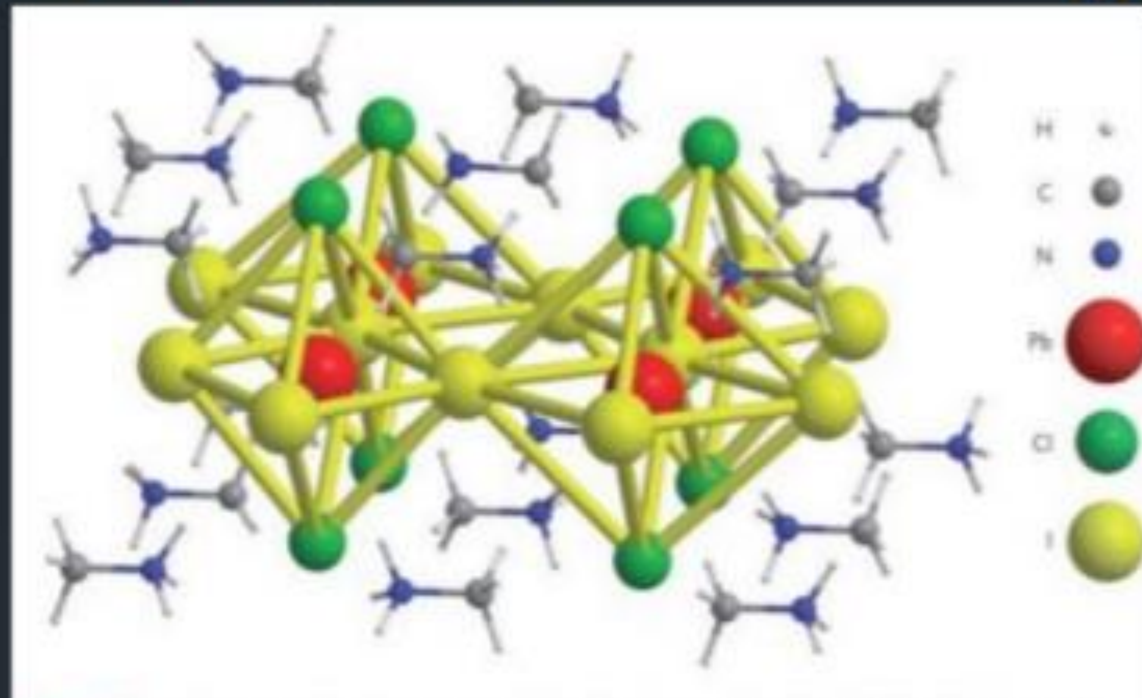
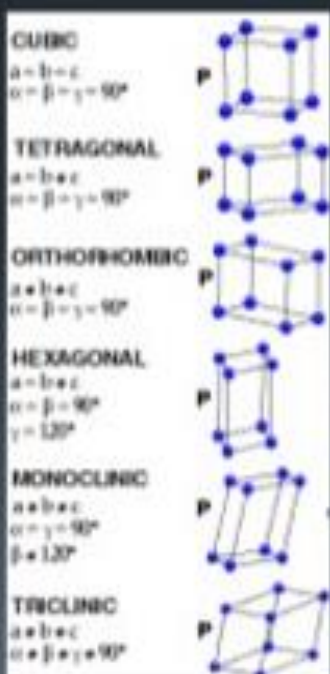


Figure 1 | Crystal structure. Possible structure of the hybrid perovskite $CH_3NH_3PbI_{3-x}Cl_x$. At present, crystallographic data on the precise position of the organic ligands are not available.



Phase Transition ($CH_3NH_3PbI_3$):

Orthorhombic → Tetragonal → Cubic

162 K 327 K (54 C)

The organic ligand is disordered in Tetragonal and Cubic phase.

Nature, 2013, 12, 1087

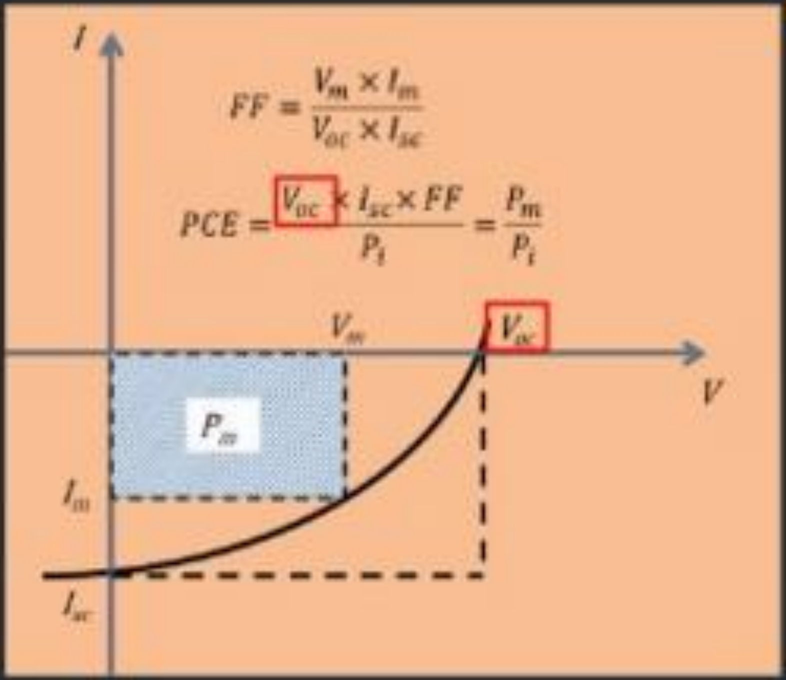
Material Properties: Good for Photovoltaics, but with Caution

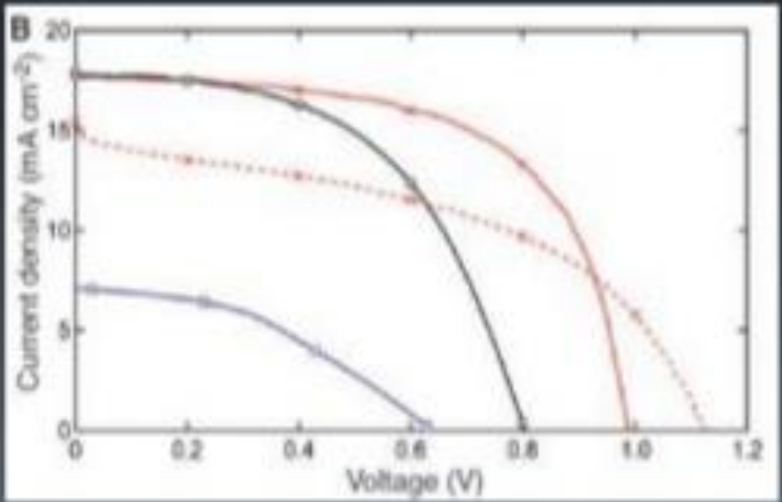
- Cheap Manufacturing:
  - Lower manufacturing costs expected: directly deposited from solution
  - Caution: Encapsulation needed, which may increase cost
- Material Properties for High Efficiency Photovoltaics:
  - 1. High Optical Absorption Coefficient
  - 2. Excellent Charge Carrier Transport (crystallinity, diffusion length, carrier mobility)
  - 3. Promising Device Parameter: High V_{oc} of >1.1 V is reported
- Stability:
  - Study shows it can maintain more than 80% of its initial efficiency after 500 hours.
  - Caution: More studies needed. Lifetime of 15 years has not been demonstrated. The ultimate goal of 15-year-lifetime not demonstrated.
- Other Real World Concerns (equally important but omitted here):
  - Toxicity from Pb
  - Scaling Problem

Nature. 2013, 12, 1
Nature Comm. 2013, DOI: 10.1038/ncomms3

High V_{oc}

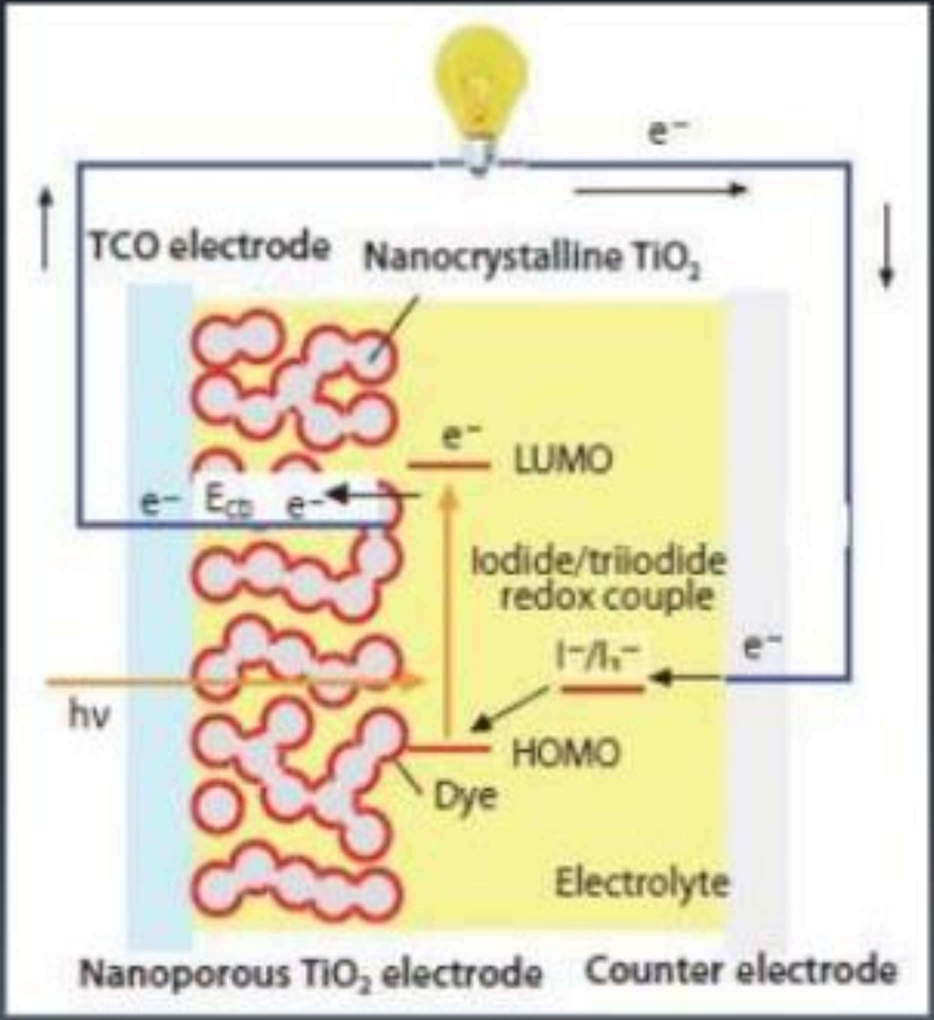
- Perovskite solar cells are quite effective in generating a high electric voltage, which is represented by a high open circuit voltage (V_{oc}):
- $CH_3NH_3PbI_2Cl$:
  - optical bandgap of 1.55 eV
  - V_{oc} of **1.1 V**
  - A voltage drop of only 0.45 eV, competitive with the best thin-film technologies (CIGS: 1.15 eV → 0.7 V; Si: 1.1 eV → 0.7 V)
- Compares favorably to DSSC or OPV, which has a larger 0.7-0.8 V voltage drop, resulting in a small portion of the bandgap being extracted as V_{oc}.
- Other optimization predictions: Higher FF is possible (60-70% → over 80%), current can also be higher.





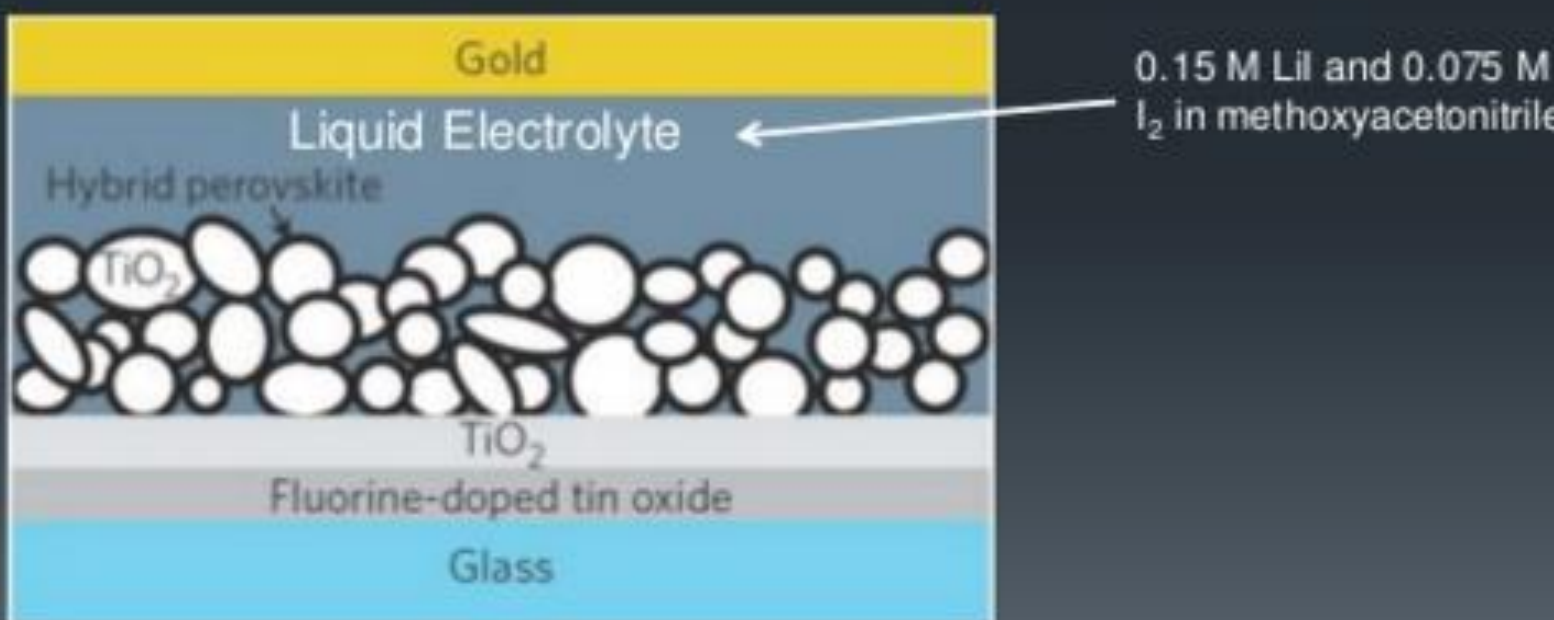
DSSC: Predecessor to Perovskite Solar Cells

- Current Perovskite Solar Cells are built upon the architectural basis for DSSCs
  - Pioneering work by Grätzel (EPFL, Switzerland) that has garnered ~ 17000 citations



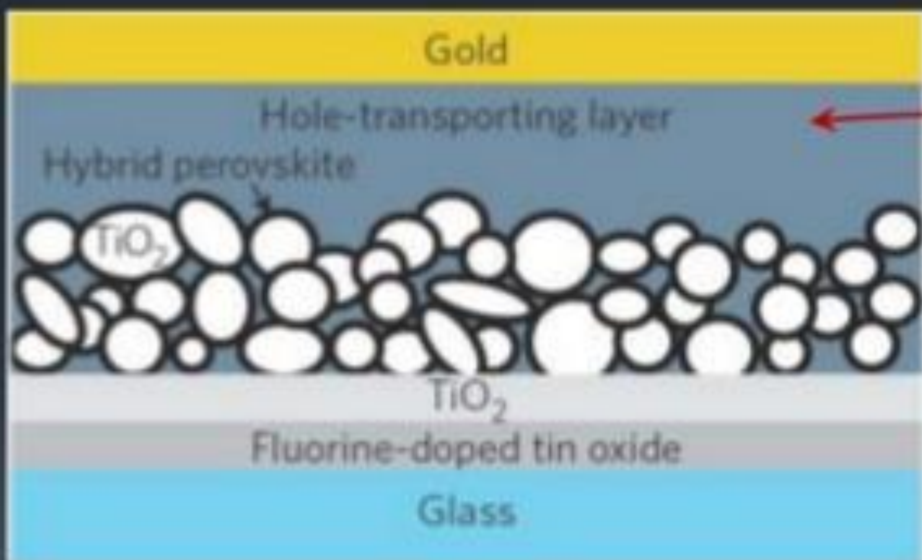
Replacing Dye with Perovskite

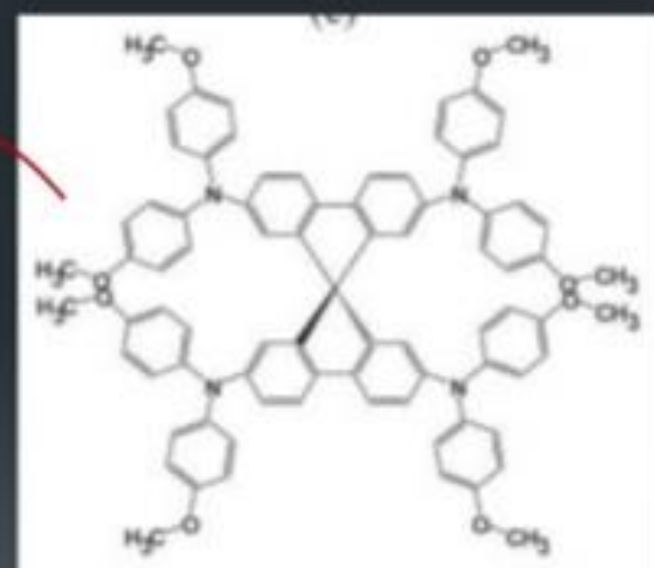
- Dyes do not absorb all the incident light, reducing DSSC efficiency.
- In 2009, Miyasaka (Toin U. of Yokohama, Japan) turns to perovskite as possible replacement of the dye and achieved 3.8% efficiency.
- Problem: Liquid electrolyte dissolved away the perovskite within minutes.



Replace Liquid Electrolyte with a Solid Hole Transporting Layer (HTL)

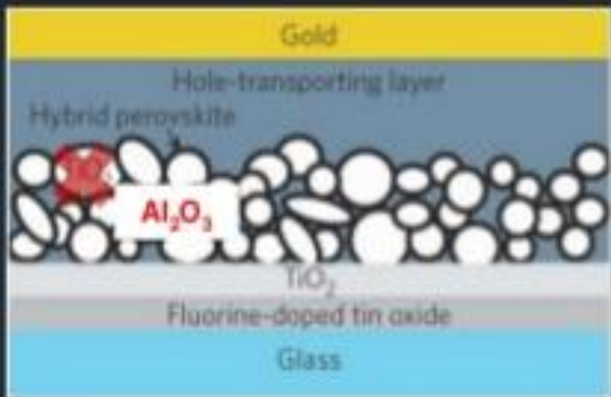
- 2012, Nam-Gyu Park (Sungkyunkwan U., South Korea) teamed up with Grätzel, over 9% efficiency.





HTL layer: spiro-OMeTAD

Al_2O_3 Scaffold and Single Layer

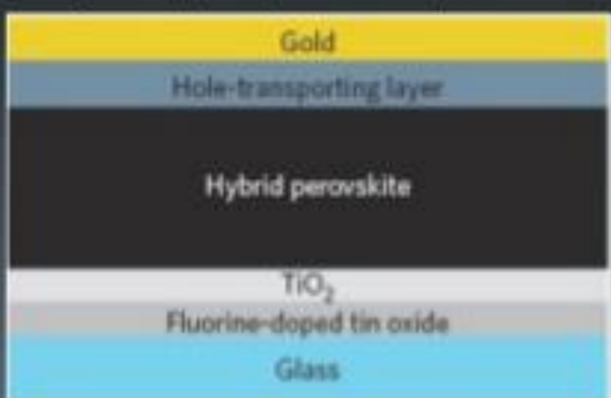


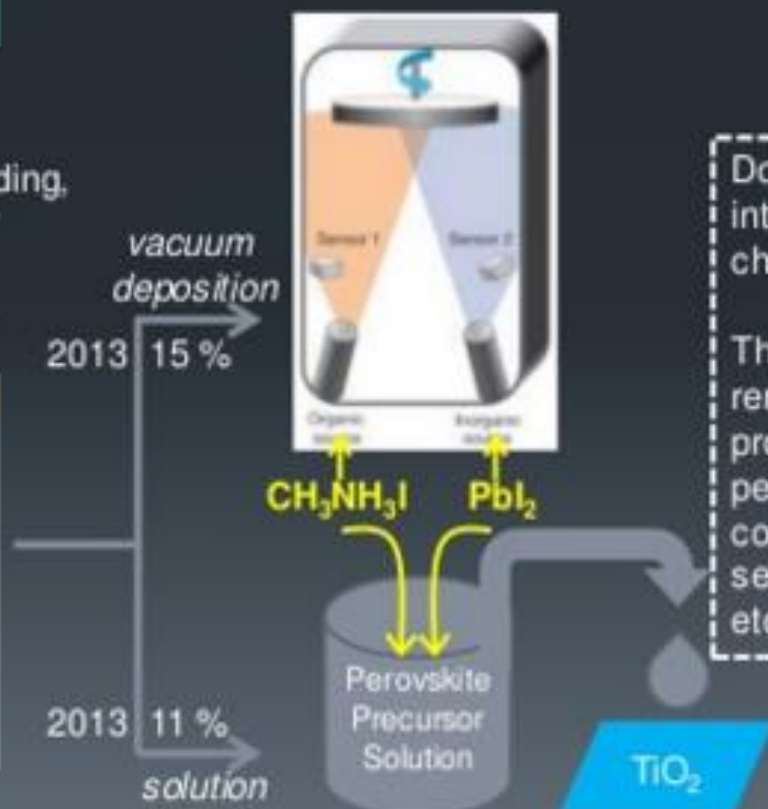
2012, **Henry Snaith (Oxford U.)**: Is TiO_2 essential for high efficiency?

Switched to an insulating Al_2O_3 scaffold, expected to see a decrease in efficiency. Surprisingly, the device with Al_2O_3 has a higher efficiency than that with TiO_2 (11% vs. 7.6%).

If all that Al_2O_3 does is scaffolding, what if we get rid of it as well?

single layer (thin film) device





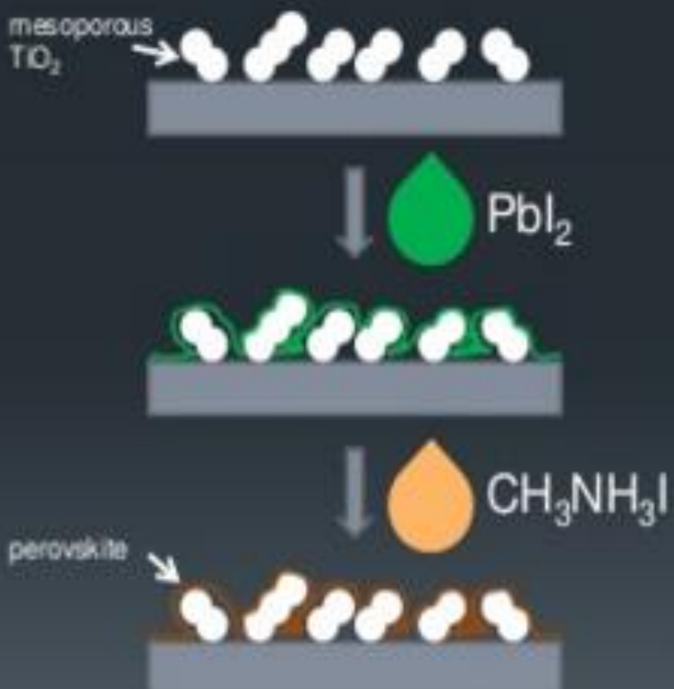
Do not need artificial interfaces for efficient charge separaton!

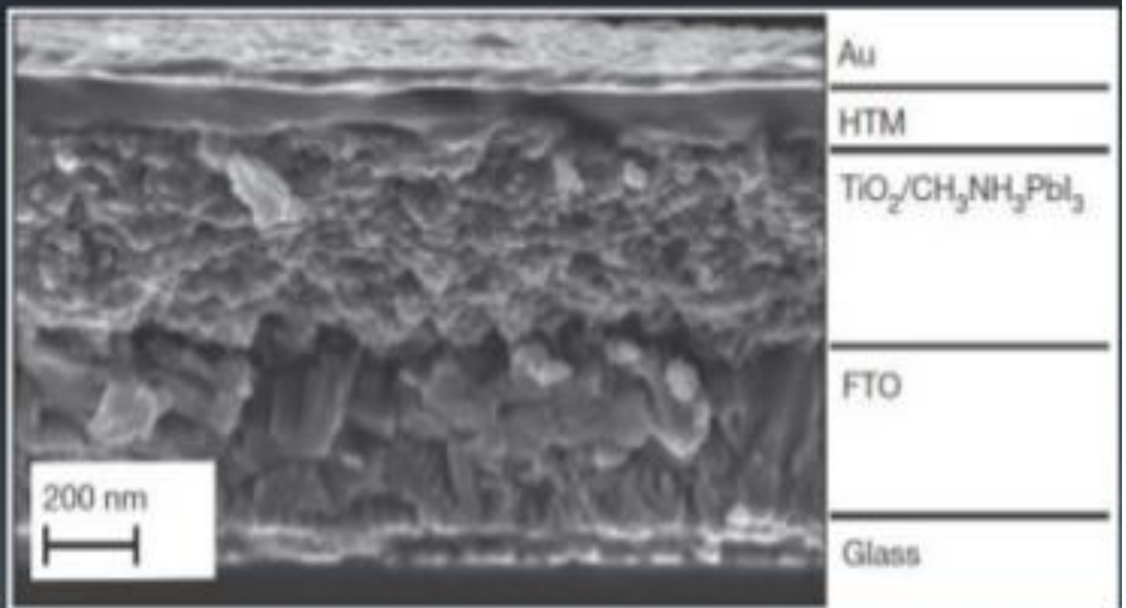
These two results are remarkable, in that they prove that these perovskites work as conventional semiconductors (Si, GaAs, etc).

Science. 2012, 338, 643.
Nature. 2013, 501, 395.
Adv. Funct. Mater. 2014, 24, 151

Sequential Deposition

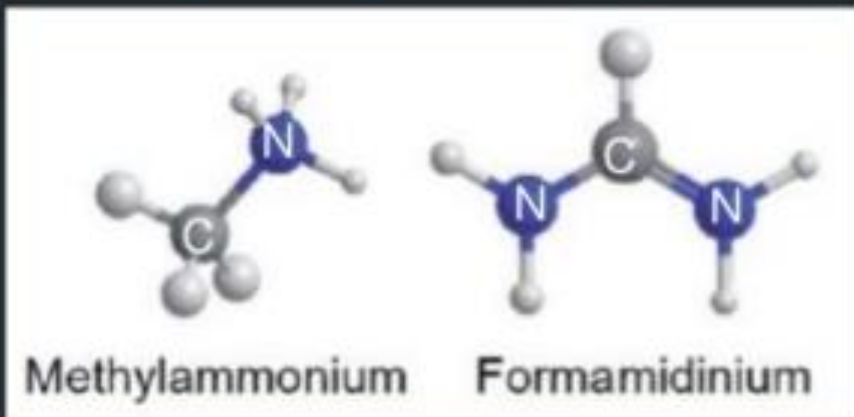
2013, Grätzel sticks with the TiO_2 structure and tinkered with the deposition step.

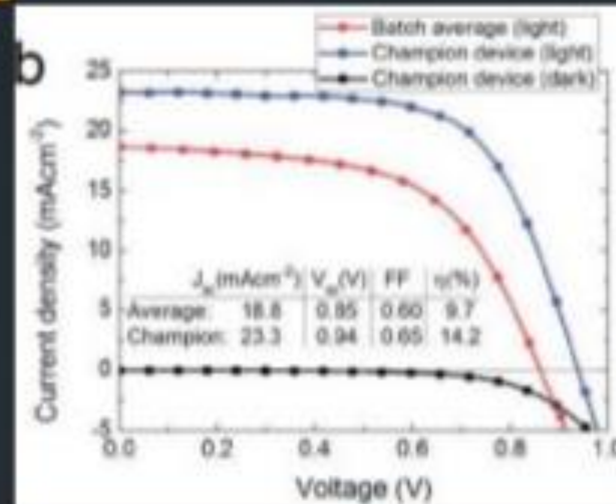




Efficiency: 15%

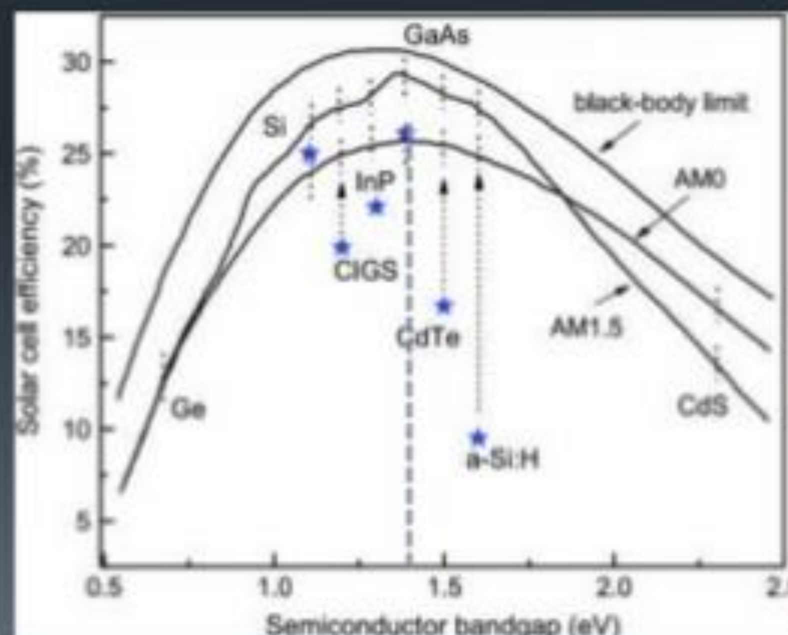
Cation: CH_3NH_3 vs. $HC(NH_2)_2$





- Formamidinium cation slightly larger → Bandgap shrunk from 1.55 eV to 1.48 eV
- Retained favorable transport property
- Best solution-based thin film perovskite solar cell (efficiency: 14.2%).

Energy Environ. Sci. 2014, 7, 982

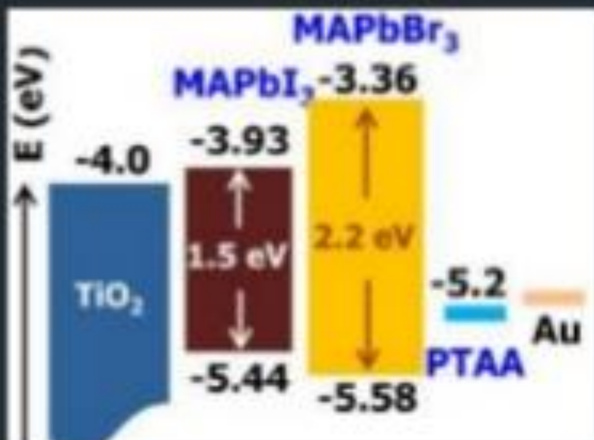


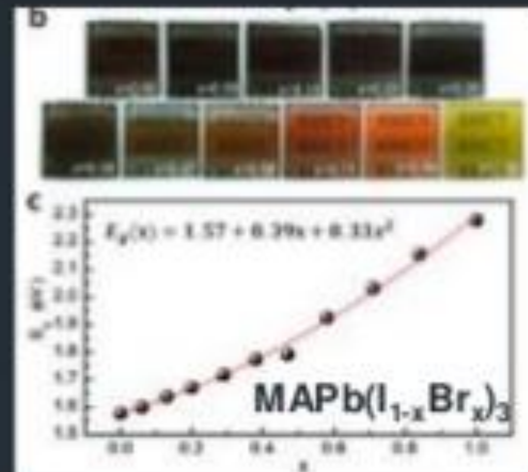
Metal

- In principle, perovskite is a flexible structure type:
  - Many elements in the periodic table (such as Co^{2+}, Fe^{2+}, Mn^{2+}, Pd^{2+}, and Ge^{2+}) can be incorporated
- Sn:
  - Earlier work by Mitzi showed that perovskites with Sn show metallic character with small bandgap (not the semiconductors ideal for PV)
  - Recent work confirmed this notion.
  - It was also found that the facile oxidation of Sn^{2+} to Sn^{4+} gives a metal-like behavior in the semiconductor which lowers the photovoltaic performance.
- Cu:
  - At 2013 Fall MRS meeting, a group from Hokkaido U., Japan, is studying Cu-based materials with a general formula of R_2CuBr_4. Field effect transistor by inkjet deposition showed weak n-type properties.
- In general, replacing Pb with other less or non toxic metals remains a challenge.

Halogen:
$MAPbI_3$, $MAPbBr_3$, $MAPbCl_3$, $MAPbI_{3-x}Cl_x$

- $CH_3NH_3PbI_3$ bandgap 1.5 eV, $CH_3NH_3PbBr_3$ 2.3 eV, bandgap tailoring can be simply achieved by alloying of both.





- Why don't researchers use $CH_3NH_3PbCl_3$?
  - Bandgap (3.1 eV) too large for good absorption, appearance is colorless.

- Mixed Halide $CH_3NH_3PbI_{3-x}Cl_x$: Currently the best perovskite material.
  - The extent of incorporation of Cl into the perovskite is <u>in debate</u>. Recent results indicate that the Cl incorporation is very low (3-4%), due to the large difference in the ionic radii of Cl- and I- anions. Another XPS study shows Cl:I exactly at 1:2.
  - This mixed halide have <u>similar</u> bandgaps as $CH_3NH_3PbI_3$ (another indication that the Cl incorporation is low)
  - This mixed halide has <u>superior</u> charge transport property than iodide one (diffusion length >1000 nm)
  - <u>Better stability</u> in air (reason unclear)

Nano Lett. 2013, 13, 1764
J. Mater. Sci., 2002, 37, 3585
Chem. Mater. 2013, 25, 4613
Adv. Mater. 2013, DOI: 10.1002/adma.201304803