ESP5403 Nanomaterials for Energy Systems

Nanostructured Solar Cells

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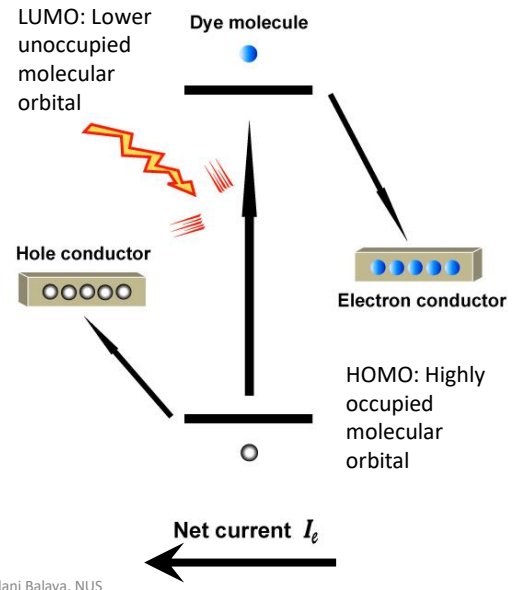
Dye-sensitized Solar Cell

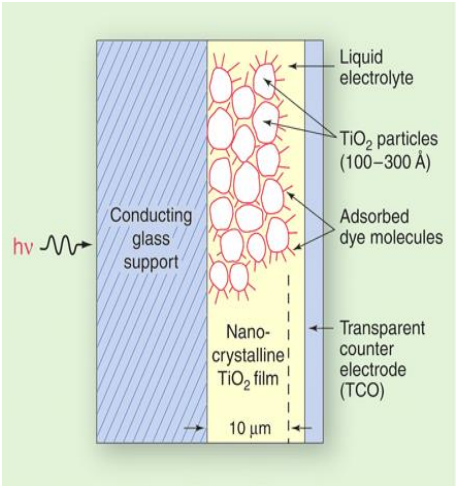
Nanostructured Solar Cell

- **Dye molecule**
  - electron hole pair splits because radiation interacts with the dye
  - the electron shifts over to the electric conductor and the hole shifts to the hole conductor



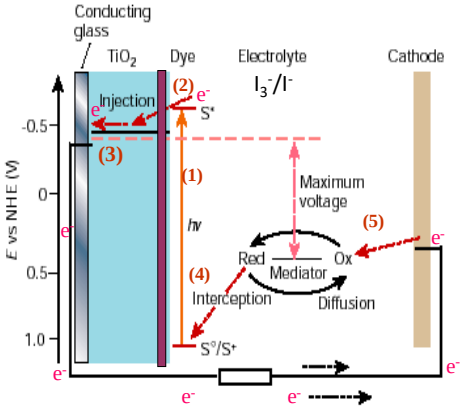
Design of Dye-sensitized Solar Cells

- Conducting electrode
  conducting glass support coated with conducting oxide.
- Nano structured dye-sensitized TiO_2 film
- Liquid electrolyte
- Counter electrode
  coated with conducting oxide with small amount of Pt



Working Principle of DSC

1. Photoexciton of dye
2. Injection of e^- into CB of TiO_2
3. Transport of e^- working electrode
4. Regeneration of oxidized dye by donation from electrolyte
5. Regeneration of electrolyte



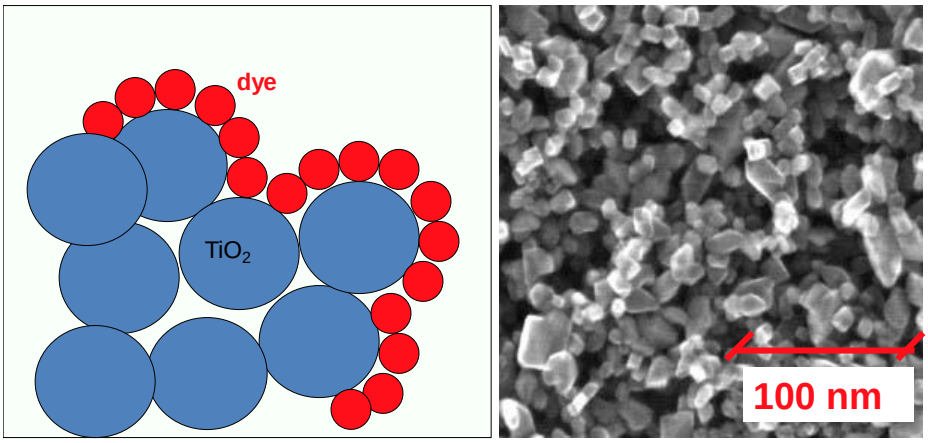
Dye sensitized nanocrystals achieve quantitative conversion of photons into electric current

The incident photon to electrical current conversion efficiency (external quantum efficiency) can reach close to 100 %

$$\eta = \eta_{abs} * \Phi_{inj} * \eta_{coll}$$

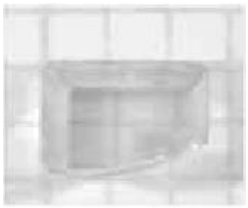
A key question is how electrons are quantitively collected from the disordered network of nanoparticles.

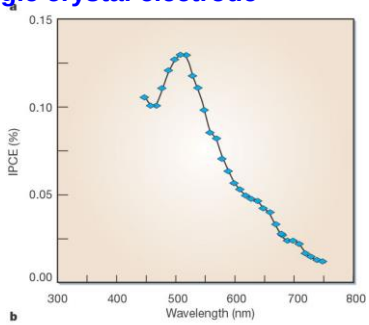
Role of nanoparticles in DSSC



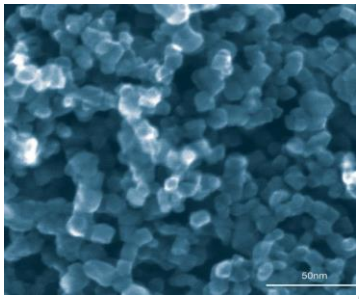
A dye sensitized nanocrystalline film generates over 1000 times more photocurrent than a single crystal electrode

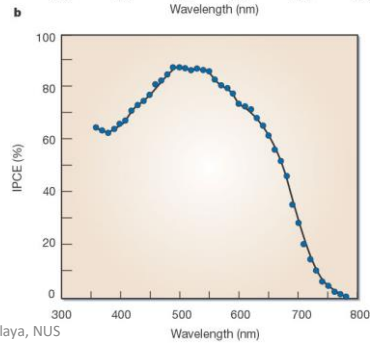
single crystal of anatase





Nanocrystalline anatase film





Electrochemical junctions

As $\Phi_e > \Phi_n$, upon contact electrons flow from n-semiconductor into electrolyte until the Fermi level equalize, establishing a positive space charge layer in the n-semiconductor and an electric field at the interface which drives charge separation

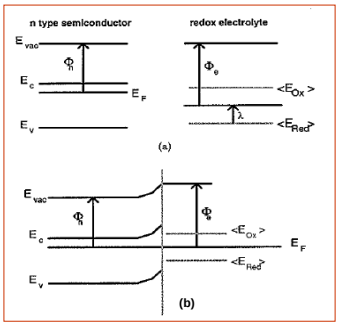


Fig. Band profile of electrochemical junction (a) before & (b) after contact

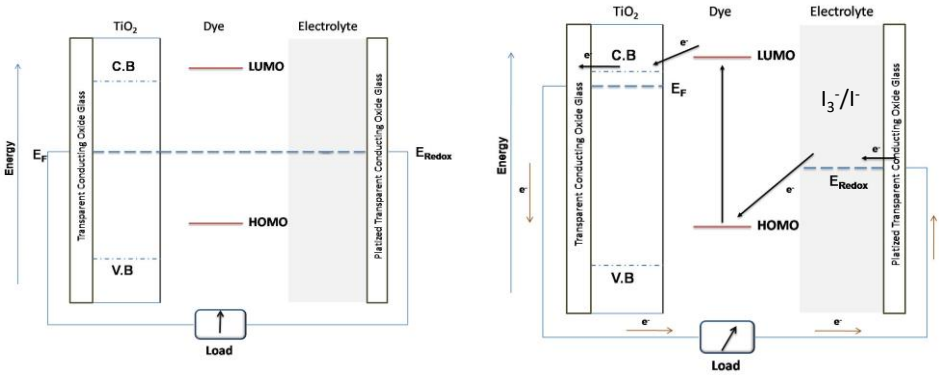
Under illumination, electrons will be transferred to the semiconductor surface, resulting in the semiconductor gaining a *negative charge and the* electrolyte a *positive charge, so providing a* ***photovoltage***

The oxidized species move away from semiconductor to electrolyte and recovers an electron at the counter electrode and regenerate the reduced form

Advantage:
The field is established spontaneously upon wetting the semiconductor surface
Disadvantage
In many material systems, the semiconductor surface is prone to react chemically with the electrolyte under illumination

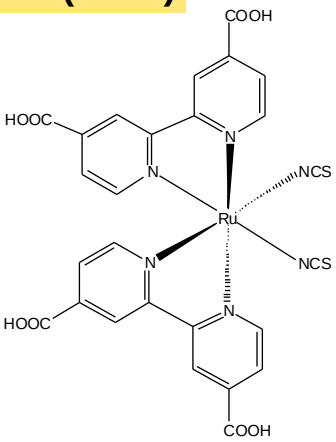
Dye sensitized solar cell in dark and upon illumination

Show the energy level diagram for a DSC when it is in dark. Draw the corresponding energy level diagram when the cell is illuminated with light. Indicate the direction of electron movement with arrows.

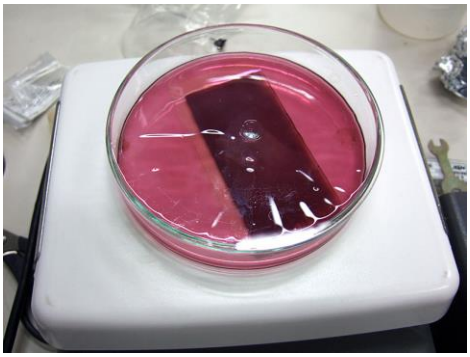


Ruthenium complexes are widely used as sensitizers due to their extraordinary performance and excellent stability

N3 (N719)

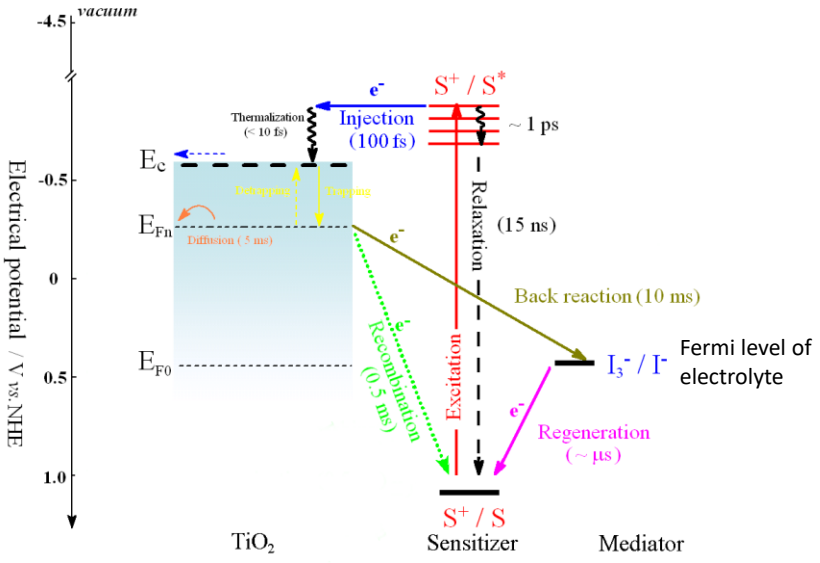


Spontaneous uptake of N3 sensitizer by a nanocrystalline TiO2 film supported on conducting glass

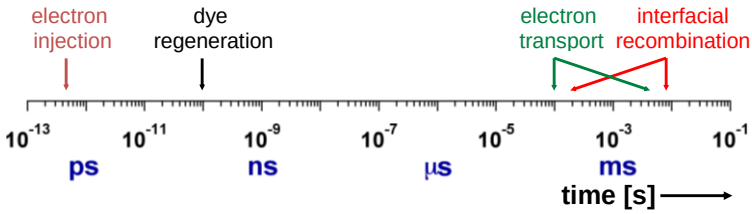


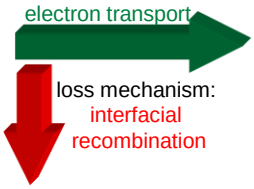
Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Mueller, E.; Liska, P.; Vlachopoulos, N.; Graetzel, M. J. American Chemical Society (1993), 115(14), 6382-90.

Photo-induced interfacial charge separation occurs within femtoseconds



Dynamic Competition





Competition ⇒

Electron diffusion length

$$L_n = \sqrt{D_n \cdot \tau_n}$$

τ_n: electron lifetime
D_n: electron diffusion coefficient

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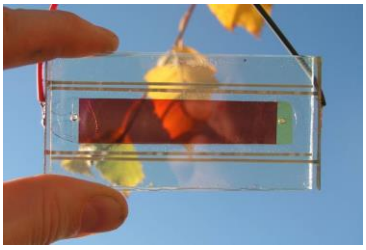
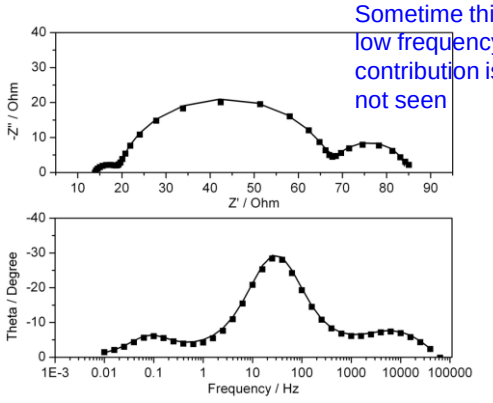
Impedance studies of mesoscpic solar cells

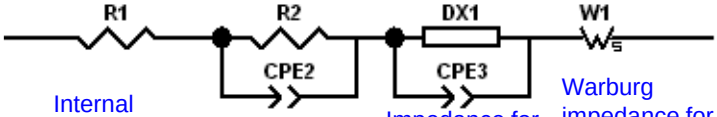


Sometime this low frequency contribution is not seen



Abayev, A. Zaban, F. Fabregat-Santiago, J. Bisquert

Physica Status Solidi (a), 196, R4-R6 (2003).



Internal resistance

Impedance for charge transport

Impedance for back transfer - recombination

Warburg impedance for ions or redox molecules

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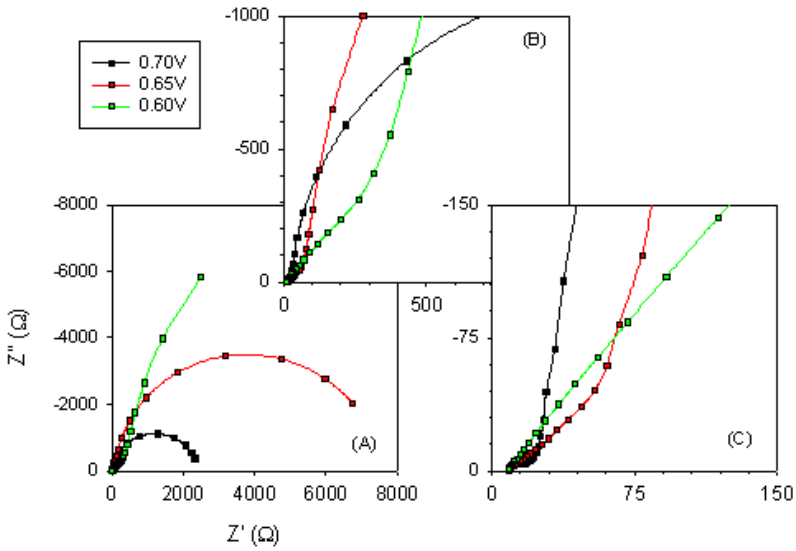
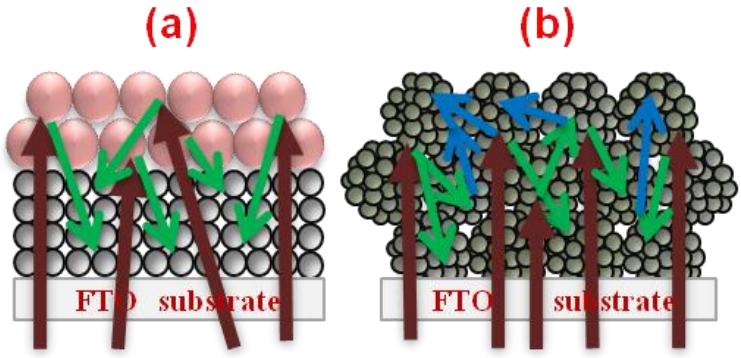
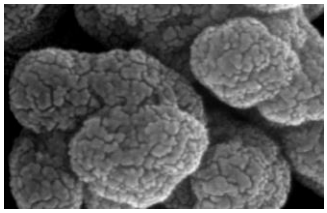
Nyquist impedance plot for a 11.2 % cell reveals electron diffusion and interfacial back reaction dynamics



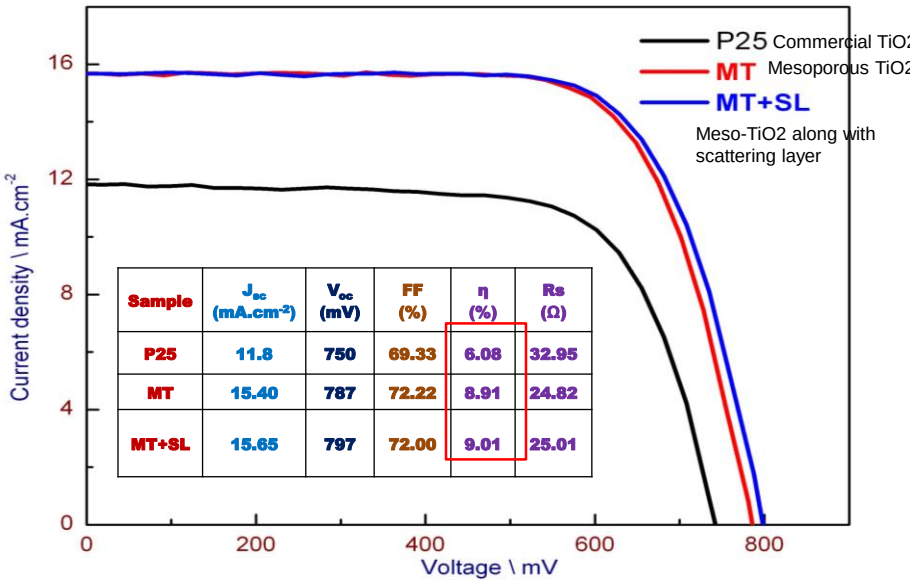
Schematics of structure of bifuctional (a) and multi-functional (b) photoanodes



Mesoporous TiO2 helps with multifunctional properties



Photovoltaic performance



Sample	J_{sc} (mA.cm^{-2})	V_{oc} (mV)	FF (%)	η (%)	Rs (Ω)
P25	11.8	750	69.33	6.08	32.95
MT	15.40	787	72.22	8.91	24.82
MT+SL	15.65	797	72.00	9.01	25.01

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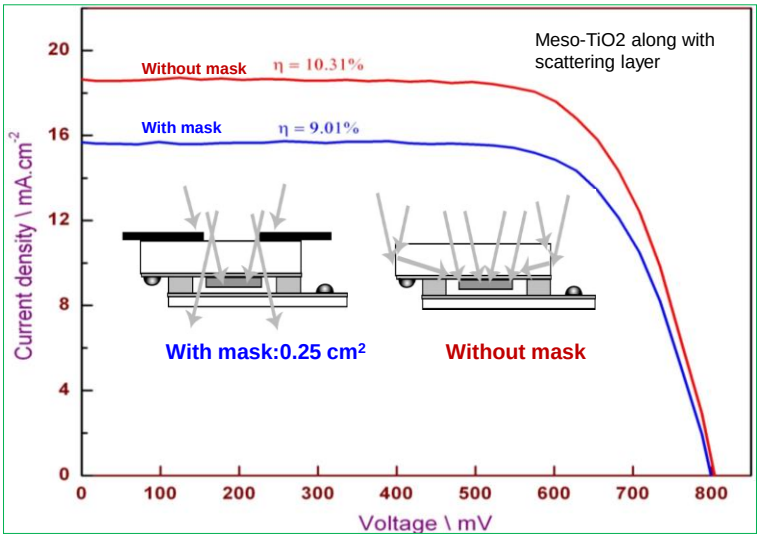
Photovoltaic performance



Eletrode:15 µm MT+ 4 µm SL

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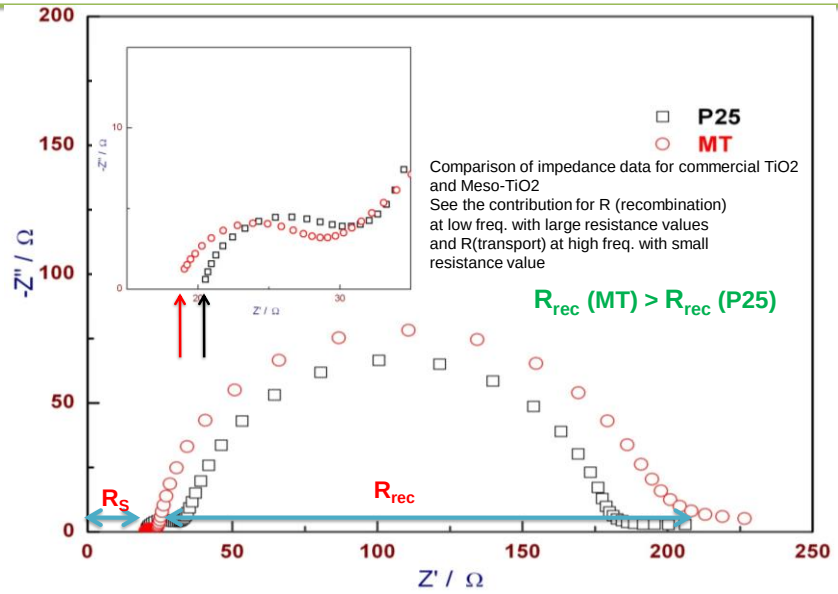
Nyquist plots: charge transfer & transport



R_S : Series resistance ; R_{rec} : Charge recombination resistance

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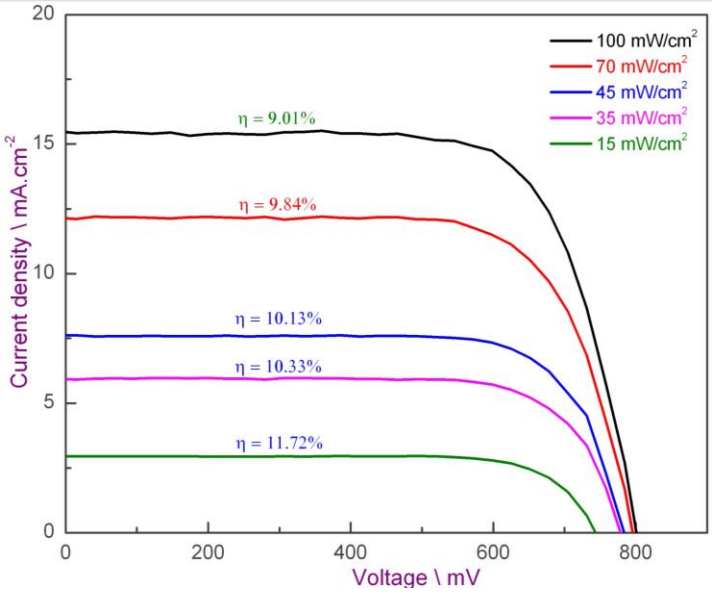
PV performance under different illuminations



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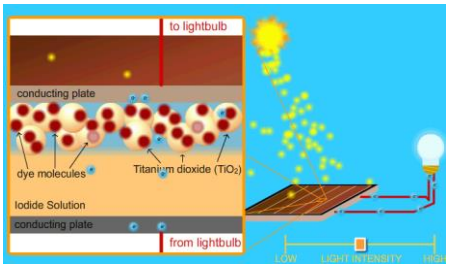
How does a dye-sensitized solar cell work?

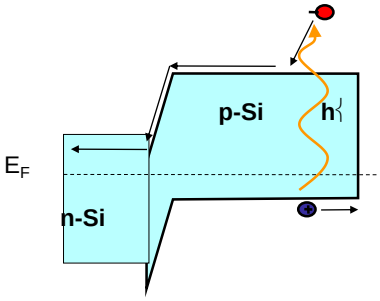
- Light with high enough energy excites electrons in dye molecules
- Excited electrons infused into semiconducting TiO_2, transported out of cell
- Positive "holes" left in dye molecules
- Separation of excited electrons and "holes" creates a voltage



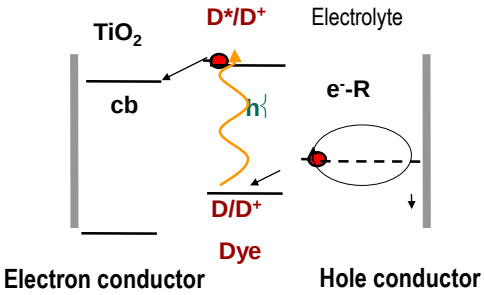
Source: http://www.compadre.org/portal/items/detail.cfm?ID=12726

Dye sensitized solar cells separate light absorption from carrier transport

p-n junction photovoltaic cells



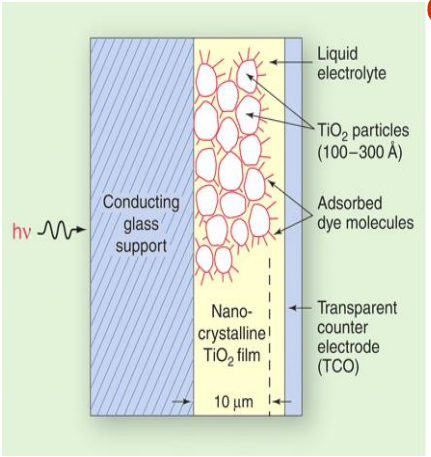
dye sensited solar cells DSC

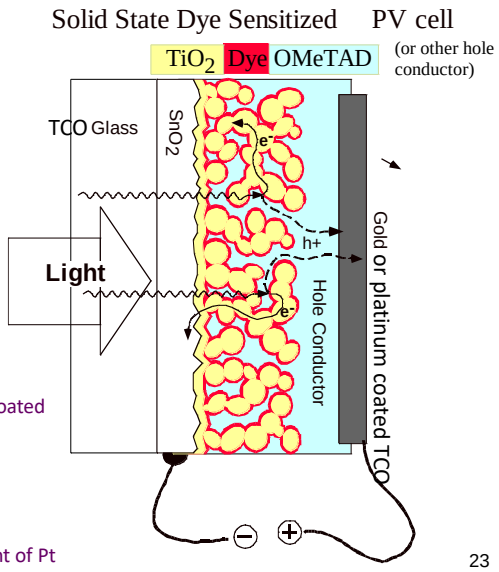


Charge separation by electric field at the p-n junction

Charge separation by kinetic competition as in photosynthesis

Design of solid state dye-sensitized solar cells





Conducting electrode conducting glass support coated with conducting oxide.

Nano structured dye-sensitized TiO_2 film

Liquid electrolyte

Counter electrode

coated with conducting oxide with small amount of Pt

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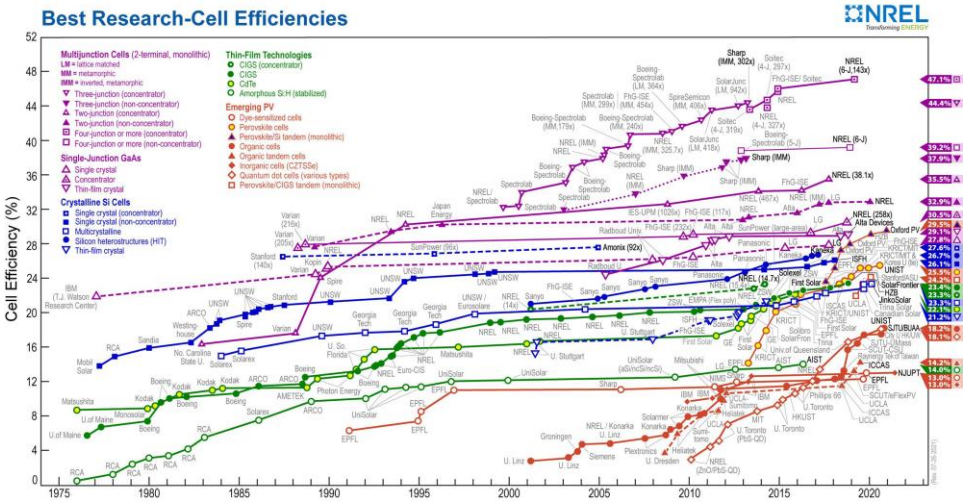
Perovskite Solar Cells

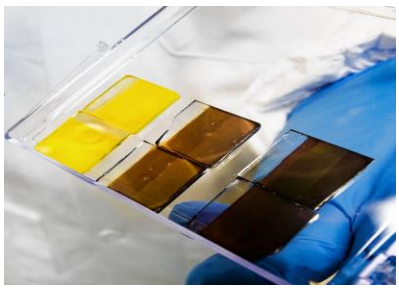
Best solar cells (lab scale) efficiencies chart



Latest update by NREL, USA

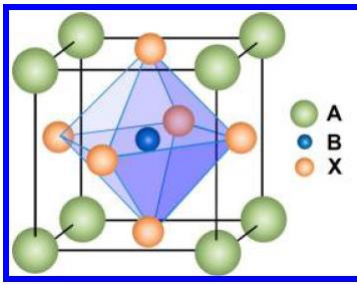
Why perovskite solar cells are promising?

- ❑Promising Photovoltaic Conversion Efficiency (PCE) of 23.3 %.
- ❑High V_{oc}'s of > 1.1 V .
- ❑Good light absorber of the whole visible solar spectrum - thin films (less materials & low costs) .
- ❑Manufacturing: Simple wet chemistry techniques using solution process--vastly simpler than other solar technologies, from c-Si to liquid DSSC .
- ❑Perovskites are available as mineral.



Perovskites

"Perovskites" is a material that has general ABX3 crystal structure e.g. calcium titanate
First discovered by Guatav Rose in 1839 and named after Russian mineralogist L.A.Perovski



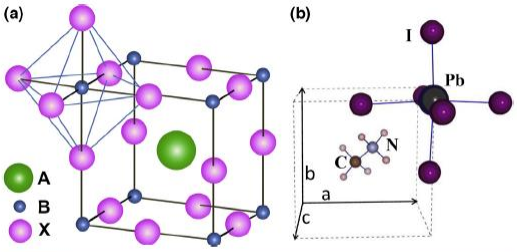


FIGURE 2
(a) ABX_3 perovskite structure showing BX_6 octahedral and larger A cation occupied in cubo-octahedral site. (b) Unit cell of cubic $CH_3NH_3PbI_3$

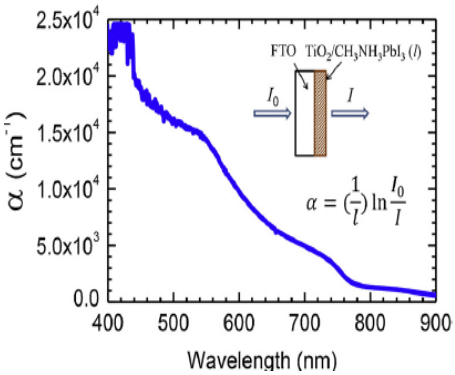
Fig.: ABX_3 Perovskite Structure ($SrTiO_3$ is a famous example)
A,B are cations & X= oxygen, carbon, nitrogen, or halogen

E.g. $CH_3NH_3PbI_3$

Material properties: Good for high efficiency solar cells

- ❑ Optical band gap ~1.55 eV ; absorption onset occurs at 800nm
  - ➢ good light absorber over the whole visible solar emission spectrum

- ❑ High Optical Absorption Coefficient
  - ➢ @ 700 nm, $\alpha = 0.5 \times 10^4\ cm^{-1}$, equal to a penetration depth of 2 µm



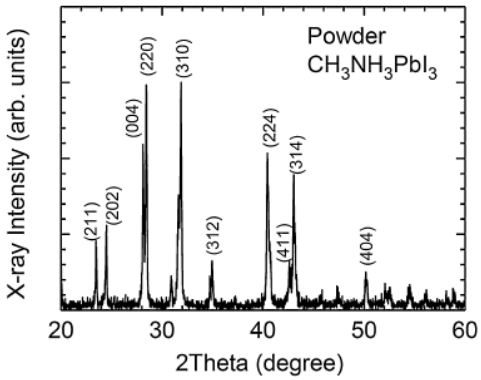
Absorption coefficient (α) as a function of wavelength for perovskite CH3NH3PbI3 nanodot coated with 1.4 mm TiO2 film

http://dx.doi.org/10.1016/j.mattod.2014.07.007

Material properties: Good for high efficiency solar cells

❑Highly crystalline

➢Excellent charge carrier mobilities - diffusion length > 1 μm.



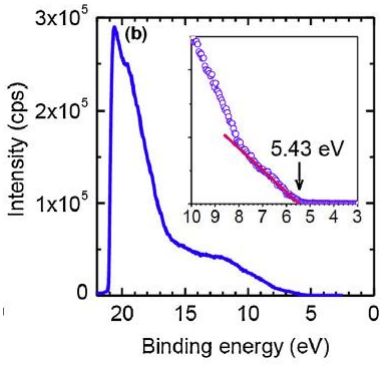
X-ray diffraction patterns for $CH_3NH_3PbI_3$ powder

http://dx.doi.org/10.1016/j.mattod.2014.07.007

Material properties: Good for high efficiency solar cells

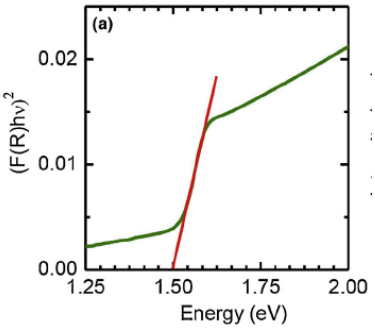
❑ Weak binding energy of excitons i.e. about 30 meV (close to 26 meV, kT @ 25°C)

Valance band edge



Ultra-violet Photoelectron Spectroscopy of $CH_3NH_3PbI_3$ adsorbed TiO_2 film

Band gap



Diffuse reflectance spectral data for $CH_3NH_3PbI_3$ adsorbed TiO_2 film

http://dx.doi.org/10.1016/j.mattod.2014.07.007

Energy level comparison

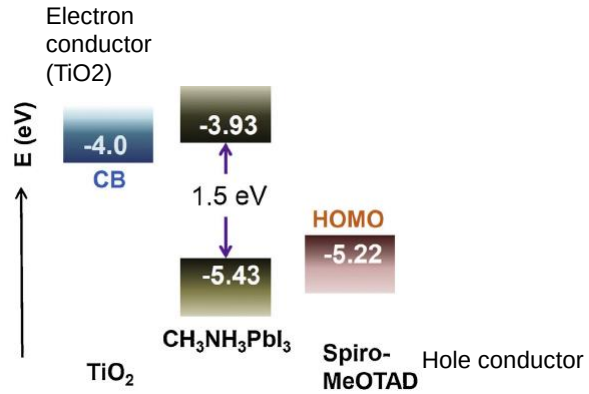
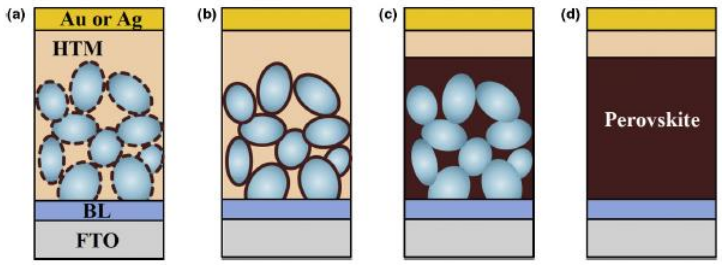


Figure shows valance band maximum (VBM), band gap (Eg) and conduction band minimum (CBM) for the perovskite $CH_3NH_3PbI_3$

From thermodynamic point of view: VBM is suitable for hole separation and CBM is suitable for electron separation

On the basis of bandgap energy, absorption onset wavelength is expected around 826 nm.

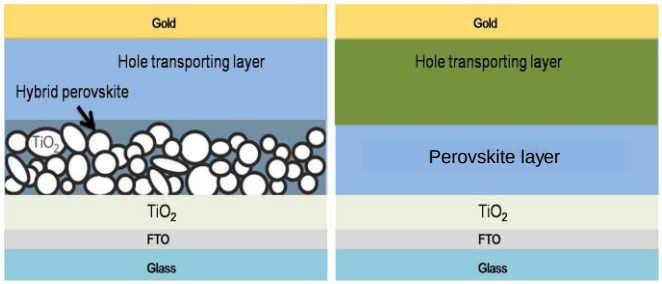
Structural evolution of perovskite solar cells



Structural evolution of perovskite solar cells: (a) sensitization concept with surface adsorption of nanodot perovskite, (b) meso-superstructure concept with non-injecting scaffold layer, (c) pillared structure with a nano oxide building block, and (d) planar pin heterojunction concept. Spheres represent TiO_2 in (a) and (c) and Al_2O_3 in (b).

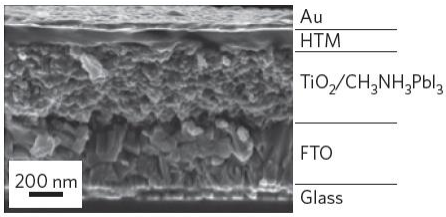
Device Architecture

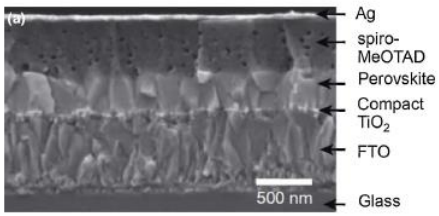
❖Current Perovskite Solar Cells are built upon the architectural basis for solid state DSSC



Hydbrid perovskite solar cell

Thinfilm perovskite solar cell



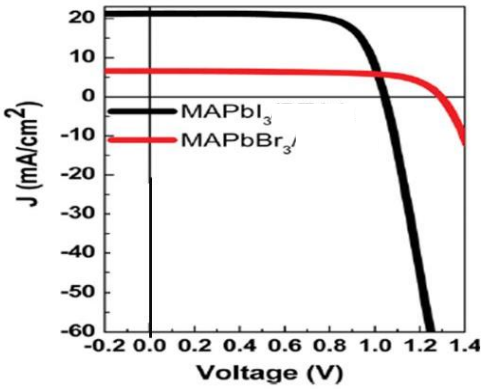


Cross-sectional SEM view

Material properties: Good for high efficiency solar cells

❑ Low voltage losses of about 0.4 eV during PV action

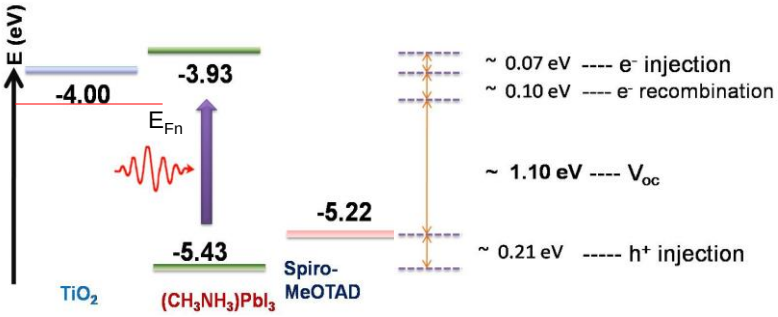
➢ High V_{oc}'s of > 1.1 V
example: 1.1V for $CH_3NH_3PbI_3$ versus 1.4 V $CH_3NH_3PbBr_3$



MA = CH_3NH_3

Energy Environ. Sci., 2014,7, 2614-2618

Working principle

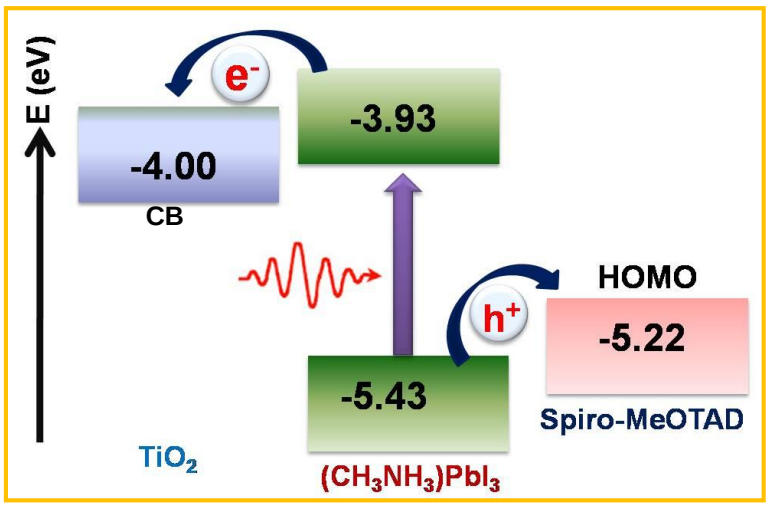


Energy losses in Perovskite solar cells

- V_{oc} is probably saturated at a mere drop of 0.4 V.
- V_{oc} is 1.1 V.
- A voltage drop of only 0.4 eV, competitive with the best thin-film technologies (CIGS: 1.15 eV @ 0.7 V; Si: 1.1 eV @ 0.7 V).

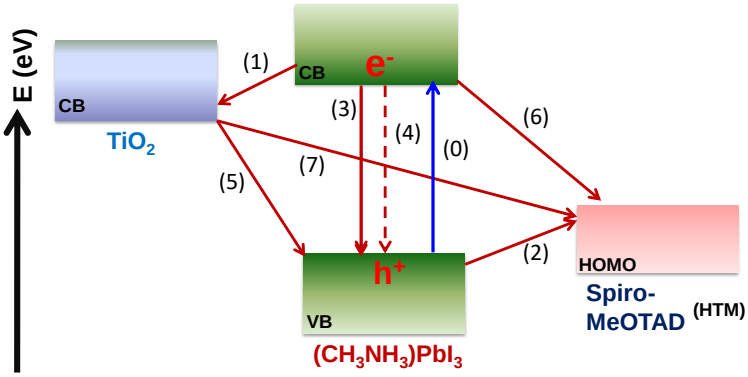
Energy Environ. Sci., 2014, 7, 2518–2534

Working principle



Energy levels in the mesoporous TiO_2 perovskite solar cells

Schematic diagram of energy levels and electron transfer processes in a TiO_2 based perovskite solar cell



(1) Electron injection; (2) hole injection; (3) radiative exciton recombination;
(4) non-radiative exciton recombination; (5) back electron transfer at the TiO_2 surface;
(6) back charge transfer at the HTM surface; (7) charge recombination at the TiO_2/HTM interface.

 Energy Environ. Sci., 2014, 7, 2518–2534

Progress in perovskite solar cell efficiency

❖ On the basis of the recent achievements, a power conversion efficiency as high as 22% is realistically possible from an optimized perovskite-based solid-state solar cells

CAUTION

Toxicity of Pb

Scalability

Challenges are to be addressed for market penetration

Quantum Dot Solar Cells

Quantum Dots – Quantum Confinement

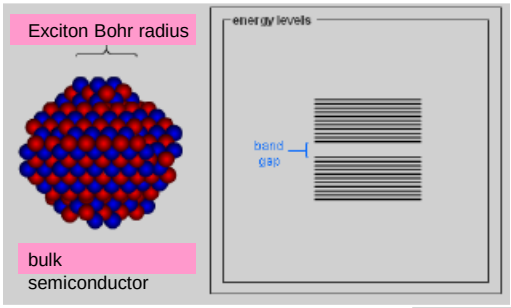
Quantum dots - semiconductor material. The electrons in quantum dots have a range of energies. The concepts of energy levels, bandgap, conduction band and valence band still apply. However, there is a major difference.

Excitons have an average physical separation between the electron and hole, referred to as the Exciton Bohr Radius this physical distance is different for each material.

In bulk, the dimensions of the semiconductor crystal are much larger than the Exciton Bohr Radius, allowing the exciton to extend to its natural limit.

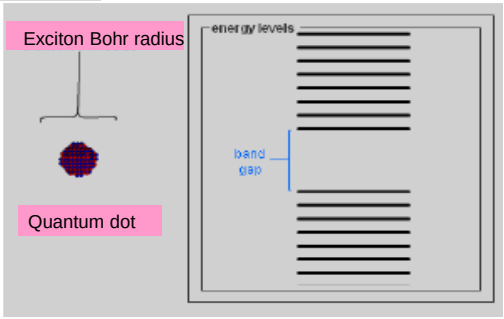
However, if the size becomes small enough - comparable to size of the material's Exciton Bohr Radius, then the electron energy levels can no longer be treated as continuous - they must be treated as discrete, meaning that there is a small and finite separation between energy levels. This situation of discrete energy levels is called **quantum confinement**, and under these conditions, the semiconductor material ceases to resemble bulk, and instead can be called a **quantum dot**. This has large repercussions on the absorptive and emissive behavior of the semiconductor material.

Quantum Dots – A tunable range of energies

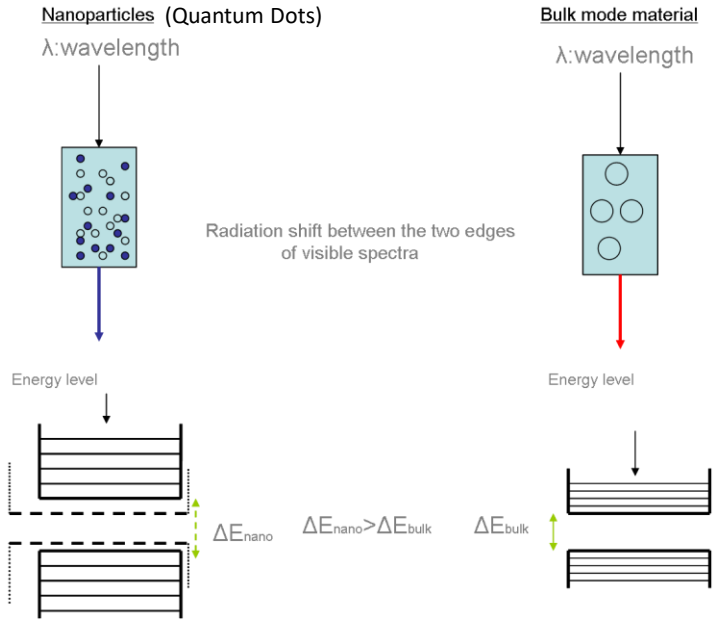


Because the bandgap of the bulk is fixed, the transition results in fixed absorption/emission frequencies.

Quantum dots offer the unnatural ability to tune the bandgap and hence the absorption/emission wavelength.



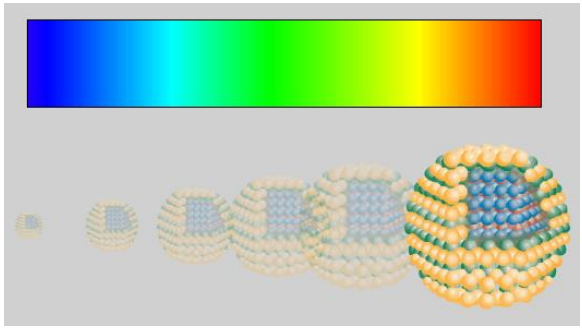
Energy levels in quantum dots



Quantum Dots – A tunable range of energies

- Because quantum dots' electron energy levels are discrete rather than continuous, the addition or subtraction of just a few atoms to the quantum dot has the effect of altering the boundaries of the bandgap.
- Changing the geometry of the surface of the quantum dot also changes the bandgap energy, owing again to the small size of the dot, and the effects of quantum confinement.
- The bandgap in a quantum dot will always be energetically larger; therefore, we refer to the radiation from quantum dots to be "blue shifted" reflecting the fact that electrons must fall a greater distance in terms of energy and thus produce radiation of a shorter, and therefore "bluer" wavelength.

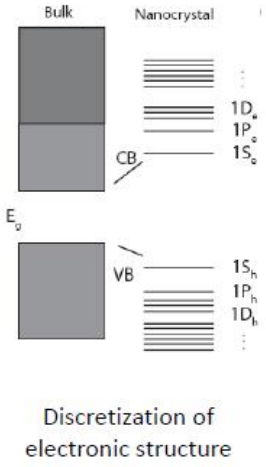
Size Dependent Control of Bandgap in Quantum Dots



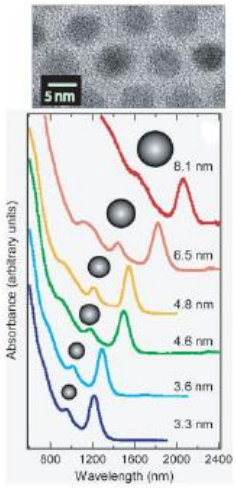
In bulk semiconductor material, electrons tend to make transitions near the edges of the bandgap.

- However, with quantum dots, the size of the bandgap is controlled simply by adjusting the size of the dot.
- Because the absorption/emission frequency of a dot is dependent on the bandgap, it is therefore possible to control the output wavelength of a dot with extreme precision.
- In effect, it is possible to tune the bandgap of a quantum dot, and therefore specify its "color" output depending on the needs of the customer.

Effects of quantum confinement

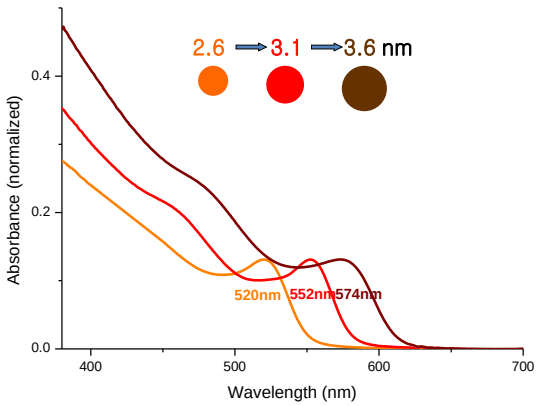


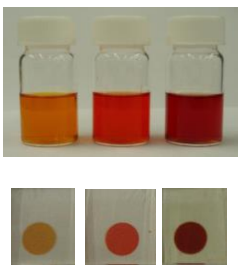
Discretization of electronic structure



Change in bandgap energy

Absorption spectra of different sizes of CdSe QDs





Why quantum dots for solar cells?

- To achieve very low cost PV cells – increasing the efficiency is essential
- Excess energy of incident photons compared to bandgap, create e-h pair to higher energy levels, generate heat through phonon emission
- Highly excited electrons and holes – termed hot electrons and hot hole (hot carriers)
- Photogenerated e-h pairs are correlated and are termed excitons
- The extraction of useful work from hot carriers – difficult as the cooling process occurring through carrier-phonon scattering and subsequent hot-carrier cooling is very fast (sub-ps)
- Formation of discrete quantum levels in quantum dots affects the relaxation and cooling dynamics of high-energy excitons and could enhance power conversion efficiency – using excess energy to create more excitons – "multiple exciton generation" (MEG).

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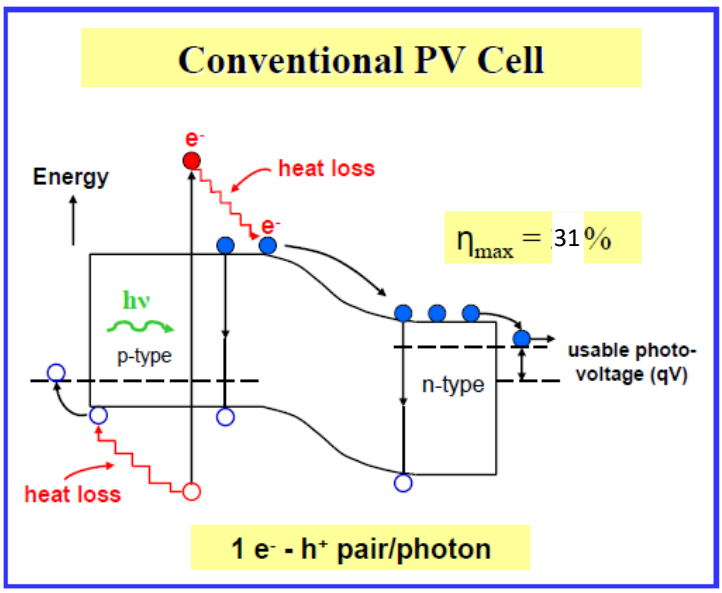
Solar Energy Conversion



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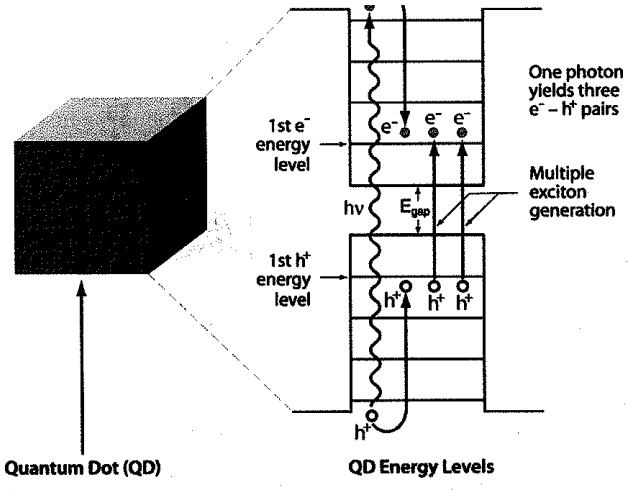
How to enhance conversion efficiency

- Shockley-Queisser analysis suggests 31% efficiency for a single p-n junction
- Enhancement possible by multiple p-n junction – limit of an infinite stack – ultimate efficiency at one sun increases above 66 %
- For practical purposes, stacks limited to 2 or 3 junctions yield 32% efficiency
- Other approach to go beyond Shockley-Queisser limit is to use quantum dots.

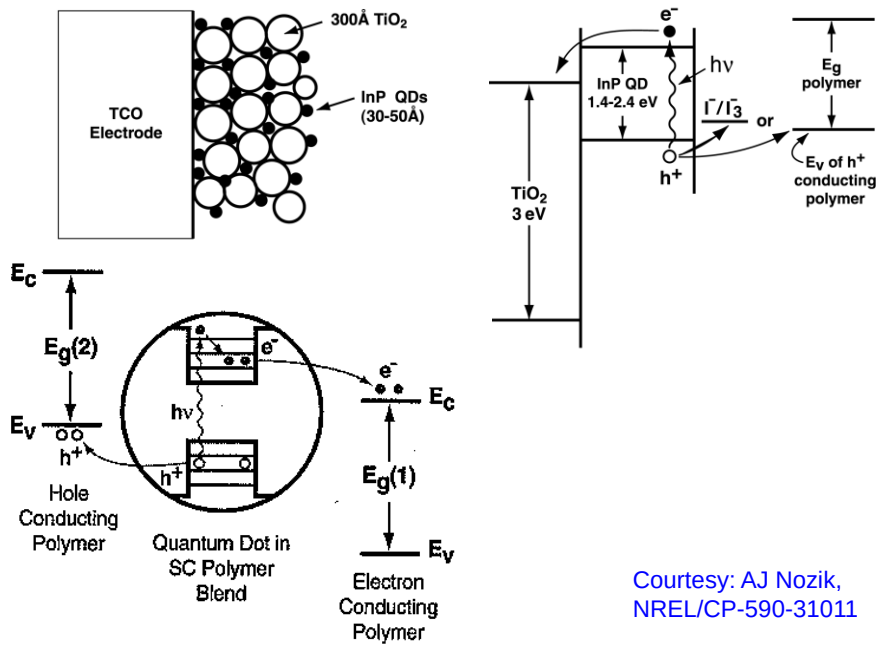
How to enhance the conversion efficiency

- Two fundamental ways to utilize hot-excitons:
- Enhanced photovoltage – where more carriers are extracted from the photoconverter before they cool
  - Rate of photogenerated carrier separation, transport and interfacial transfer across semiconductor interfaces – all must be fast compared to rate of carrier cooling
- Enhanced photocurrent – where the energetic hot carriers produce a second (or more) e-h pair through multiple exciton generation (MEG) - a process that is inverse of Auger process for recombination
  - Rate of exciton multiplication is greater than the rate of carrier cooling and forward Auger process of recombination

Enhanced PV efficiency in QD solar cells by MEG (inverse Auger effect)

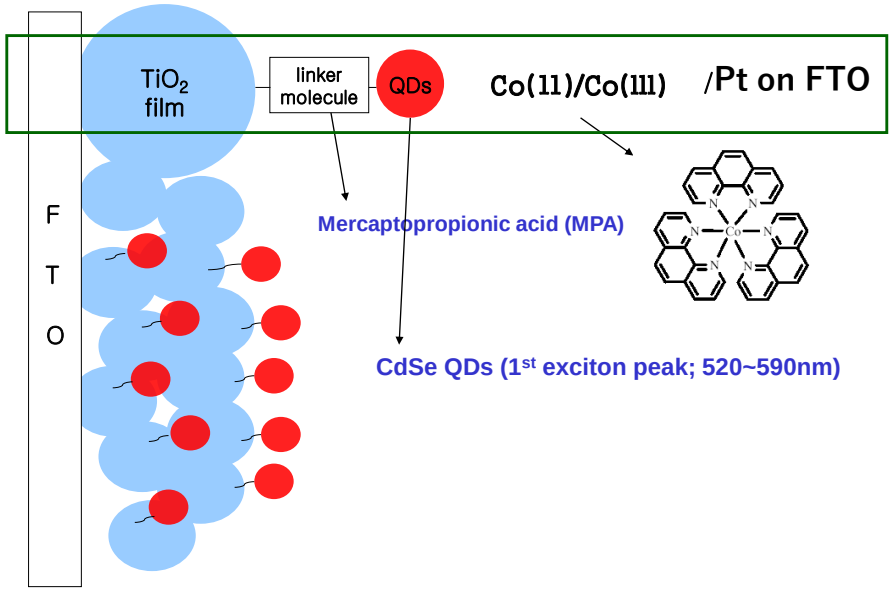


Quantum dot-sensitized nanocrystalline TiO_2 solar cells

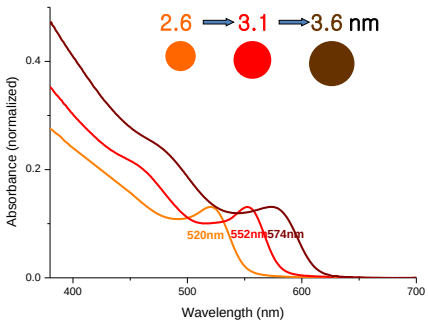


Courtesy: AJ Nozik, NREL/CP-590-31011

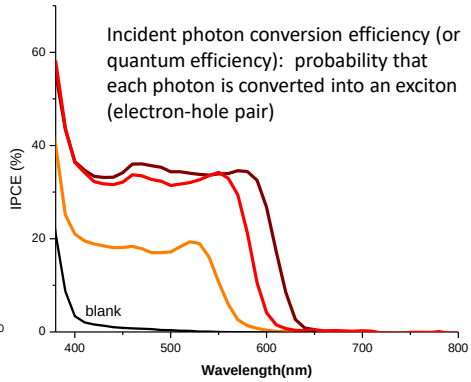
Schematic diagrams of QDs-sensitized solar cells



Absorption & IPCE spectra of different sizes of CdSe QDs

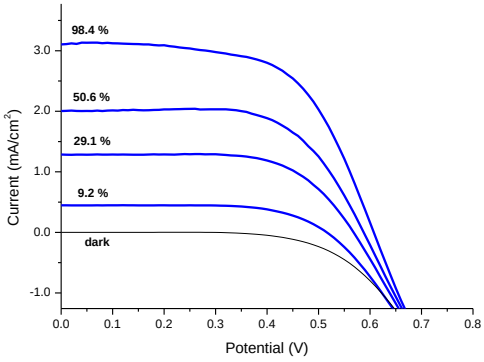


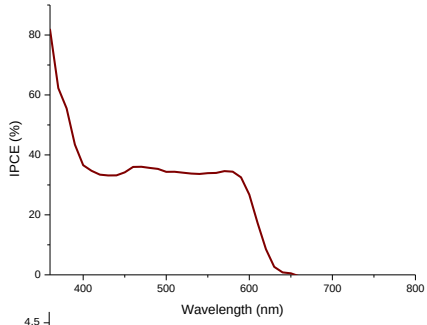
Incident photon conversion efficiency (or quantum efficiency): probability that each photon is converted into an exciton (electron-hole pair)



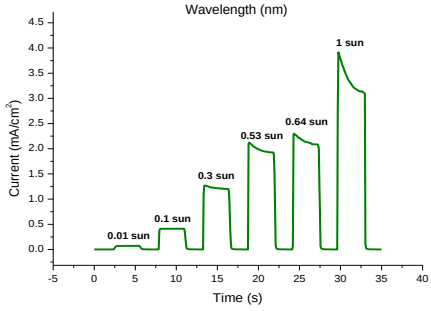
	I_{sc} (mA/cm²)	V_{oc} (V)	FF	Efficincy (%)
520 nm	1.87	0.66	0.65	0.80
552 nm	2.34	0.71	0.69	1.14
574 nm	3.15	0.61	0.61	1.17

Best results from CdSe (1st exciton peak, ~574nm) QDs-sensitized cell





Light-intensity dependency



	I_{sc} (mA/cm²)	V_{oc} (V)	FF	Efficincy (%)
9.2% sun	0.46	0.52	0.67	1.67
50.6% sun	2.10	0.59	0.65	1.50
98.4 % sun	3.15	0.61	0.61	1.17

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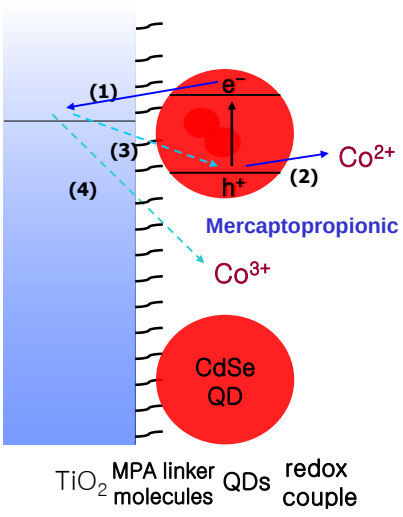
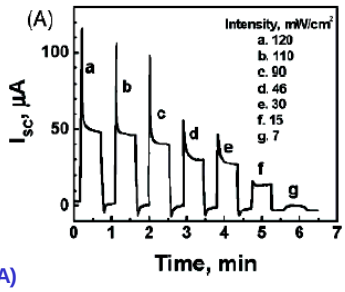
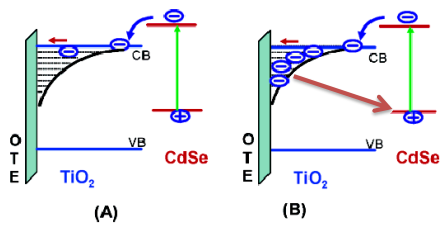
What is a limiting step in QDs-sensitized cells?



Mercaptopropionic acid (MPA)





Possible recombinations

Kamat et al. JACS (2006)

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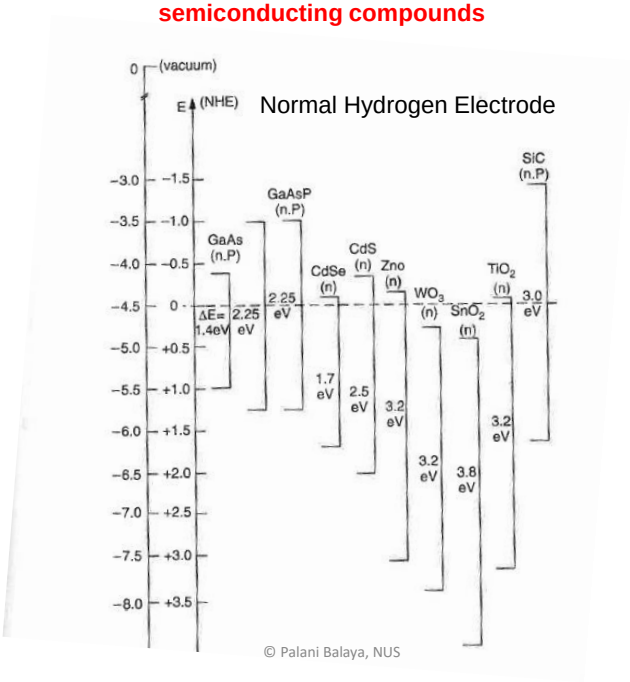
Energy levels of valance and conduction band edges of a few semiconducting compounds



- Dye-sensitized solar cells
- Perovskite solar cells
- Quantum dot solar cells