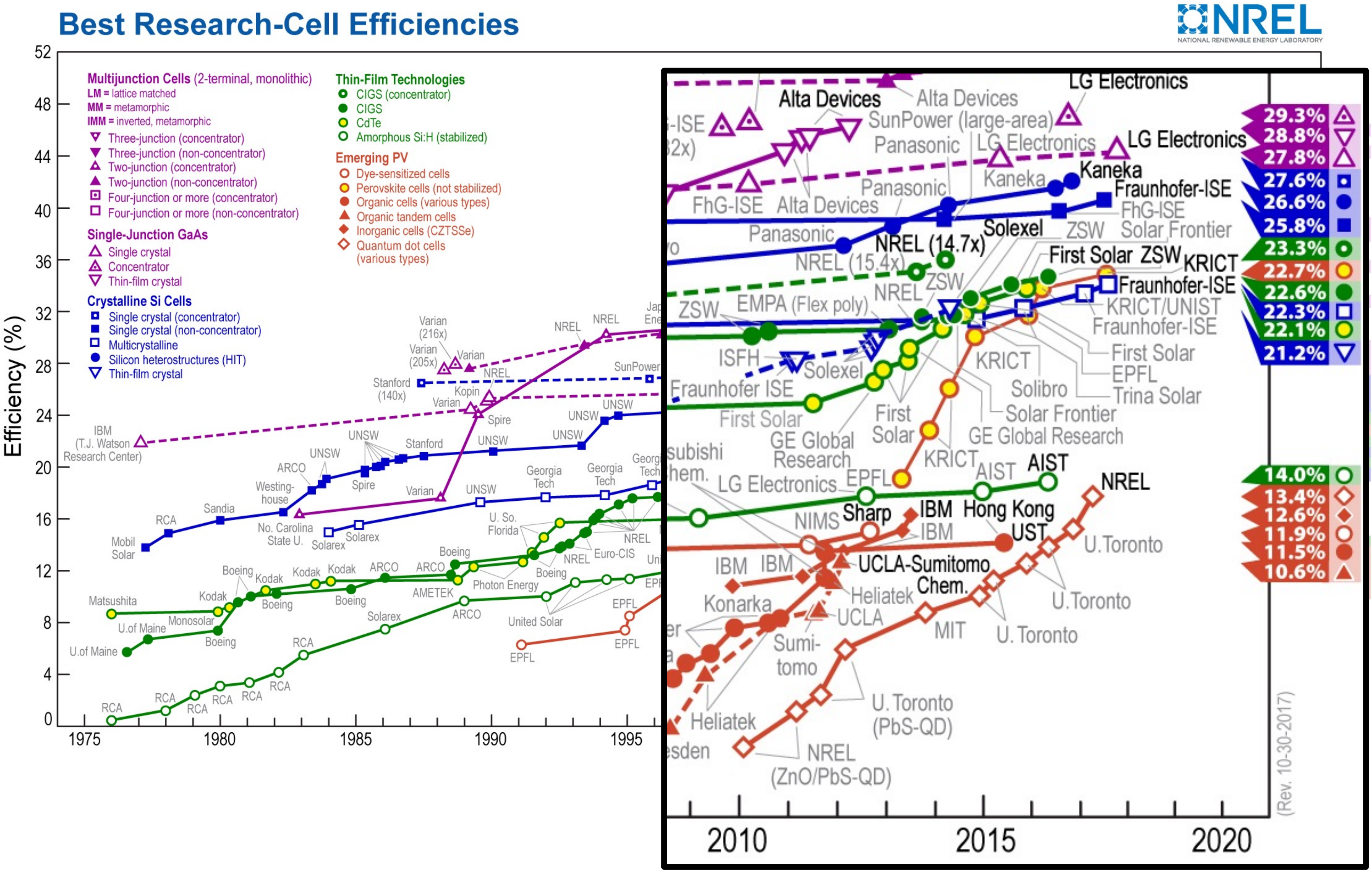
ChE 430
Colloidal synthesis of nanoparticles and their energy applications

MODULE 7: Solar Cells

7.0. History of solar cells
7.1. Characteristic of a photovoltaic cell: a bit of physic of solid state
7.2. Third generation solar cells
7.3. How to enhance QD solar cell efficiency
    7.3.1 Solar cell geometry
    7.3.2 Surface modification
7.4. State-of-the-art QD solar cells

National Renewable Energy Laboratory (NREL) track certified efficiencies



7.2. Third generation photovoltaic

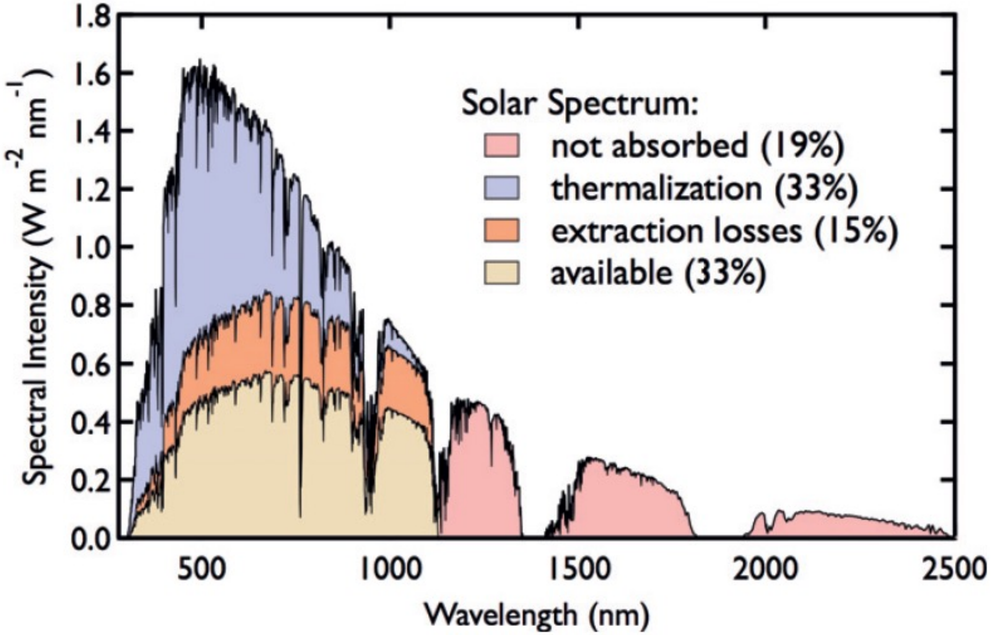
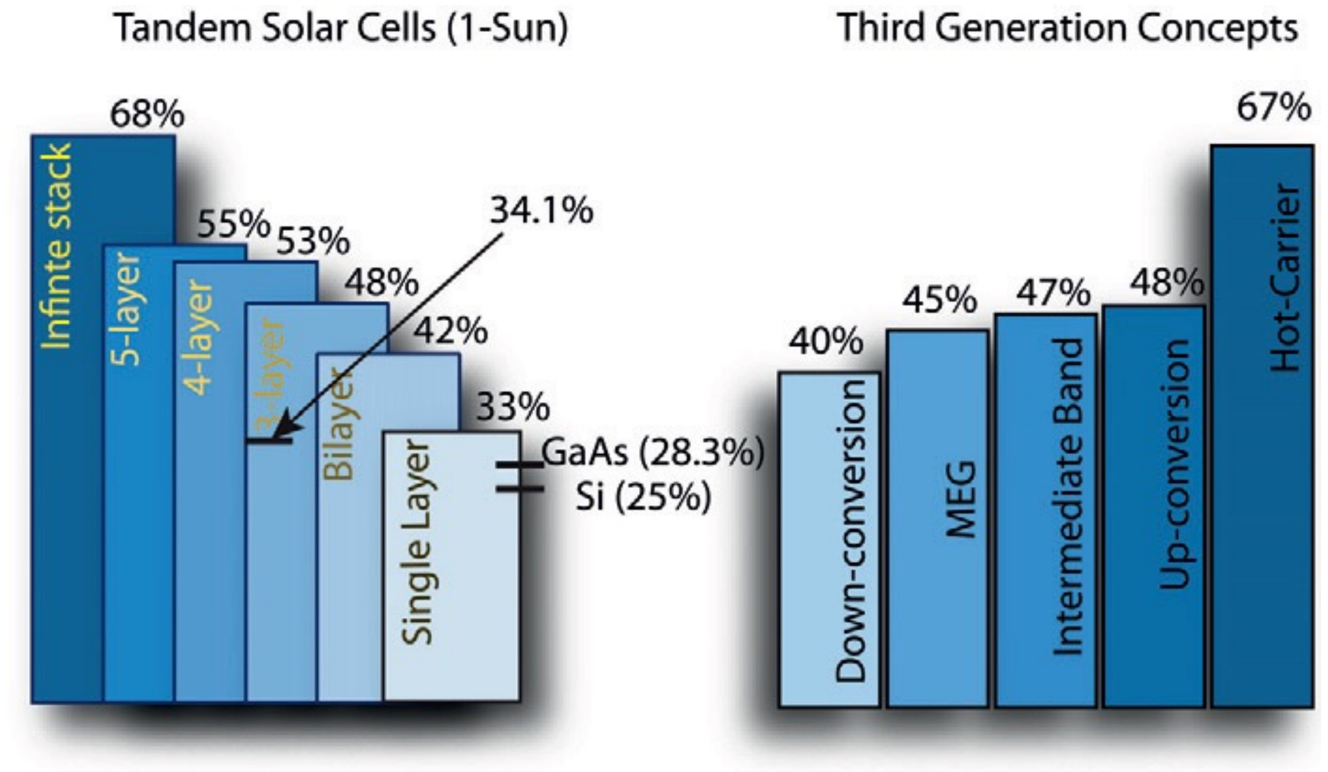


Fig. 1 Spectral analysis of the minimum losses for a silicon solar cell (band-gap = 1.1 eV). These are the losses accounted for in the Shockley-Queisser limit and represent an upper limit for solar cells made from single-junction bulk semiconductors. Thermalization represents the largest loss in this analysis, and it increases for the higher energy portions of the solar spectrum.

- 1º and 2º generation PV have the best power conversion efficiency (PCE) that have almost reached the Shockley-Queisser limit (33%)
- 3º generation PV can have **higher limiting PCE** by bypassing one of the assumption of SQ analysis and recovering some of the energy lost via thermalization or **providing paths to harvest those photons not absorbed in a standard solar cell**

Materials today, O. Semonin, J.M. Luther, M.C. Beard, **2012**

The detailed balance-derived maximum allowable PCE for a range of advanced solar conversion strategies



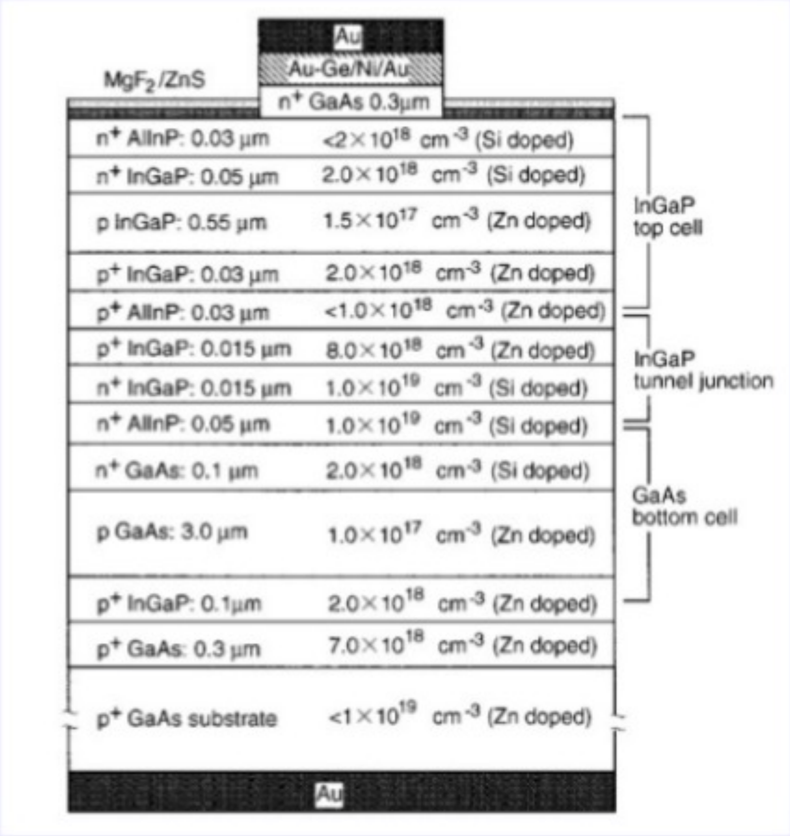
Surpassing the SQ limit for single junction solar cell is both a scientific and technological challenge and the use of CQD to enhance the primary photoconversion process is a promising avenue towards such a goal.

Materials today, O. Semonin, J.M. Luther, M.C. Beard, **2012**

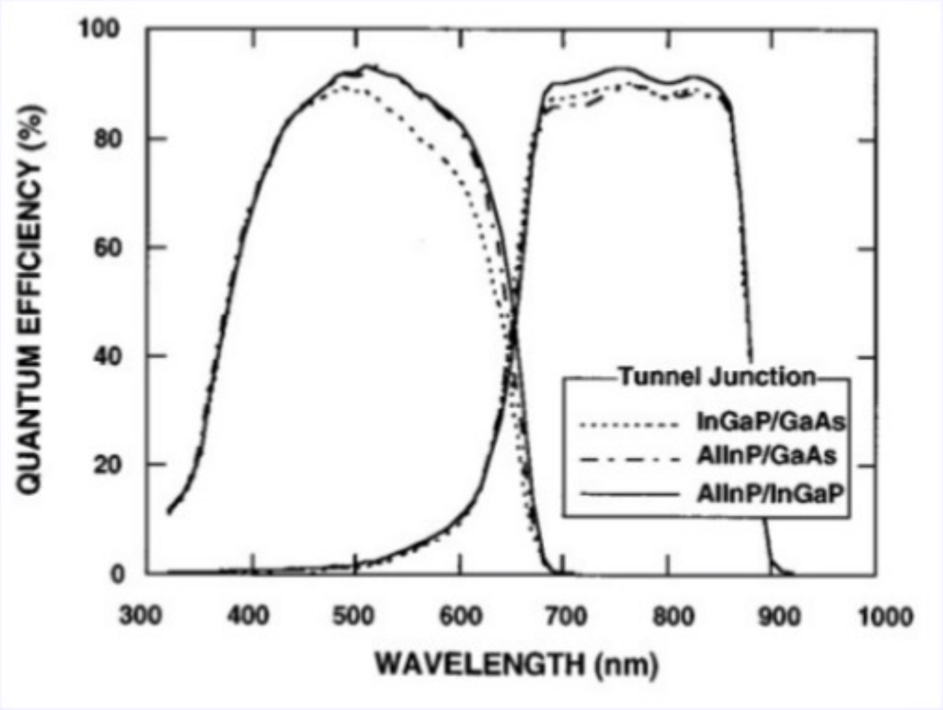
Multi-junction solar cells

Why have one junction when you can have **two?**

GaAs/InGaP



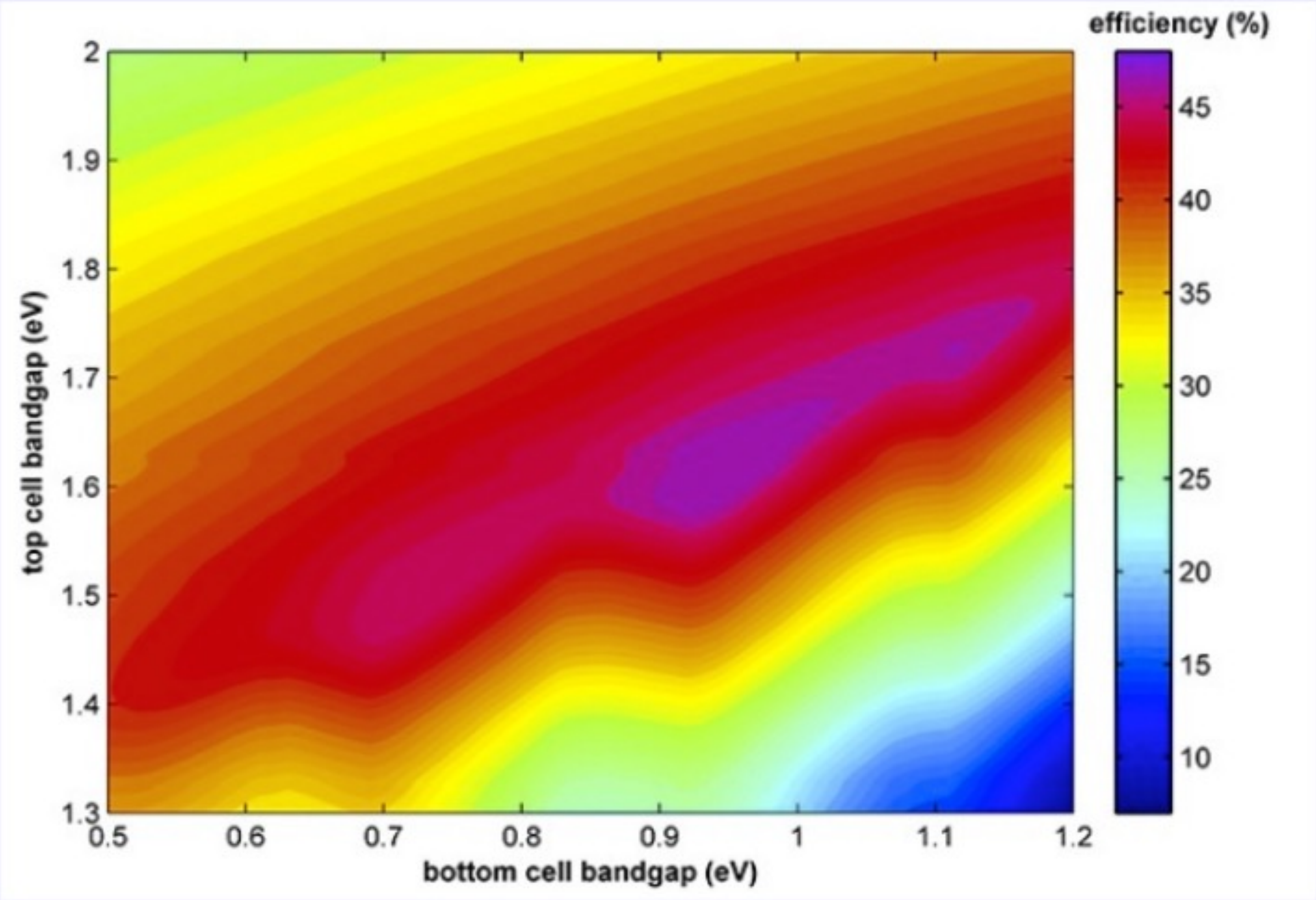
n$^+$ AlInP: 0.03 μm	$<2\times10^{18}$ cm^{-3} (Si doped)
n$^+$ InGaP: 0.05 μm	2.0×10^{18} cm^{-3} (Si doped)
p InGaP: 0.55 μm	1.5×10^{17} cm^{-3} (Zn doped)
p$^+$ InGaP: 0.03 μm	2.0×10^{18} cm^{-3} (Zn doped)
p$^+$ AlInP: 0.03 μm	$<1.0\times10^{18}$ cm^{-3} (Zn doped)
p$^+$ InGaP: 0.015 μm	8.0×10^{18} cm^{-3} (Zn doped)
n$^+$ InGaP: 0.015 μm	1.0×10^{19} cm^{-3} (Si doped)
n$^+$ AlInP: 0.05 μm	1.0×10^{19} cm^{-3} (Si doped)
n$^+$ GaAs: 0.1 μm	2.0×10^{18} cm^{-3} (Si doped)
p GaAs: 3.0 μm	1.0×10^{17} cm^{-3} (Zn doped)
p$^+$ InGaP: 0.1μm	2.0×10^{18} cm^{-3} (Zn doped)
p$^+$ GaAs: 0.3 μm	7.0×10^{18} cm^{-3} (Zn doped)
p$^+$ GaAs substrate	$<1\times10^{19}$ cm^{-3} (Zn doped)



T. Takamoto *et. al.* "Over 30% Efficient InGaP/GaAs tandem solar cells", APL, 70 381 (1997)

7.2. Third generation photovoltaic

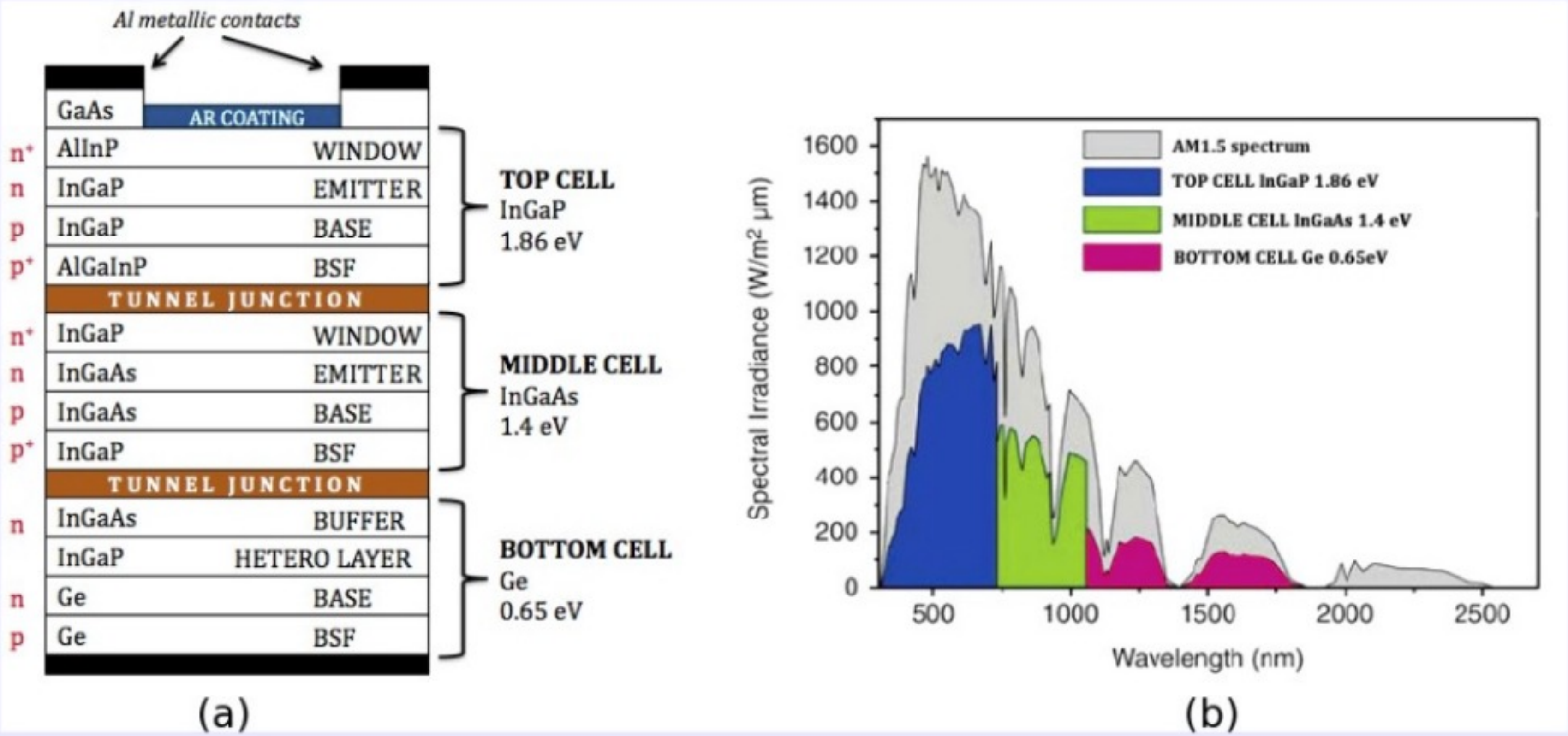
Multi-junction solar cells



Maximum theoretical efficiency ~ 46%

Multi-junction solar cells

Why have two junctions when you can have three (or more)?



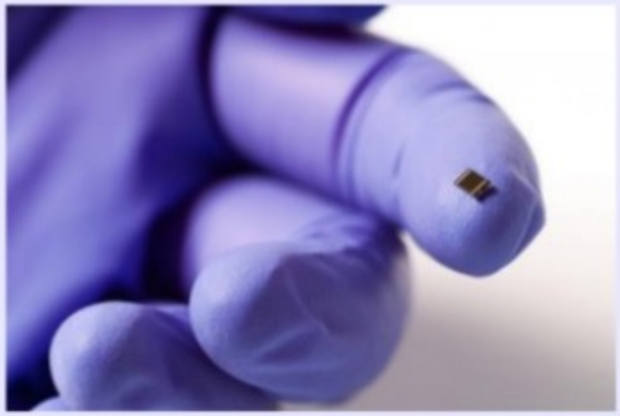
Ge/InGaAs/InGaP – Max $\eta \sim 35\%$

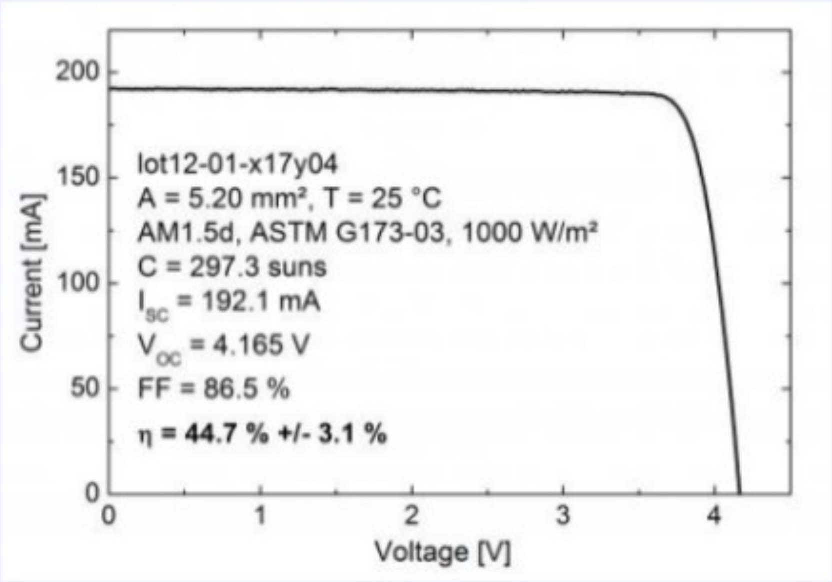
7.2. Third generation photovoltaic

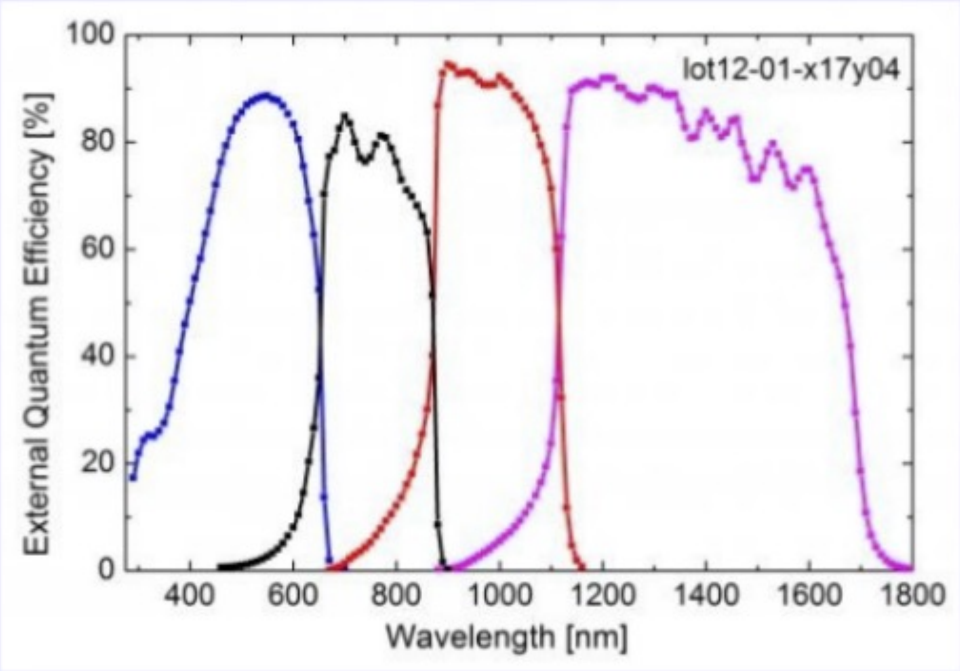
Multi-junction solar cells

44.7%!

- **Four junction cell based on III-V**
- **Fraunhofer Institute**







7.2. Third generation photovoltaic

Multi-junction solar cells

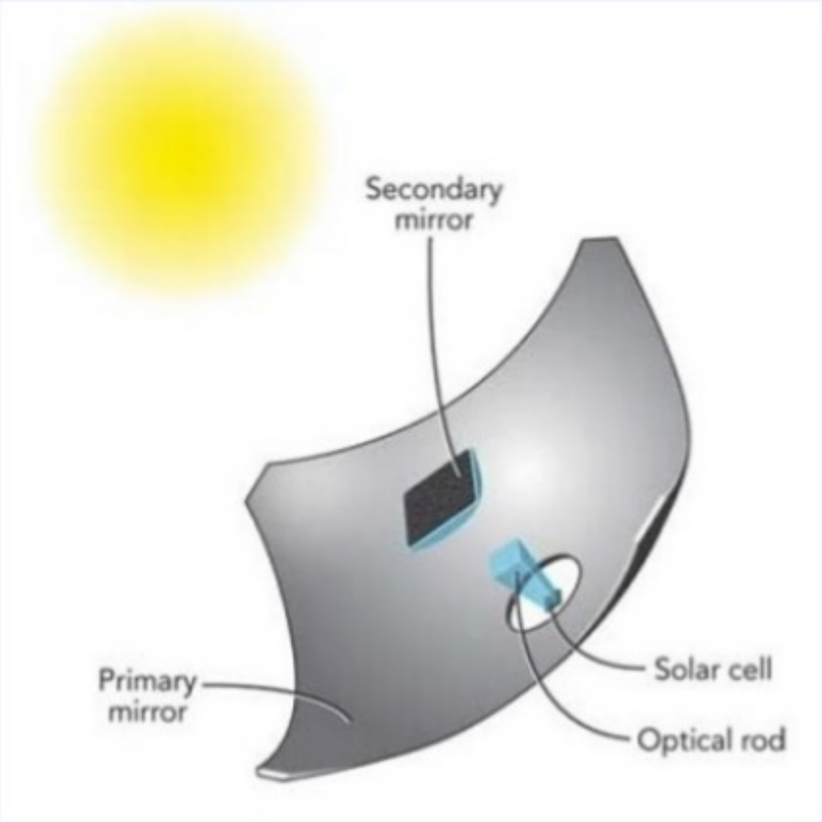
Disadvantages of tandems based on III-V's

- High precision fabrication required
- Materials balance (tunnel junction)
- High cost (materials + deposition)
- Not practical for concentrator systems

Are there other strategies?

7.2. Third generation photovoltaic

Solar concentrators

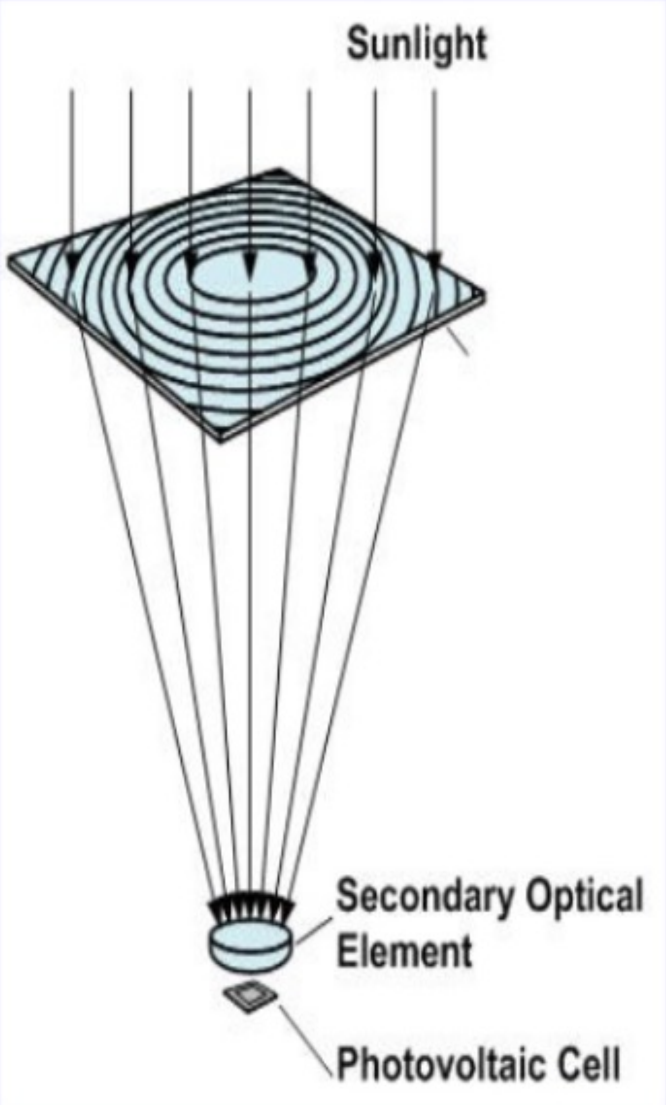


Parabolic Mirror Array

~ 500 suns
25kW output
2 axis tracking

7.2. Third generation photovoltaic

Solar concentrators



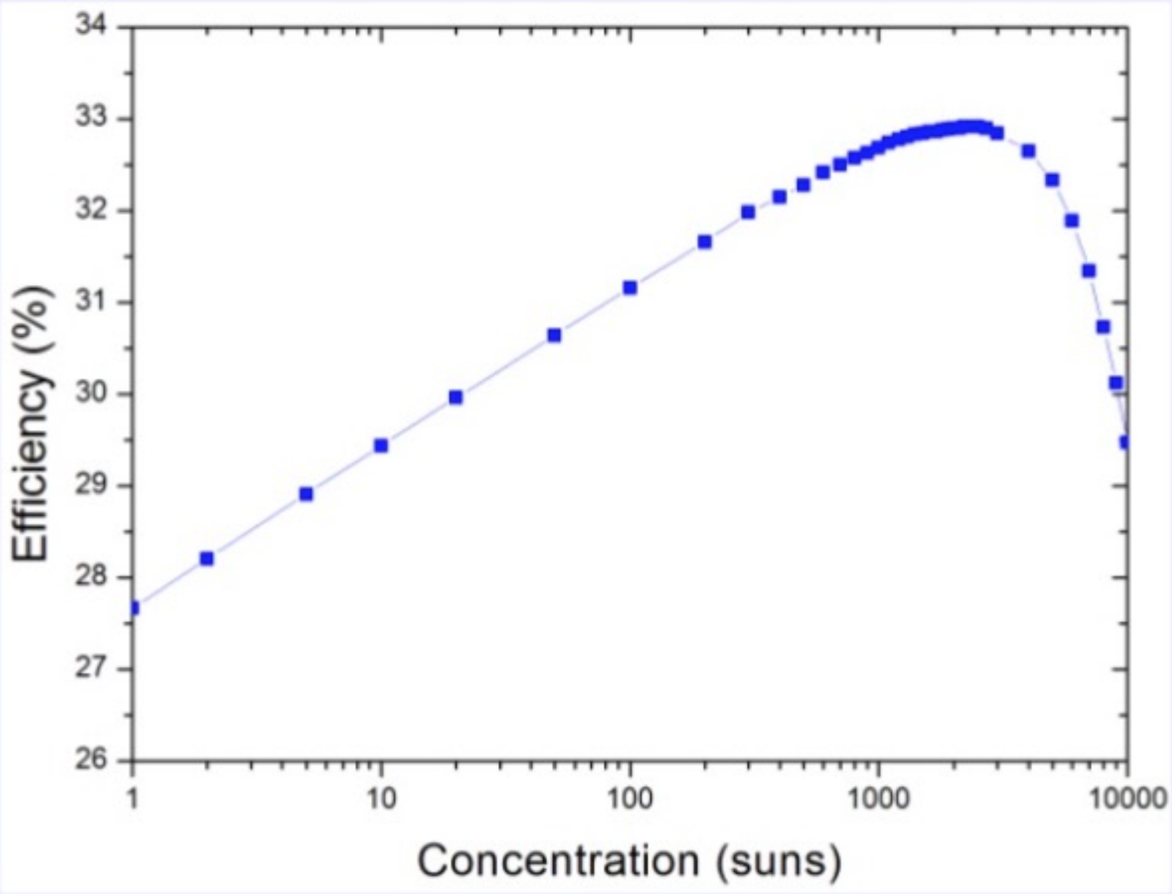
Fresnel Lenses

200 – 300 suns
1 axis tracking

7.2. Third generation photovoltaic

Solar concentrators

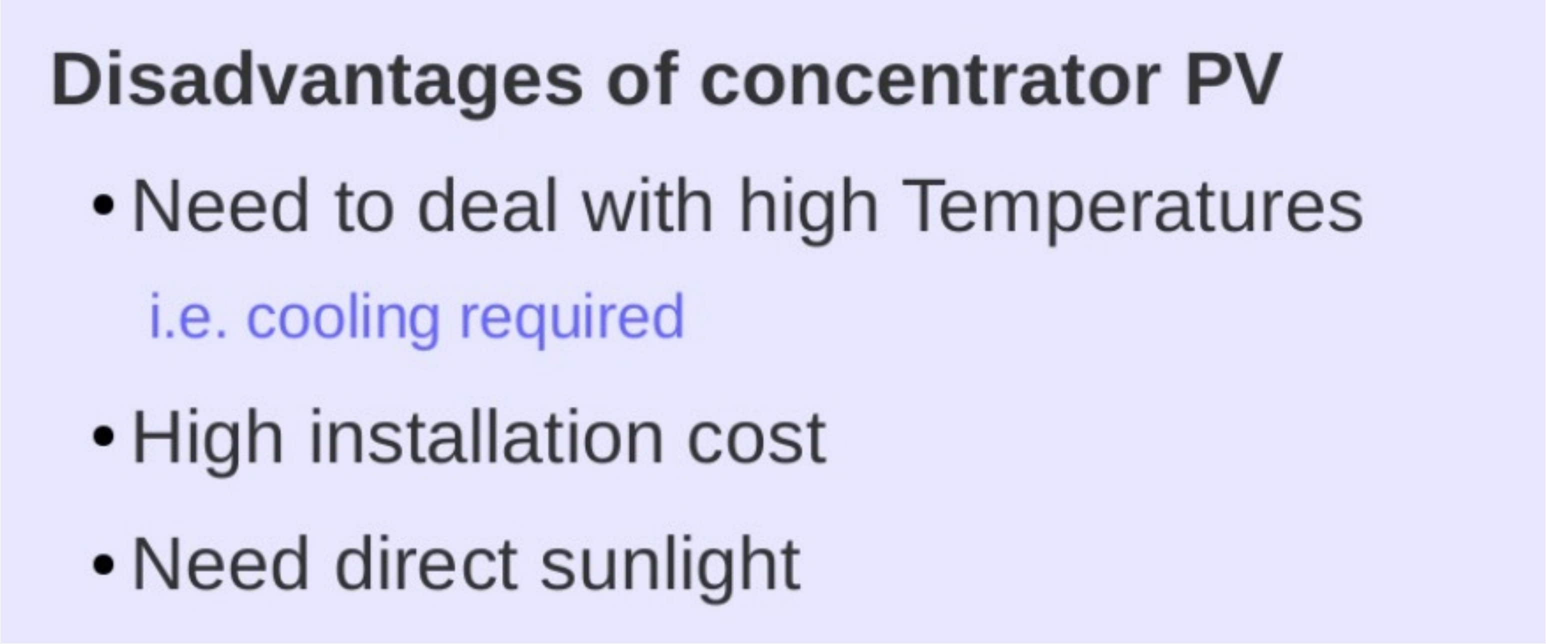
Increase photon flux → Increase efficiency



Theoretical prediction for two junction system @ T = 320K

7.2. Third generation photovoltaic

Solar concentrators



Disadvantages of concentrator PV

- Need to deal with high Temperatures

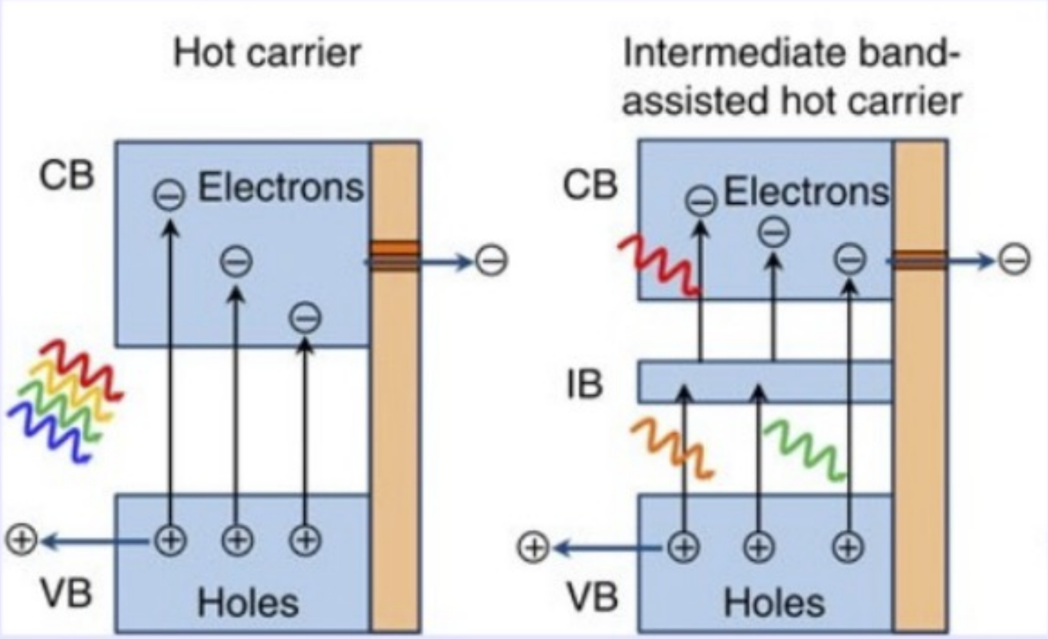
  i.e. cooling required

- High installation cost
- Need direct sunlight

7.2. Third generation photovoltaic

Hot-carriers and intermediate band

Can we get the promoted carriers out before they thermalise?

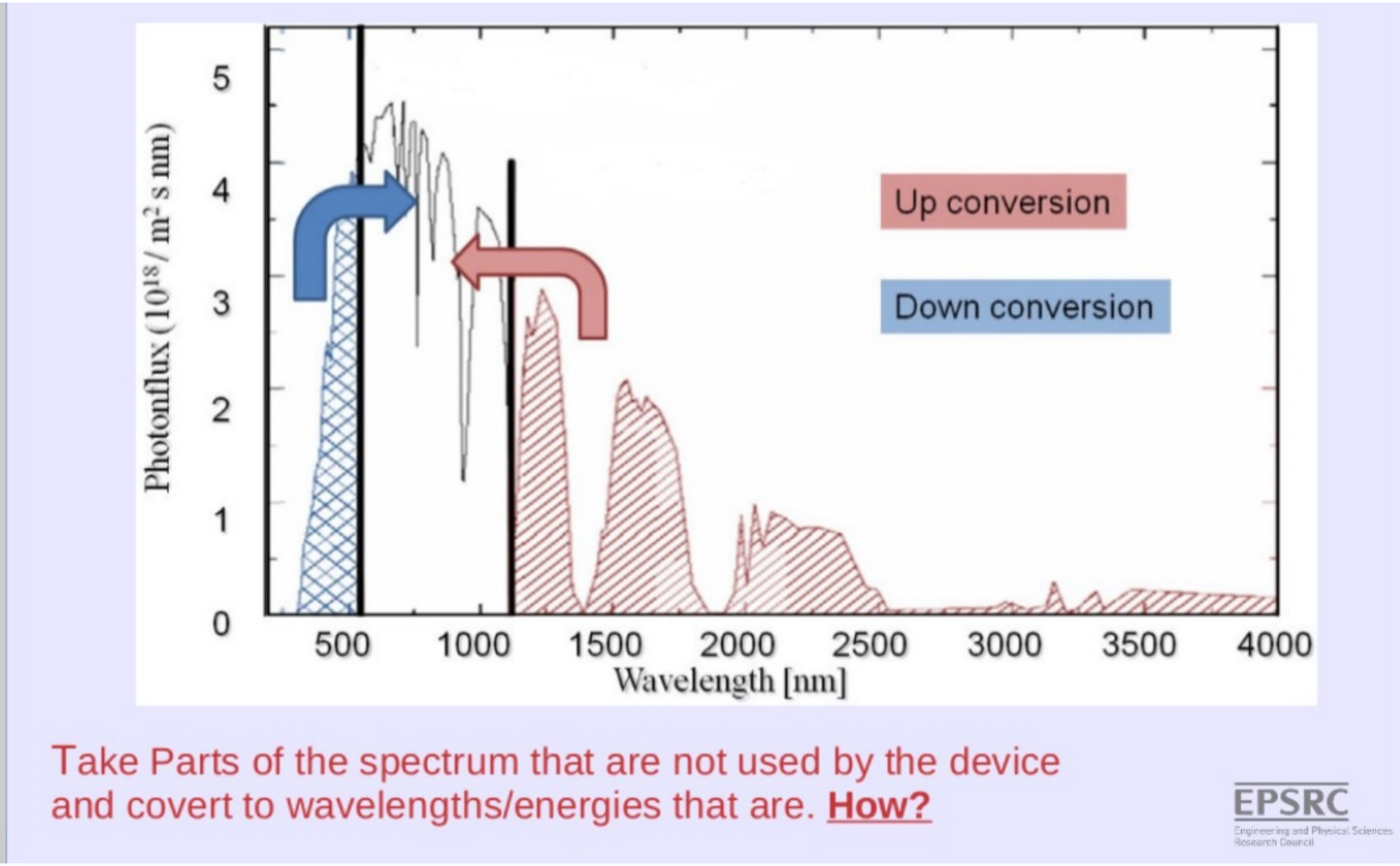


Use “selective” contacts that allow “hot” carriers to be collected before they thermalise (picoseconds!) to bottom of C.B. through scattering with phonon modes

EPSRC
Engineering and Physical Sciences Research Council

7.2. Third generation photovoltaic

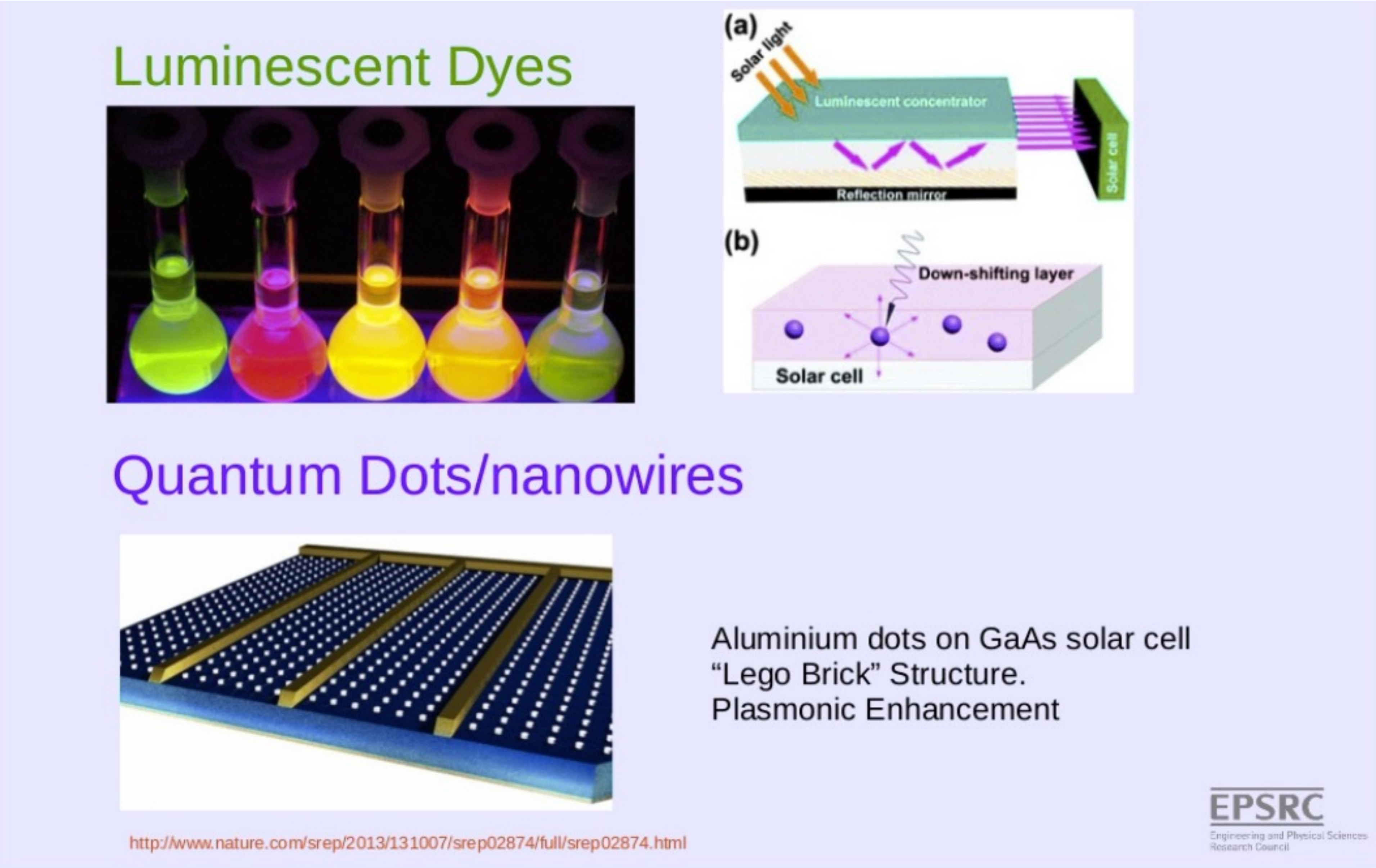
Down-conversion and up-conversion



Take Parts of the spectrum that are not used by the device and covert to wavelengths/energies that are. **How?**

7.2. Third generation photovoltaic

Down-conversion and up-conversion



Luminescent Dyes

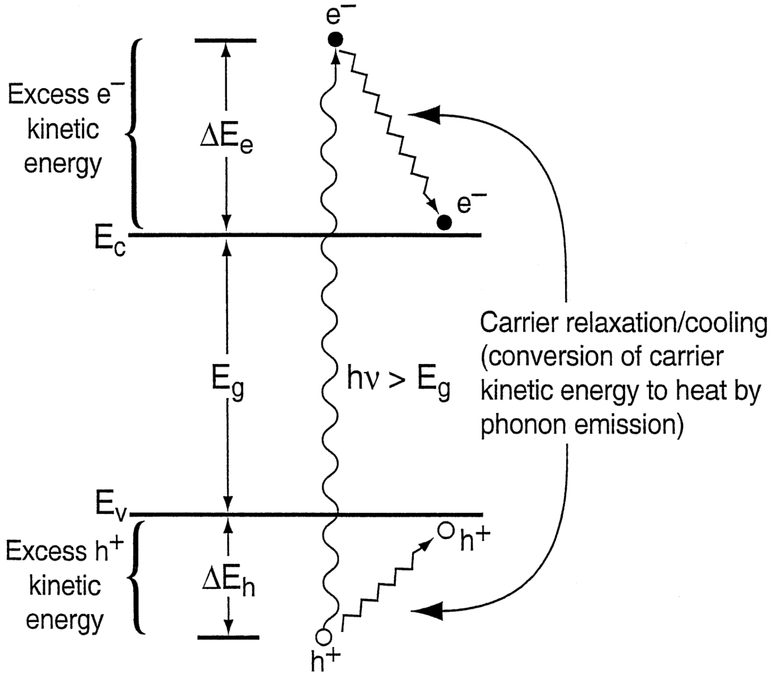
Quantum Dots/nanowires

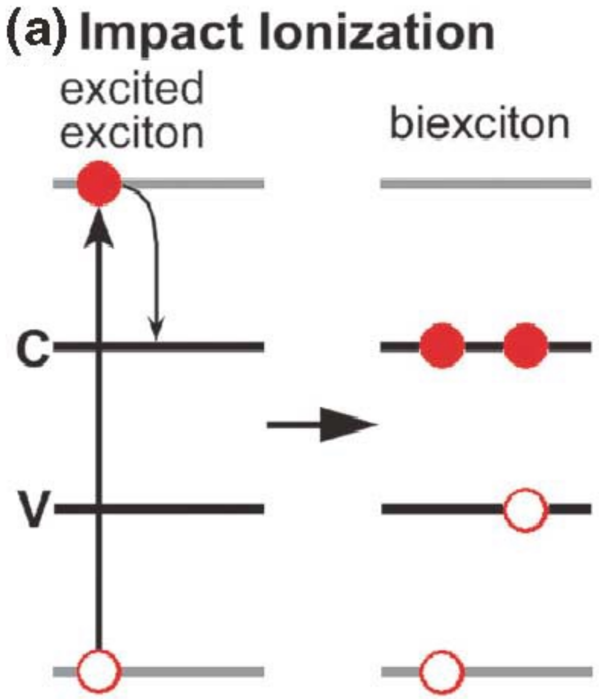
Aluminium dots on GaAs solar cell
“Lego Brick” Structure.
Plasmonic Enhancement

http://www.nature.com/srep/2013/131007/srep02874/full/srep02874.html

7.2. Third generation photovoltaic

Multi-exciton generation in QDs





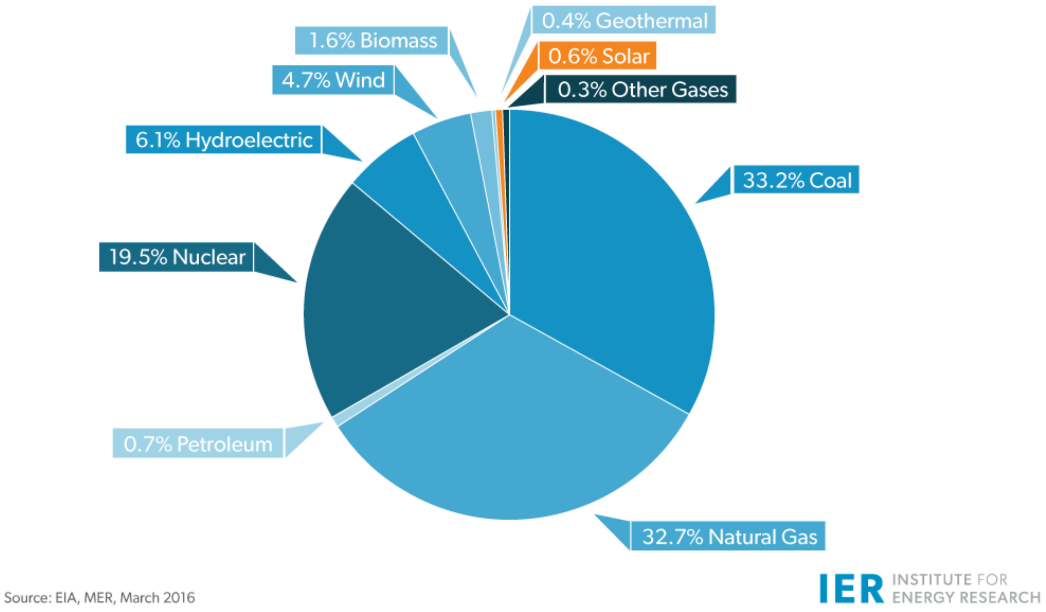
- Because of the restriction imposed by energy and momentum conservation these process are much less efficient in bulk materials
- In QDs due to enhanced Coulomb interaction and relaxation of momentum conservation they are more efficient.
- It requires 7eV (180nm) photons for Silicon

A.J. Nozik, Physica W., **2002**;
V. I. Klimov, Phy. rev. lett., **2004**

7.2. Third generation photovoltaic

Some economics

Although the Sun supplies the Earth with enough energy in 1 hour to meet the global electricity needs for 1 year, solar generated electricity supplies only 0.6% of worldwide demand.



Source: EIA, MER, March 2016

cost per system balance

cost per module

$$c_{\text{installed}}\,(W_p^{-1}) = \frac{c_{\text{module}}\,(m^{-2}) + c_{\text{BOS}}\,(m^{-2})}{CE\,(\%) \times 1{,}000\ W_p\ m^{-2}}$$

PV efficiency

We must build a technology for harvesting solar energy at an installed cost of 1 euro per Watt-peak (W_p), then we will produce electricity over its lifetime at an equivalent cost of euro 0.05kWh^{-1}.

The goal of reducing the cost has been pursued by constructing solar cells on flexible substrate and employing solution-based semiconductors and lower temperatures

7.2. Third generation photovoltaic

Perovskite solar cells

Inorganic/Organic Hybrid Tandems

- Cheap
- Easy to make (non-vacuum dep)
- Can apply to existing Si technology

Watch this space

c-Si efficiency boosted by 20% (by using perovskites)

EPSRC
Engineering and Physical Sciences Research Council

Prof. Henry Snaith, Oxford University

7.2. Third generation photovoltaic

Perovskite solar cells

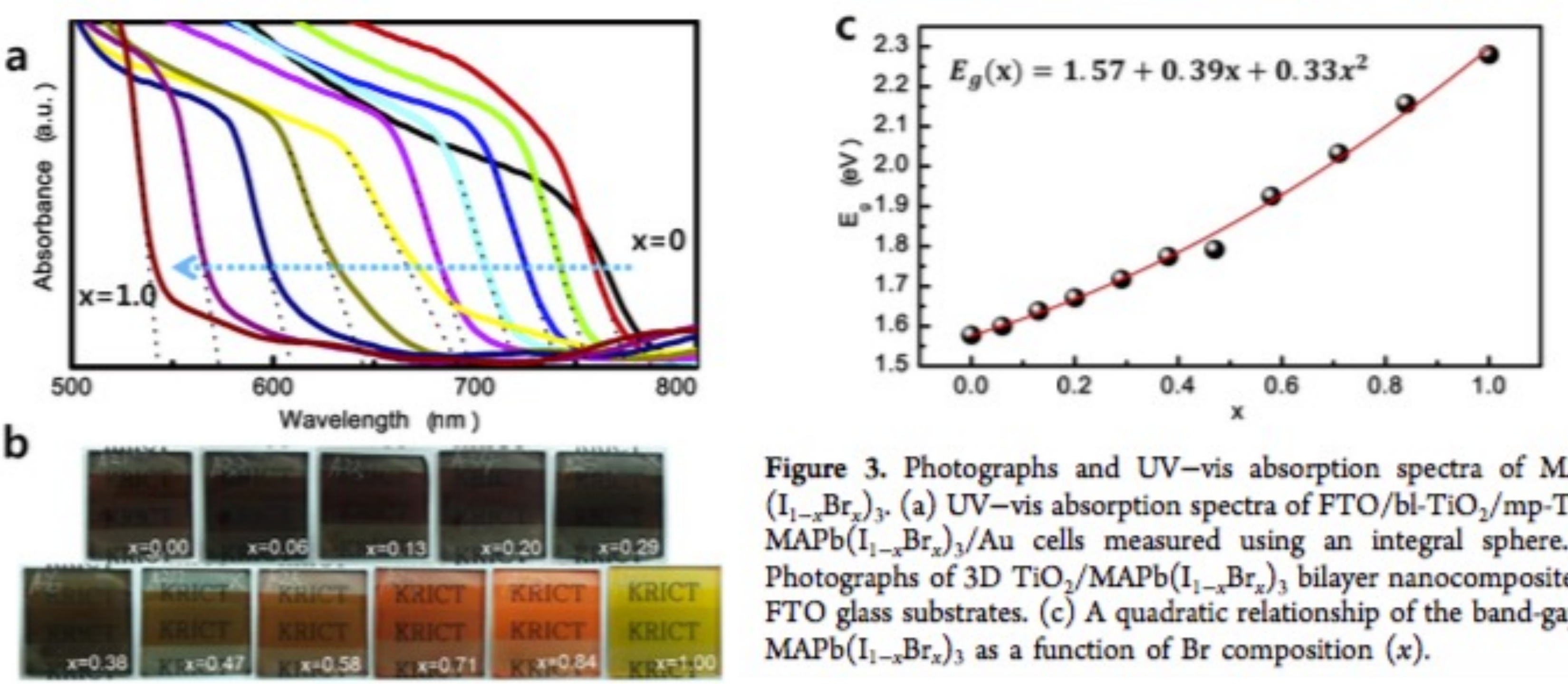


Figure 3. Photographs and UV−vis absorption spectra of MAPb($I_{1-x}Br_x$)$_3$. (a) UV−vis absorption spectra of FTO/bl-TiO_2/mp-TiO_2/MAPb($I_{1-x}Br_x$)$_3$/Au cells measured using an integral sphere. (b) Photographs of 3D TiO_2/MAPb($I_{1-x}Br_x$)$_3$ bilayer nanocomposites on FTO glass substrates. (c) A quadratic relationship of the band-gaps of MAPb($I_{1-x}Br_x$)$_3$ as a function of Br composition (x).

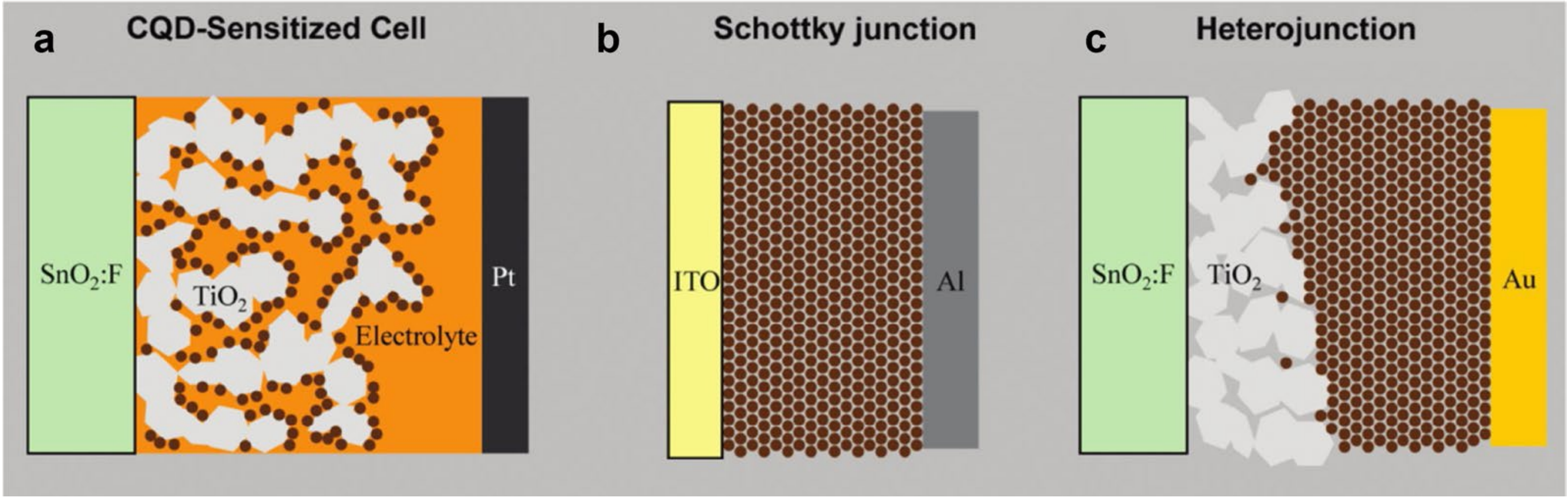
Noh et al. NanoLett 2013, 13, 1764

7.3. Enhancing QD solar cell efficiency via:

7.3.1 Solar cell geometry

7.3.2 Surface modification

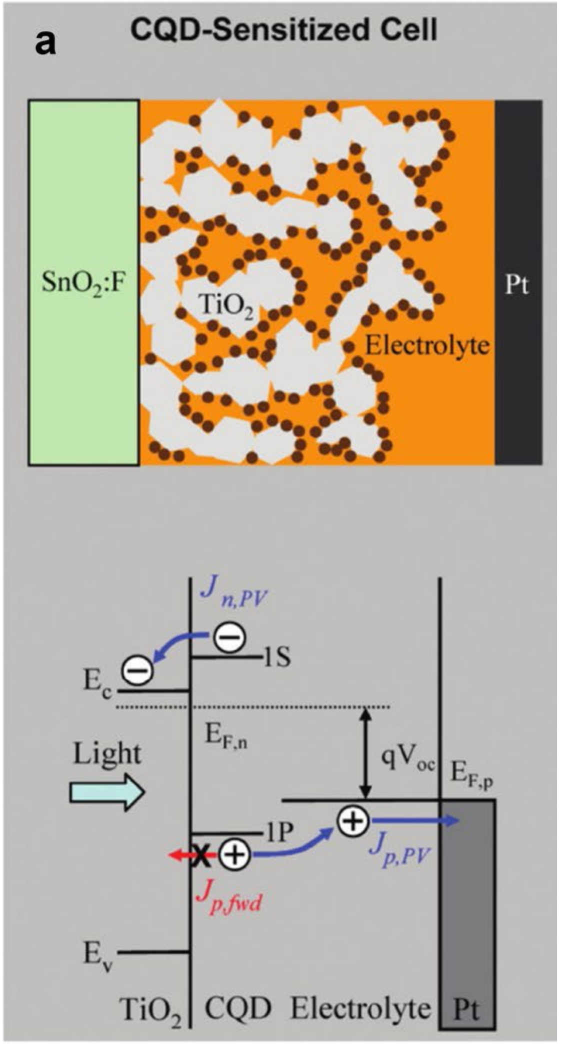
7.3.1. QD solar cell geometry



T. Sargent, ACS nano, **2012**

7.3.1. QD solar cell geometry

Quantum dots sensitized solar cells (QDSC)



Operation mechanism:

(i) Photon is absorbed in a QD, generating an exciton

(ii) The electron and hole dissociate at the interface with TiO2

(iii) The QD sensitizer is oxidized as the electron is injected into the TiO2 layer

(iv) the electron is transported to the TCO electrode

(v) The hole recombines with an electron from the electrolyte redox couple

(vi) The system is in equilibrium one the oxidized electrolyte diffuses to the counter electrode where it is reduced

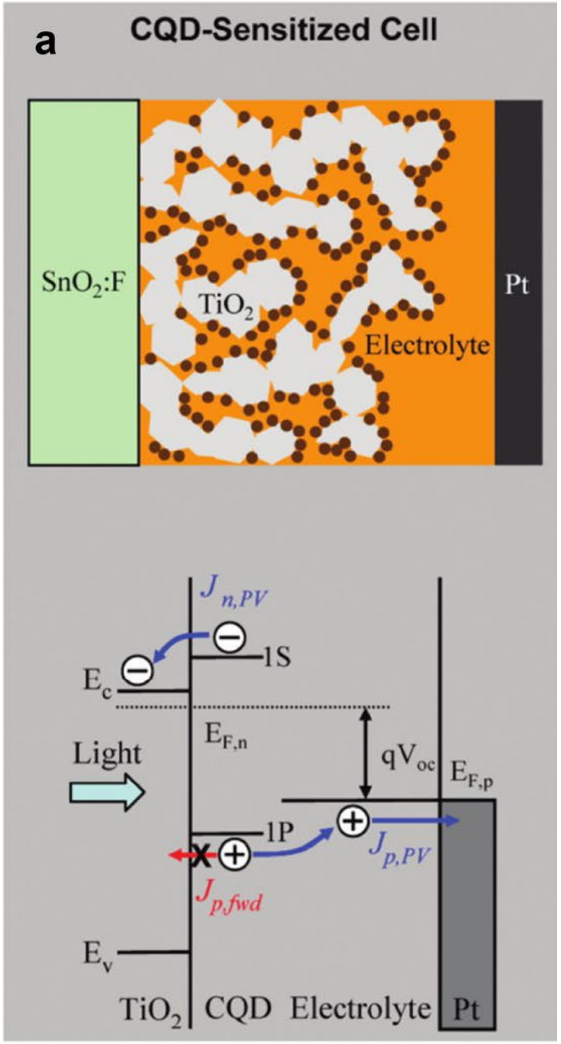
TYPICAL ELECTROLYTE: iodide/triiodide redox couple

- It is source of corrosion for the QDs
- Other: cobalt complexes or solid state hole conductors (spiro-OMeTAD)

T. Sargent, ACS nano, **2012**

7.3.1. QD solar cell geometry

Quantum dots sensitized solar cells (QDSC)



Reason for low efficiency:

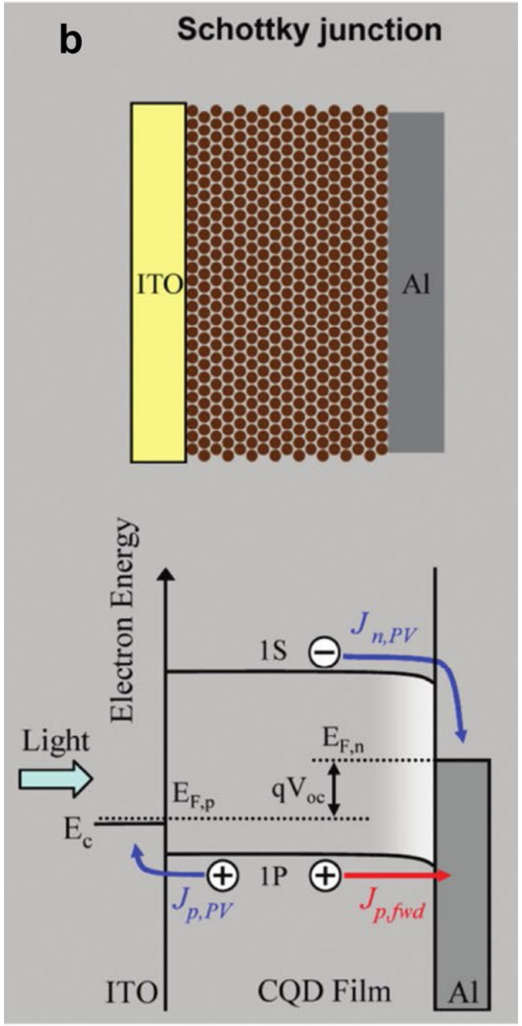
- low converge efficiency during the CQDs deposition
- Generally ZnS coating is used to reduce the back-recombination
- Just one QD monolayer will not absorb sufficient light

Highest efficiency: 5.2% with PbS CQD sensitizers

T. Sargent, ACS nano, **2012**

7.3.1. QD solar cell geometry

CQD Schottky junction solar cells (SJSC)



Operation mechanism:

(i) The architecture is based on overlaying a TCO with large work function with a film of p-type QDs to from an ohmic contact

(ii) This is followed by the evaporation of a metal with a shallow work function to generate an appropriate band-bending to extract the electron while screening holes

Disadvantage:

(i) The short diffusion length in these films limits their thickness, no sufficient light is absorbed

(ii) the barrier to hole injection into the electron-extracting electrode of the Schottky device becomes much less effective

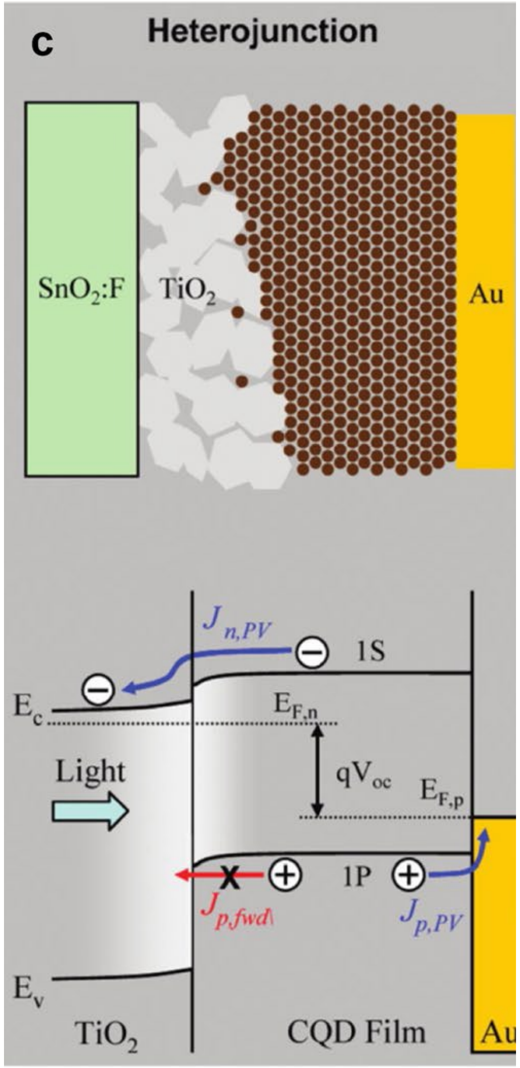
(iii) The Fermi level could be easily pinned by defect states at the metal/semiconductor interface

Highest efficiency: 5.2% with PbS CQD with engineered hole-selective contacts

T. Sargent, ACS nano, **2012**

7.3.1. QD solar cell geometry

CQD depleted heterojunction solar cells (DHJSC)



Operation mechanism:

(i) The architecture is similar to the previous one, except that it has an additional n-type layer with wide band gap (TiO2 or ZnO) between the TCO and the CQD layer to improve electron extraction

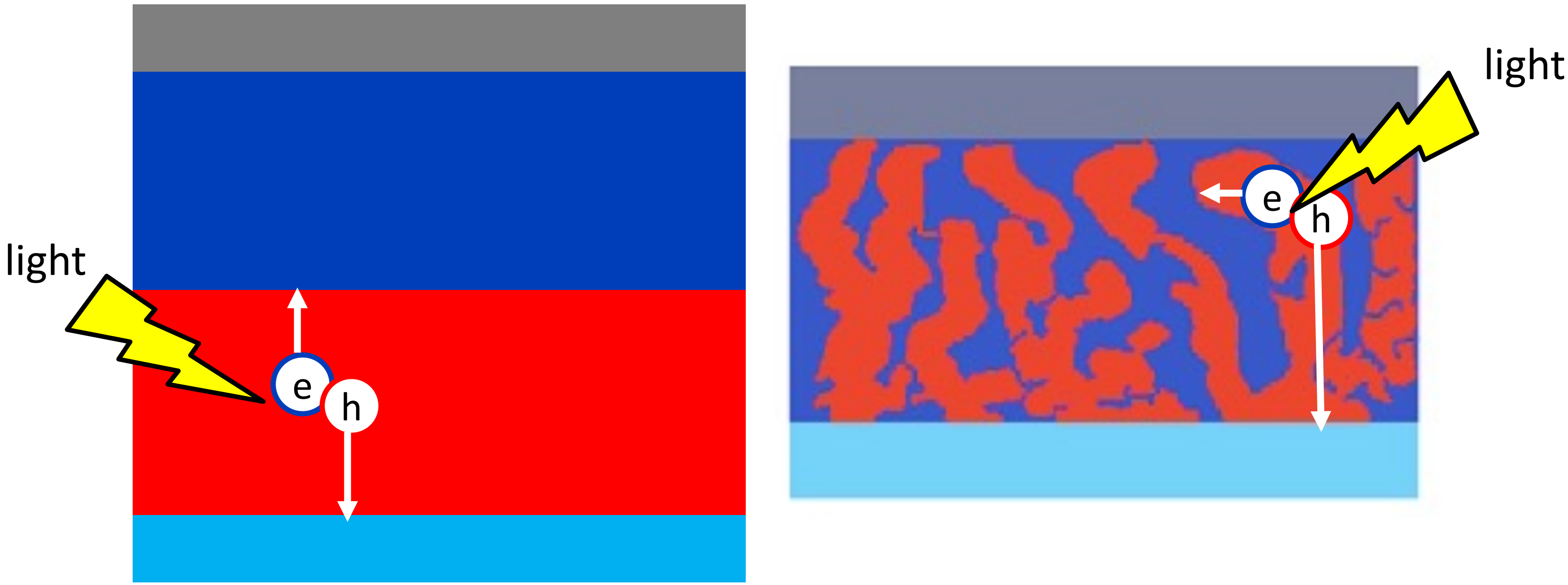
(ii) The mild depletion region at the heterojunction provides a more efficient electron-hole separation

(iii) Higher Voc is obtained because of the large difference between the Fermi level of TiO2 and the counter electrode

Highest efficiency: 7.4% with further improvement including controlled oxide doping and inorganic passivation

T. Sargent, ACS nano, **2012**

Why a bulk heterojunction is better than a planar junction?



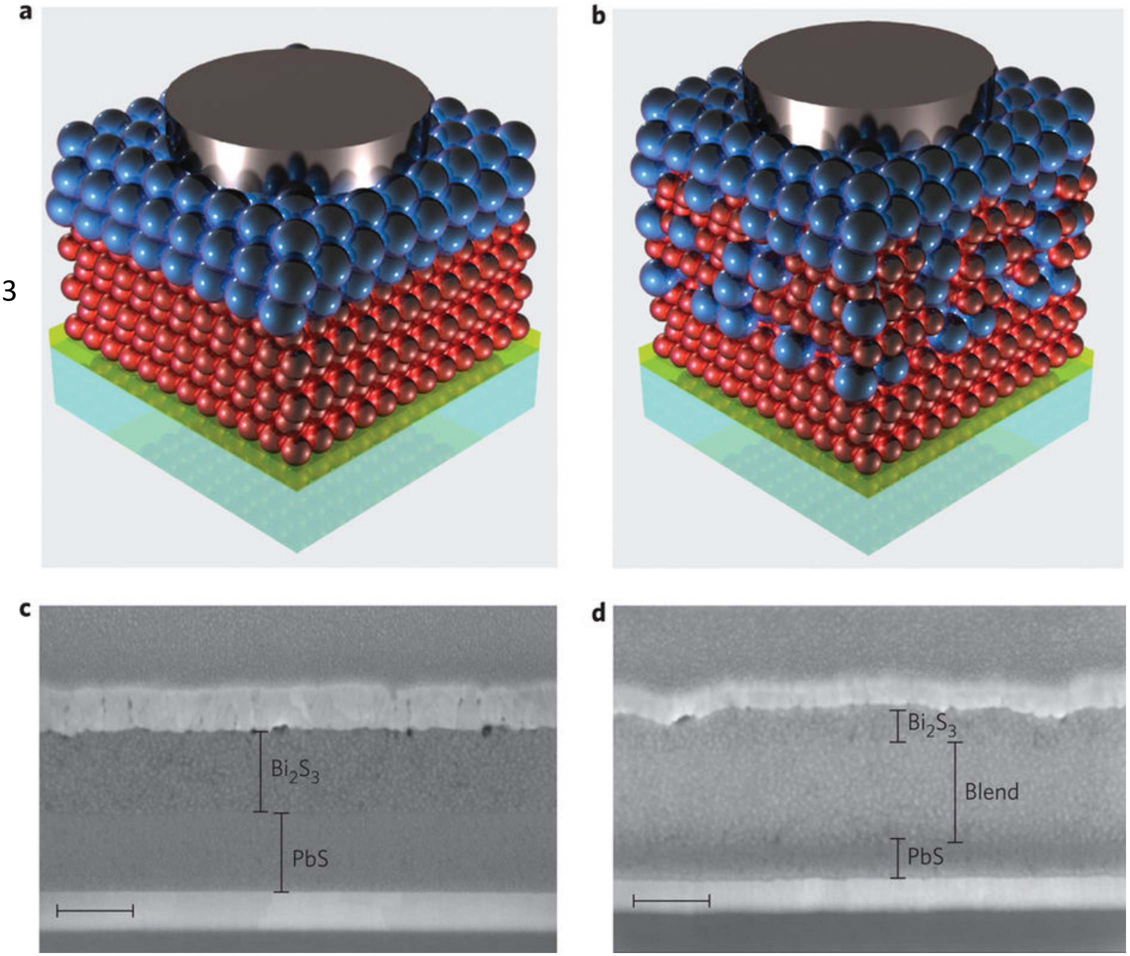
A bulk heterojunction facilitates charge separation against recombination and therefore it allows to have thickener layers of light absorbers

7.3.1. QD solar cell geometry

CQD depleted heterojunction solar cells (DHJSC)

p-type PbS

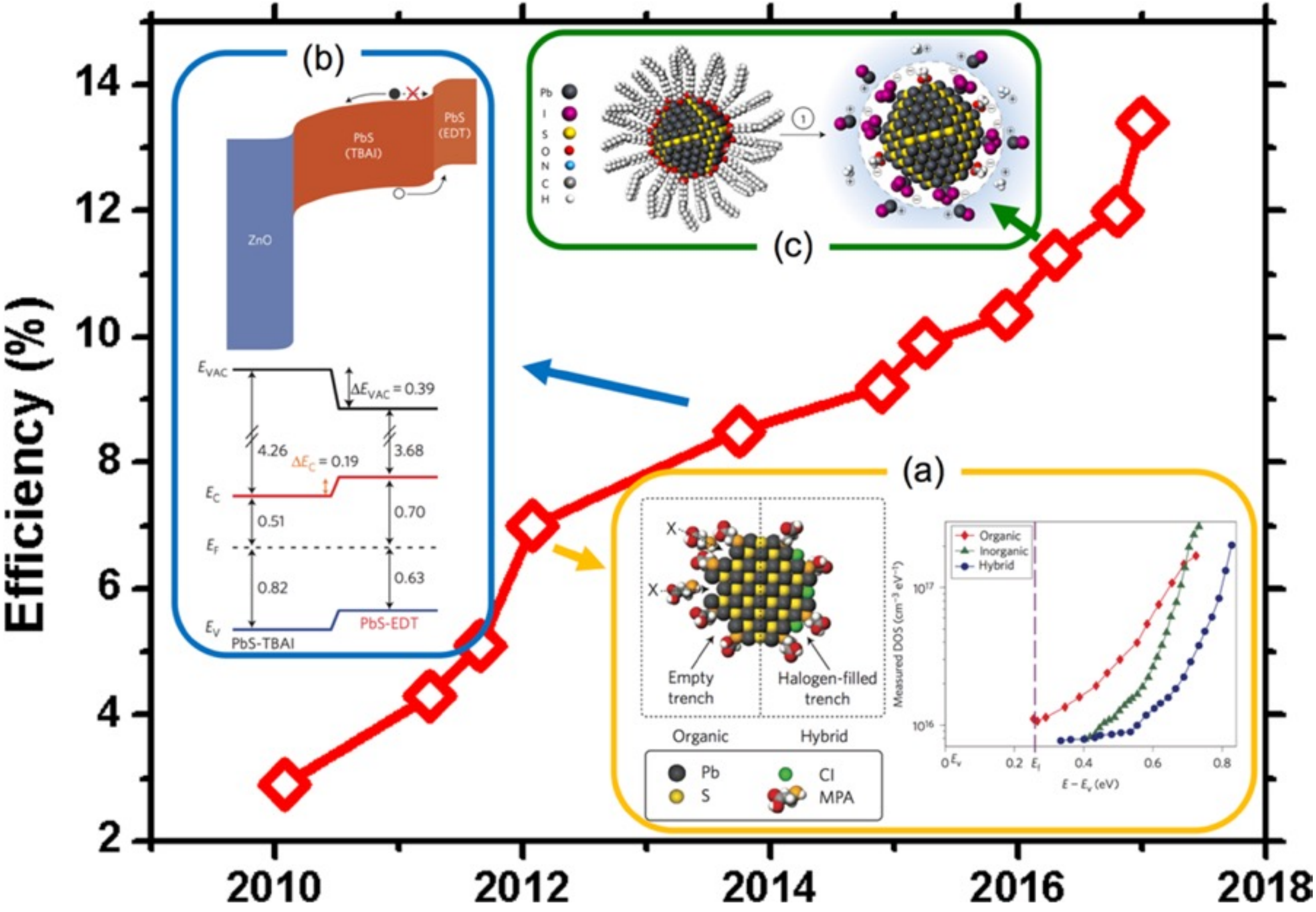
n-type Bi_2S_3



- In the bilayer a distinct interface can be noticed; on the contrary for the BHJ, 3 different layer could be distinguished.

G. Konstatatos, Nature Phot., **2012**

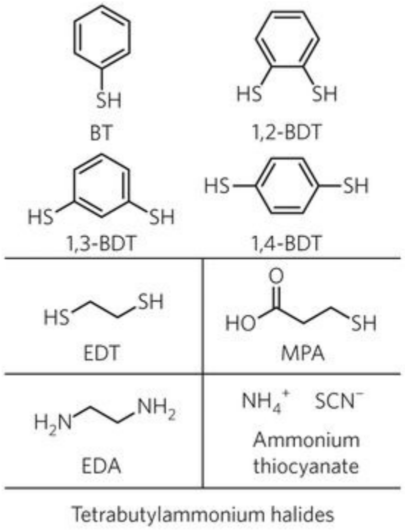
7.3.2. Surface modification

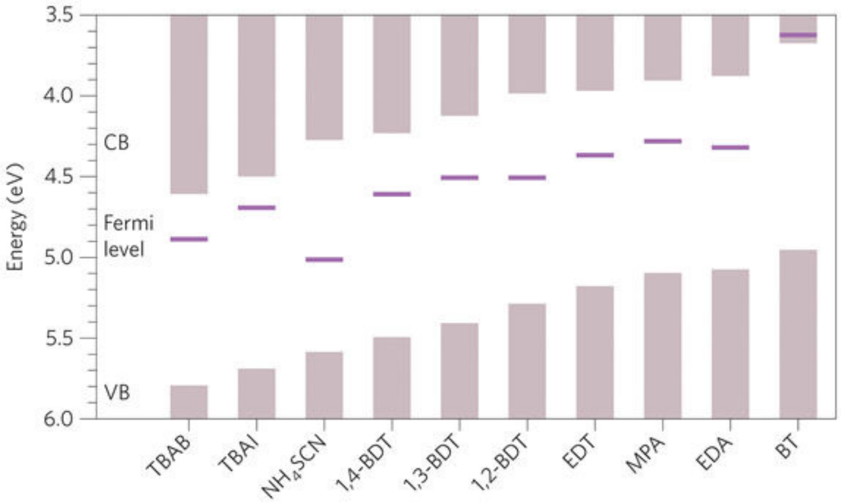


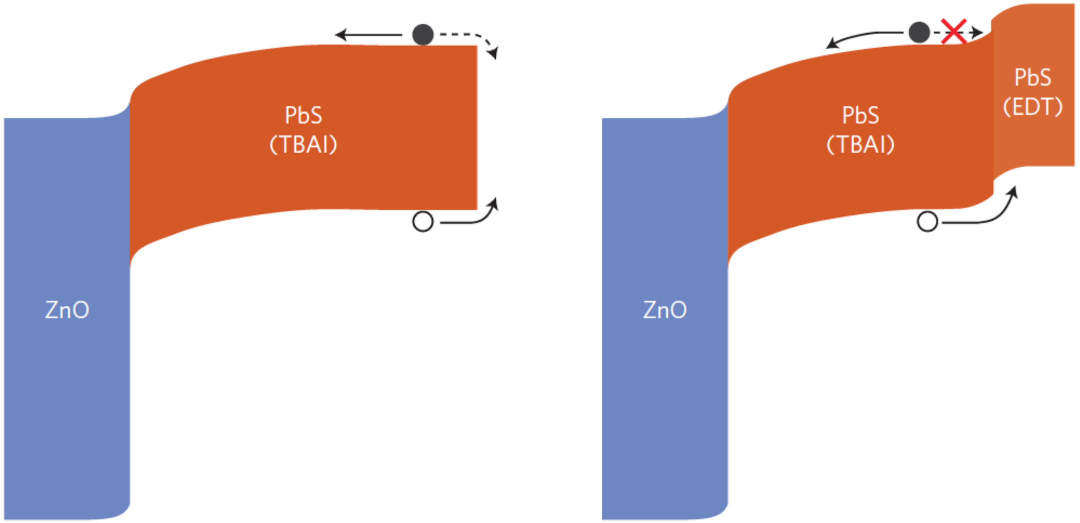
Song and Jeong Nano Convergence, 2017

7.3.2. Surface modification

The absolute energy level of CQDs is critically dependent on surface chemistry. It represents an adjustable parameter in the optimization of CQD-based optoelectronic devices.



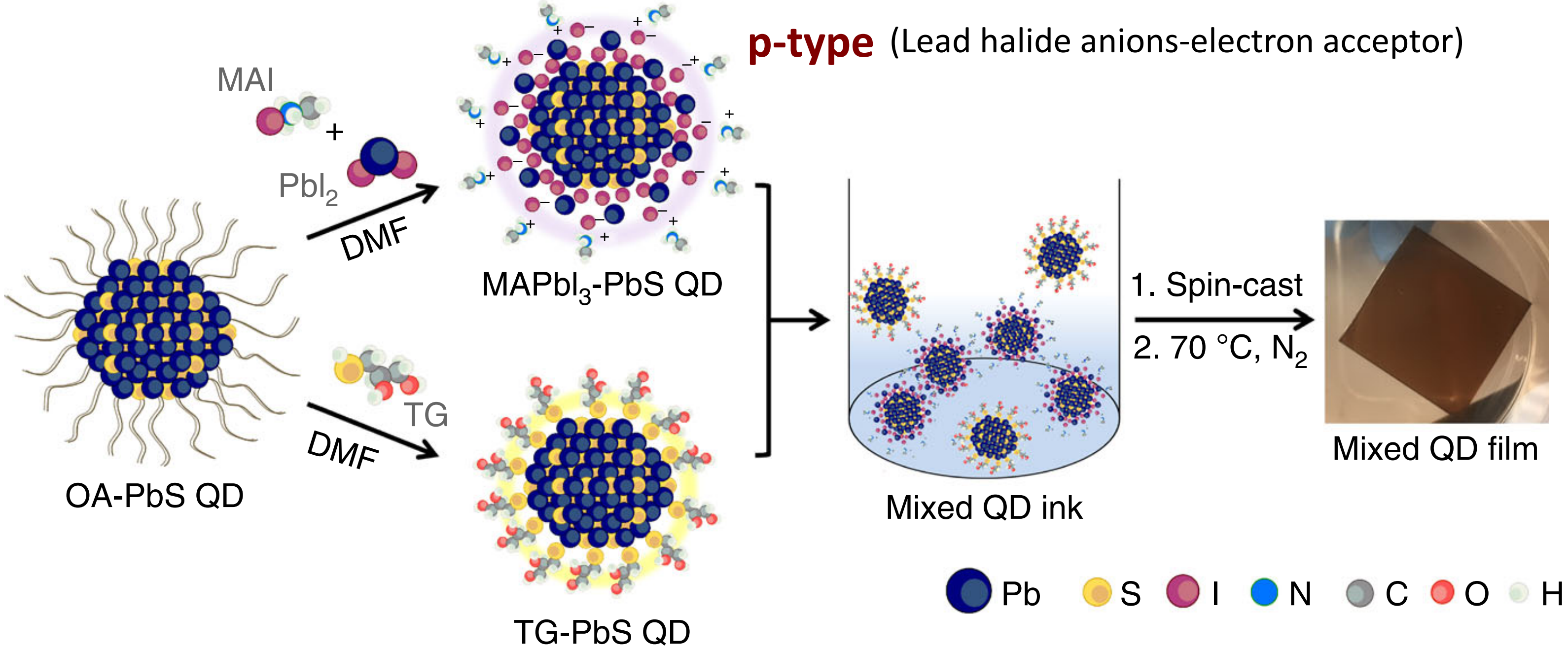




V. Bulovic, ACS nano, **2014**
M. G. Bawendi, Nat. Mat. **2014**

7.3.2. Surface modification

Mixed-quantum-dot solar cells with 10.4% efficiency



p-type (Lead halide anions-electron acceptor)

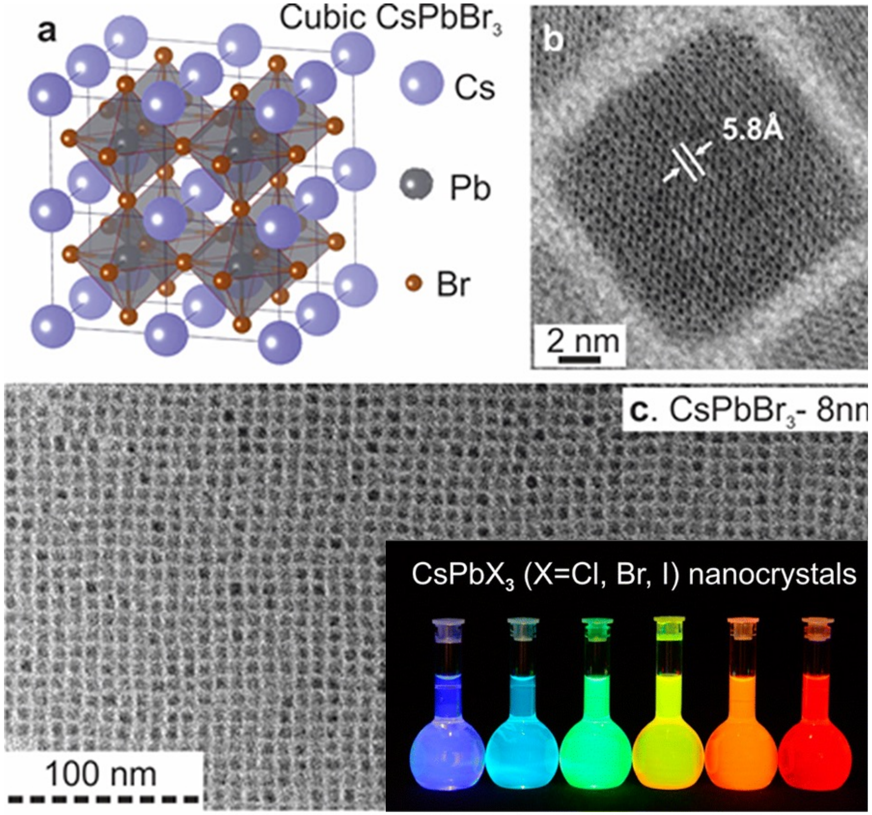
n-type

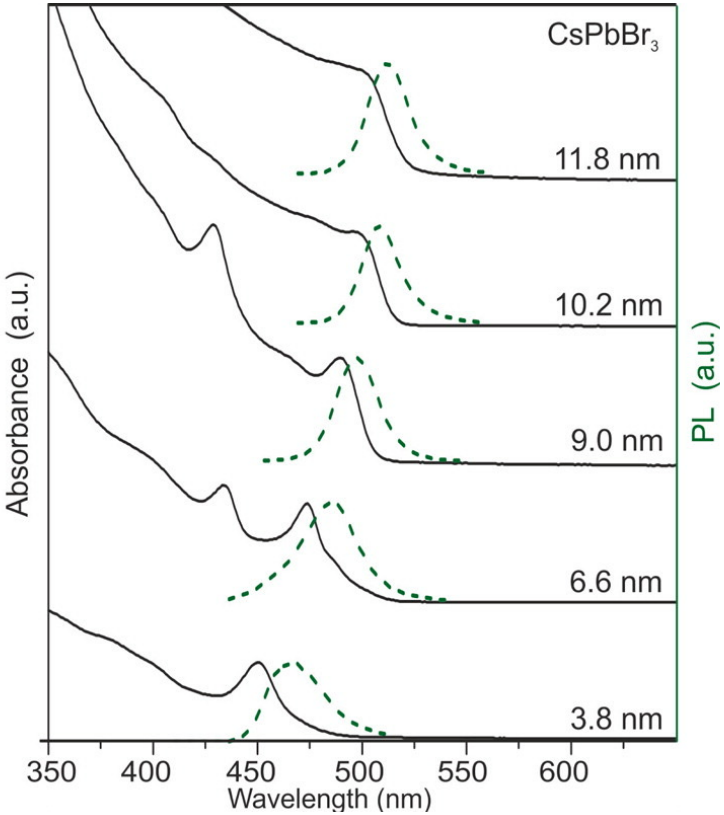
(thiol molecule-thiolgycerol, electron donor)

Surface ligands could be used to tailor electron affinity, thus to make QDs p-type or n-type

T. Sargent, Nature Comm., **2017**

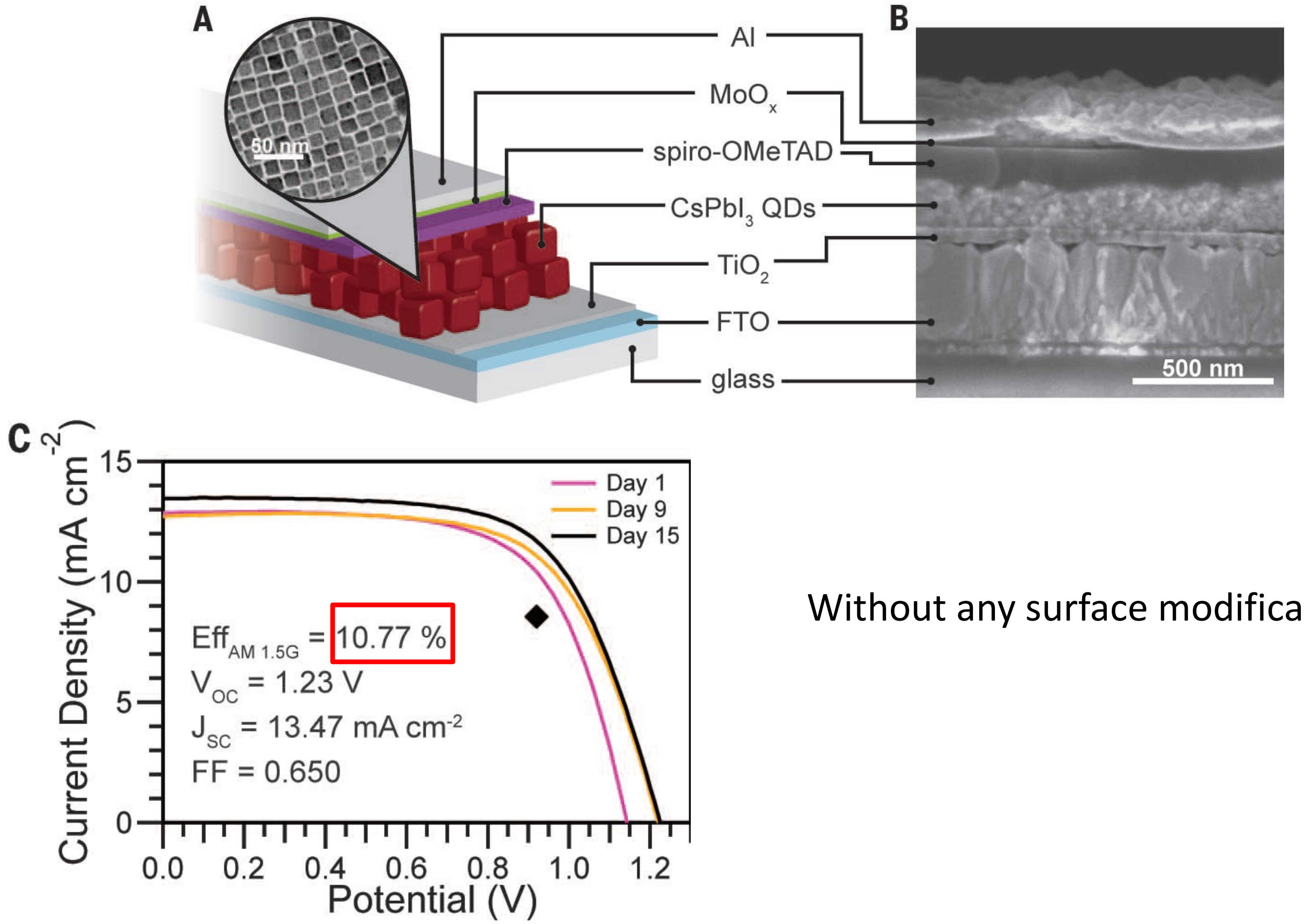
7.4. State of the art solar cells: perovskite quantum dots





- Size and composition dependent optical properties
- High QY
- Ionic compounds
- They are a platform for new science

7.4. State of the art solar cells: perovskite quantum dots



Without any surface modification!!!

J. M. Luther, Science, **2016**

7.4. State of the art solar cells: perovskite quantum dots

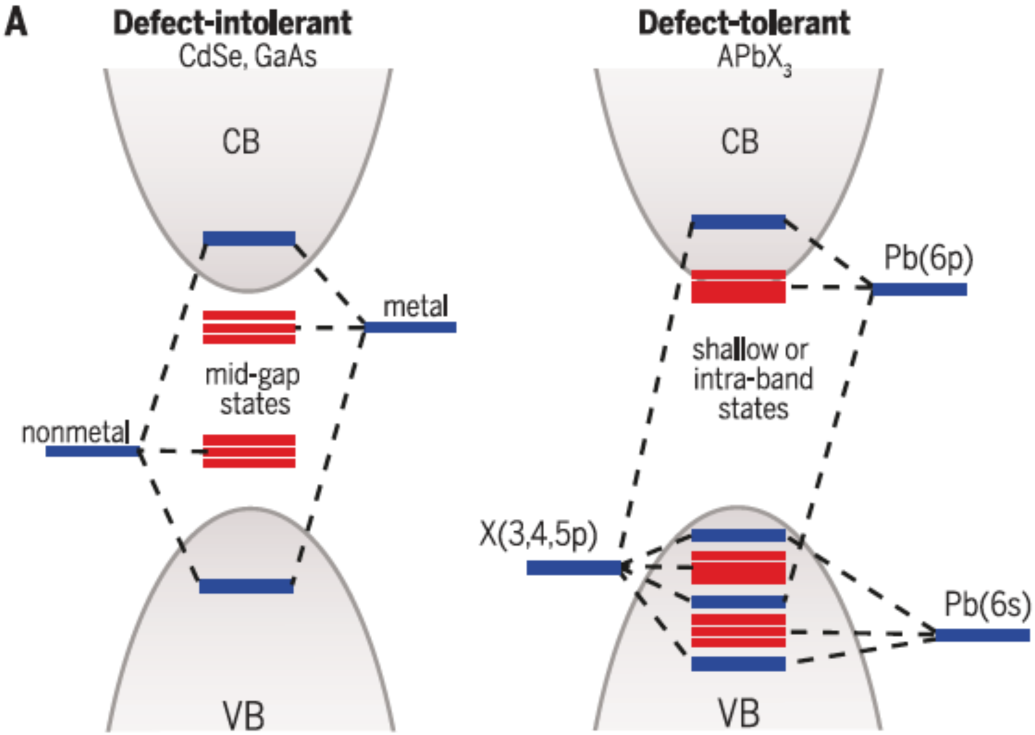
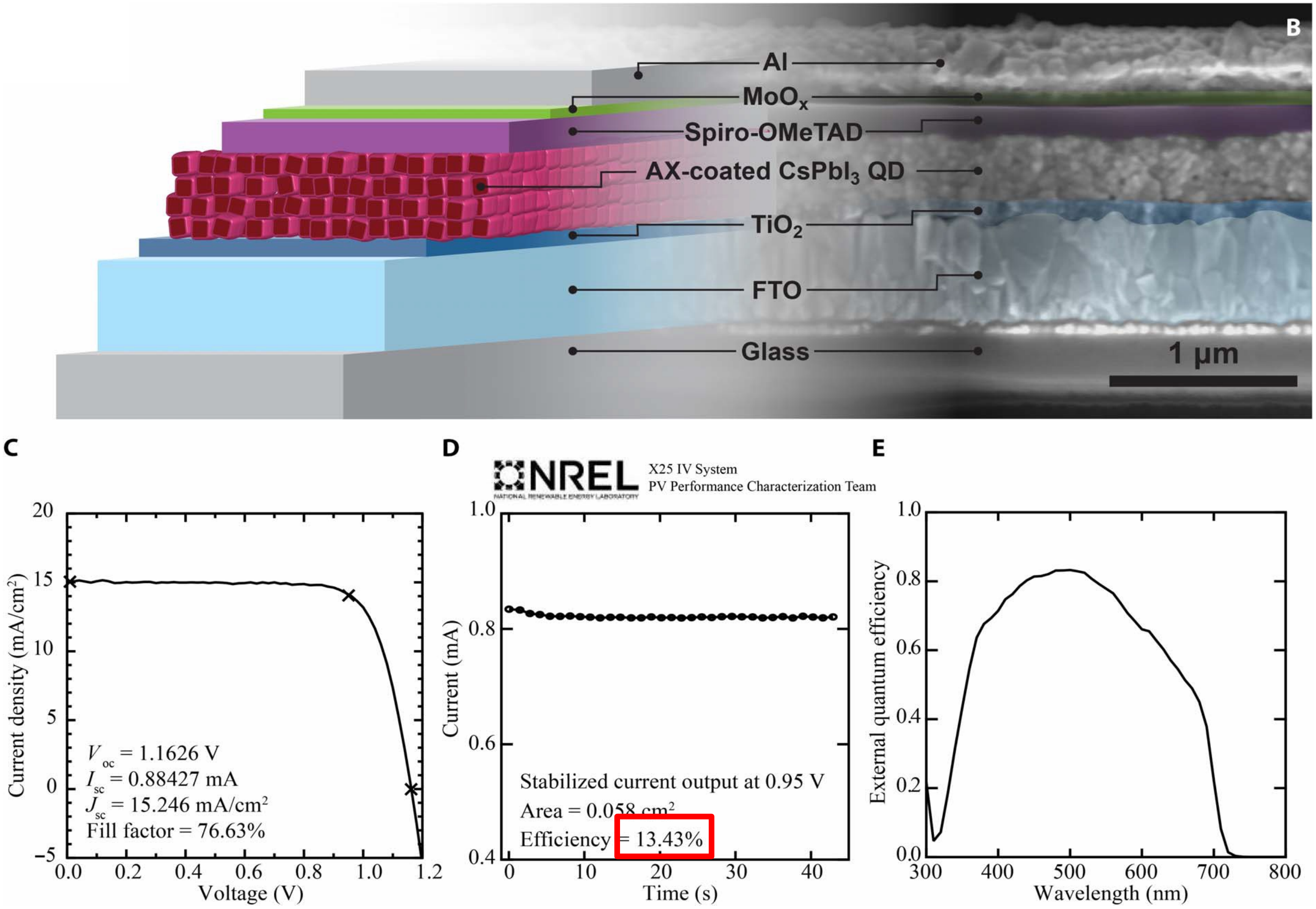


Fig. 4. Defect tolerance in LHP NCs. (**A**) Schematics comparing electronic structures that are defect-intolerant, such as for conventional semiconductors (for example, CdSe, GaAs, and InP), and defect-tolerant, such as for LHPs (*27*). Defects do not act as trap states in LHPs and are therefore benign toward their electronic and optical properties. [Adapted from (*27*)] (**B**) Electronic structure diagrams for $CsPbBr_3$ NCs at the DFT/PBE level of theory (*27*), where PBE is Perdew-Burke-Ernzerhof exchange-correlation functional. Each line

Kovalenko, Science, **2017**

Enhanced mobility $CsPbI_3$ quantum dot arrays for record-efficiency, high-voltage photovoltaic cells

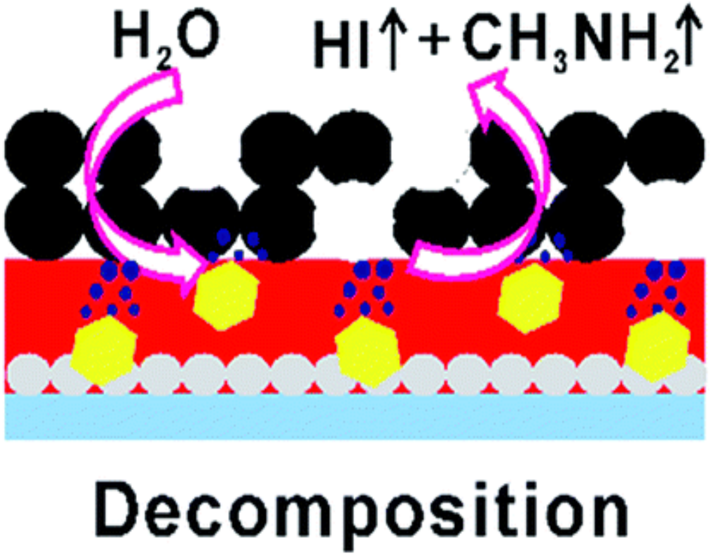


AX post-treatment [where A = formamidinium (FA^+), methylammonium (MA^+), or cesium (Cs^+) and X = I^- or Br^-] that tunes and greatly improves the electronic coupling between QDs, which enhances carrier mobility.

J. M. Luther, Sci. Advance, **2017**

7.4. State-of-the-art QD solar cells

Open challenges in perovskite quantum dots: instability



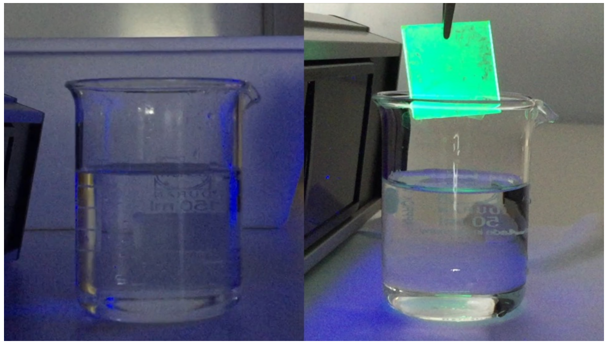
The major reason for instability is moisture!!!

7.4. State-of-the-art QD solar cells

Different strategies to protect perovskite QDs

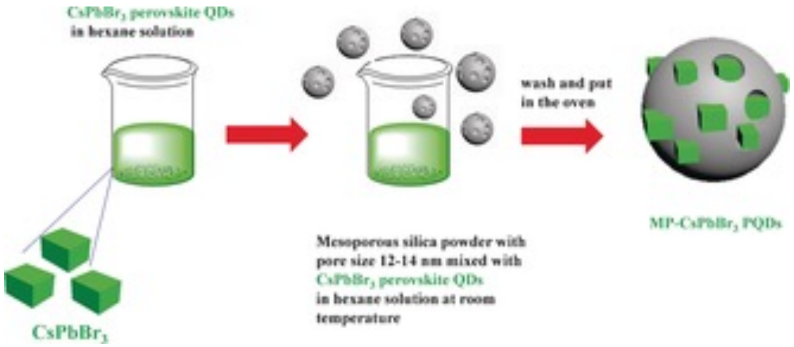
Alumina coated by ALD

$CsPbBr_3$ QDs **$CsPbBr_3$ QDs/AlOx**



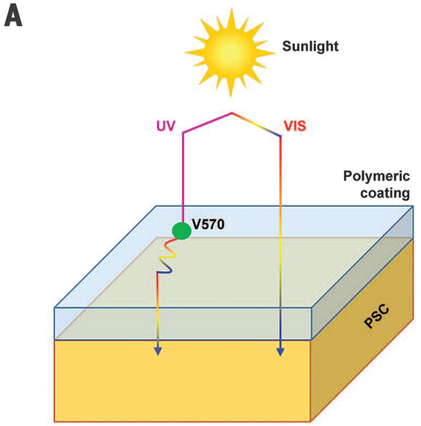
Loiudice et al., *Angew. Chem. Int. Ed.* (**2017**)

Mesoporous silica embedded



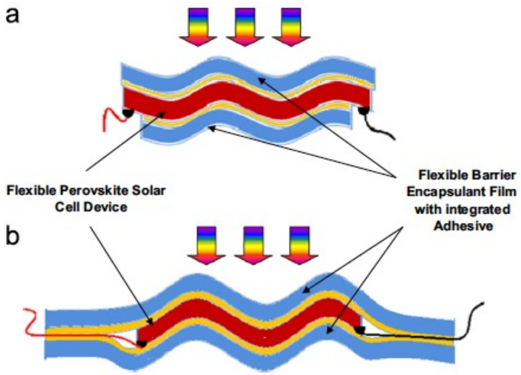
R.-S. Liu, Angew. Chem. Int. Ed, **2016**

Polymer coating



F. Bella, *Science.* (**2016**)

Plastic barrier encapsulant

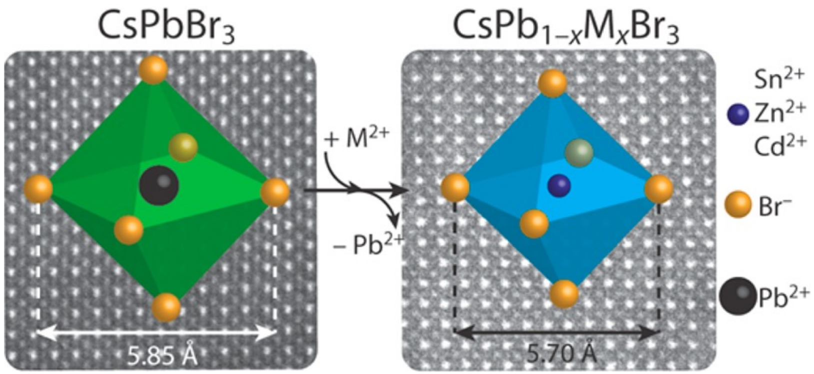


Y.B. Chang, Nano Energy, **2015**

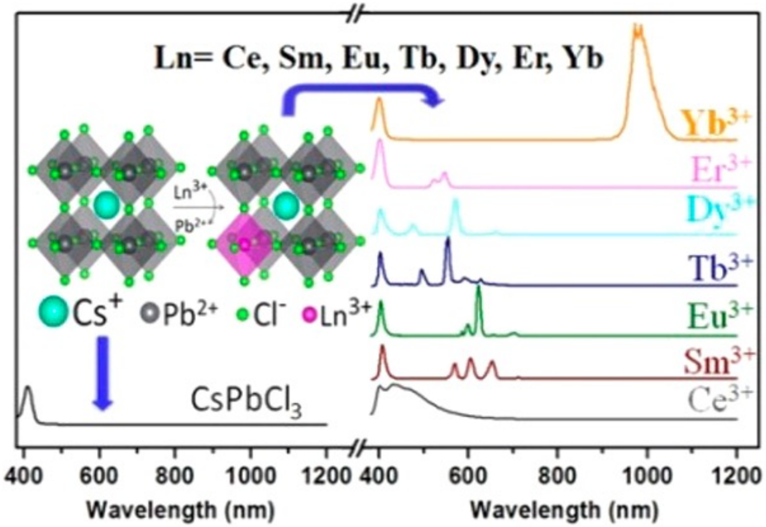
7.4. State-of-the-art QD solar cells

Open challenges in perovskite quantum dots: toxicity

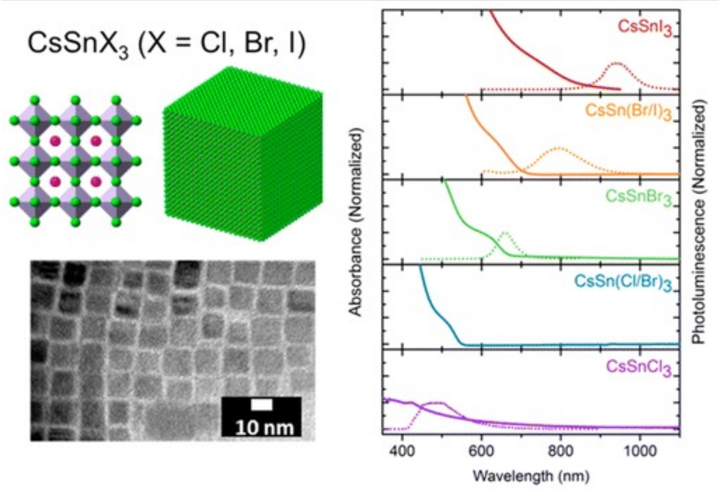
- Cation exchange of lead with divalent or trivalent atoms



M. Donega, JACS, **2016**



H. Song, Nano Lett., **2017**



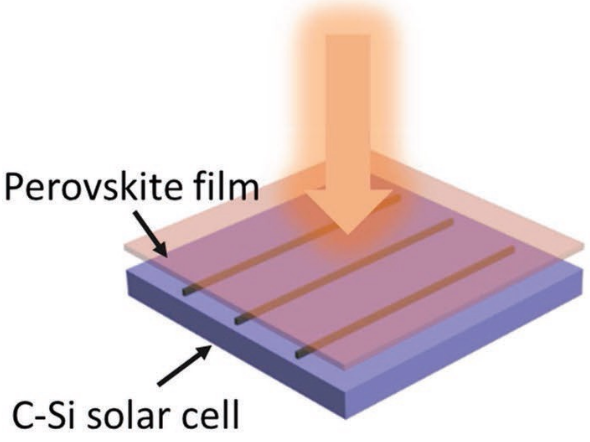
M.L. Bohm, JACS, **2016**

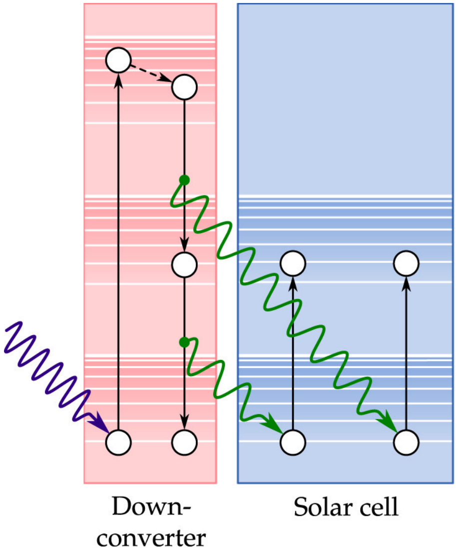
- lead-free perovskite materials are rather unstable under ambient conditions and produce lower device performances compared to their lead-containing analogues, which has been ascribed to their higher defect densities.

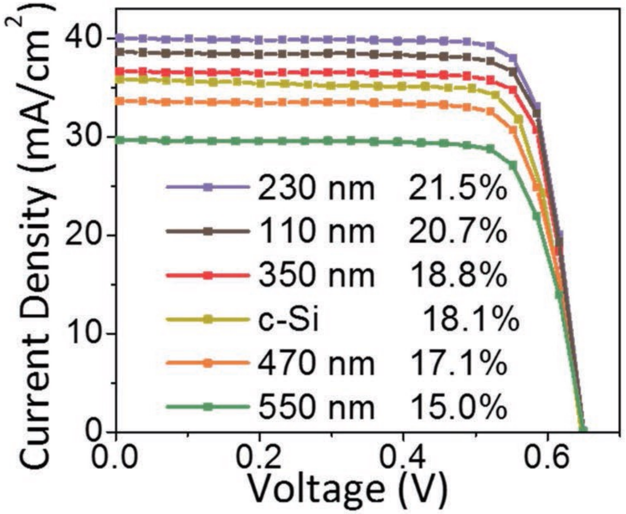
7.4. State-of-the-art QD solar cells

Combination of Si solar cell and QDs

- Cerium and Ytterbium Co-doped Halide Perovskite Quantum Dots: A Novel and Efficient Down converter for Improving t







Optimal thickness of the down-converting layer is needed.

H. Song, Adv. Mat., 2017