



SAN FRANCISCO BAY AREA
NANOTECHNOLOGY COUNCIL

June 16, 2009 Seminar

Nano-Solar cells: Solar Cells of the Future with Nanotechnology

Outline

1. Energy Research: Forefront and Challenges

Introduction – the energy challenge

Energy alternatives and the materials challenge

Think big, go small

2. Our Energy Future: Nano-Solar Cells



think it. apply it.
APPLIED MATERIALS.

Jeongwon Park, PhD.
Front End Product Group
Applied Materials

June 16, 2009



**Santa Clara
University**

Humanity's Top Ten Problems for next 100 years

1. **ENERGY**
2. WATER
3. FOOD
4. ENVIRONMENT
5. POVERTY
6. TERRORISM & WAR
7. DISEASE
8. EDUCATION
9. DEMOCRACY
10. POPULATION



2007	6.6	Billion People
2050	8-10	Billion People

<http://energysos.org/ricksmalley/top10problems/>

Source: Richard Smalley, Energy & Nanotechnology Conference, Houston.

Energy: A National Initiative

“Tonight I'm proposing \$1.2 billion in research funding so that America can lead the world in developing clean, hydrogen-powered automobiles... With a new national commitment, our scientists and engineers will overcome obstacles to taking these cars from laboratory to showroom, so that the first car driven by a child born today could be powered by hydrogen, and pollution-free.”

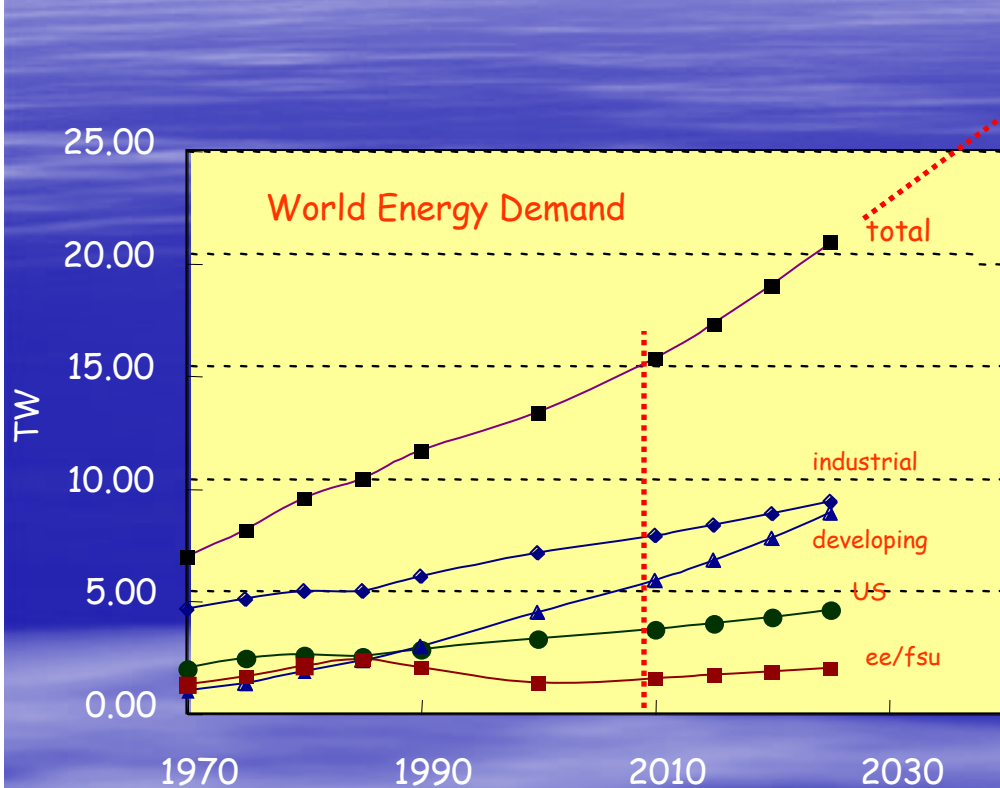
**President Bush, State-of the-Union Address,
January 28, 2003**

“To finally spark the creation of a clean energy economy, we will double the production of alternative energy in the next three years,”

**President Obama, George Mason University in Virginia,
January 8, 2009**



The World Energy Demand Challenge

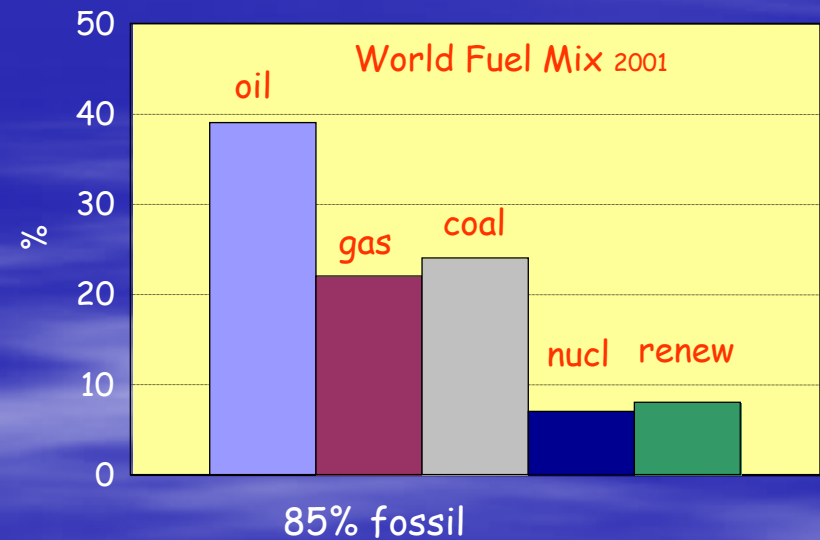


2100: 40-50 TW
 2050: 25-30 TW
 2000: 13 TW

energy gap
 ~ 14 TW by 2050
 ~ 33 TW by 2100

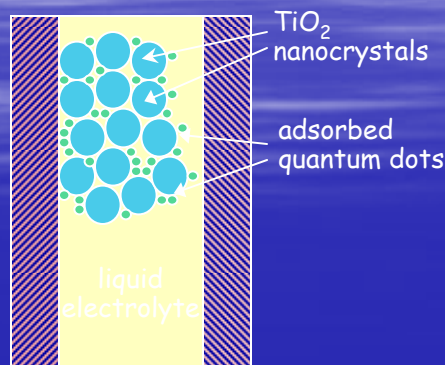
EIA Intl Energy Outlook 2004
<http://www.eia.doe.gov/oiaf/ieo/index.html>

Hoffert et al Nature 395, 883,1998

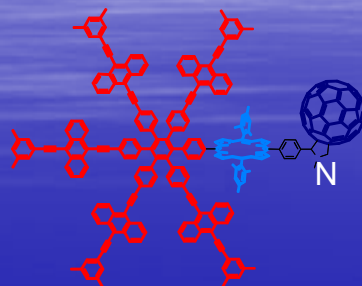


New Materials and Nanoscience will play a role

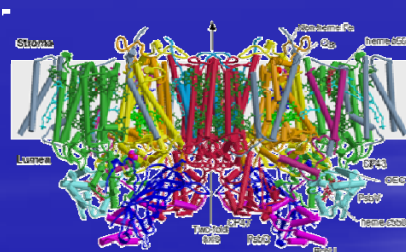
manipulation of photons, electrons, and molecules



quantum dot solar cells



artificial
photosynthesis



natural
photosynthesis



nanostructured
thermoelectrics

nanoscale architectures

top-down lithography
bottom-up self-assembly
multi-scale integration

characterization

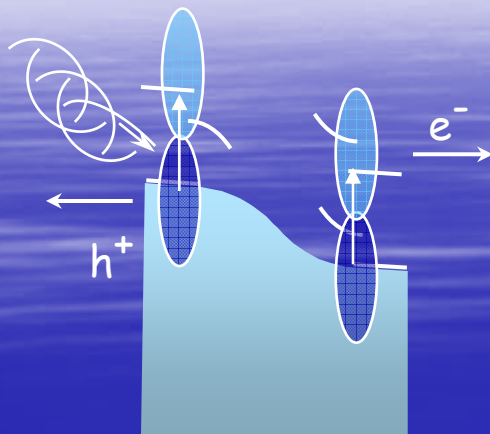
scanning probes
electrons, neutrons, x-rays
smaller length and time scales

theory and modeling

multi-node computer clusters
density functional theory
10 000 atom assemblies

Solar energy requires interdisciplinary nanoscience research

Solar Energy Utilization

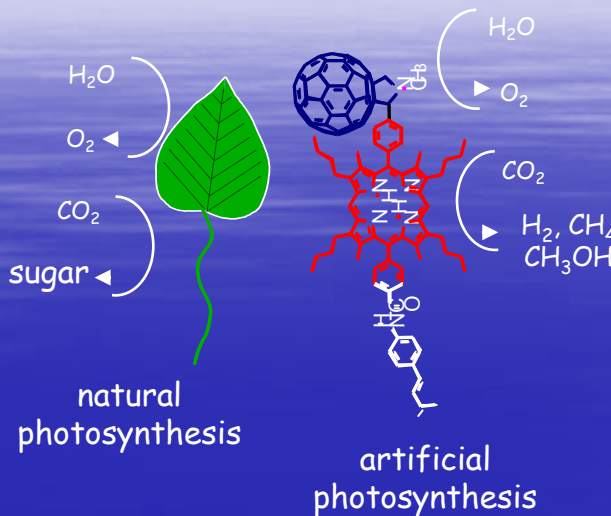


Solar Electric

.0002 TW PV (world)
 .00003 TW PV (US)
 \$0.30/kWh w/o storage



1.5 TW electricity (world)
 \$0.03-\$0.06/kWh (fossil)



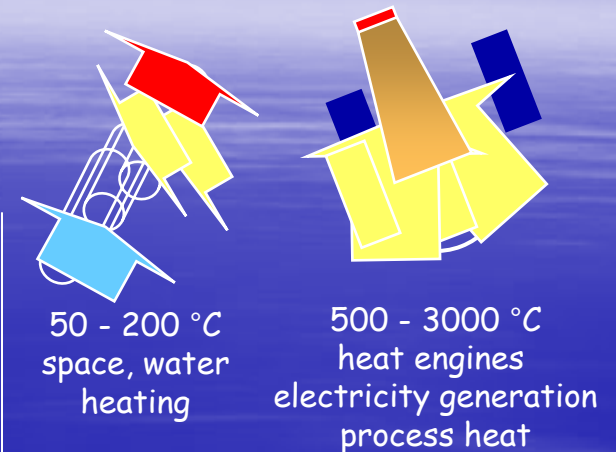
Solar Fuel

1.4 TW biomass (world)
 0.2 TW biomass sustainable (world)



11 TW fossil fuel
 (present use)

~ 14 TW additional energy by 2050



Solar Thermal

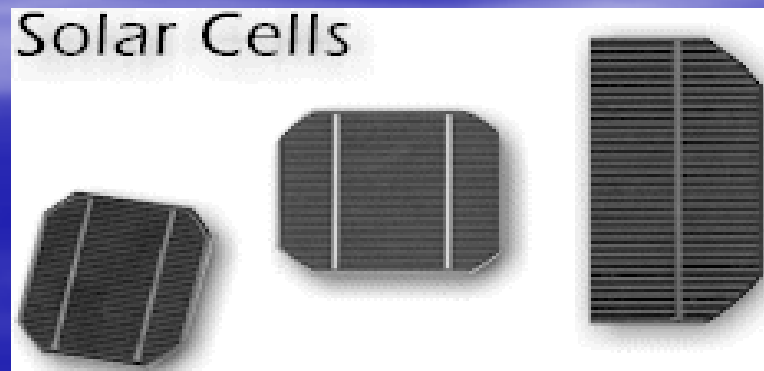
0.006 TW (world)



2 TW
space and water
heating (world)

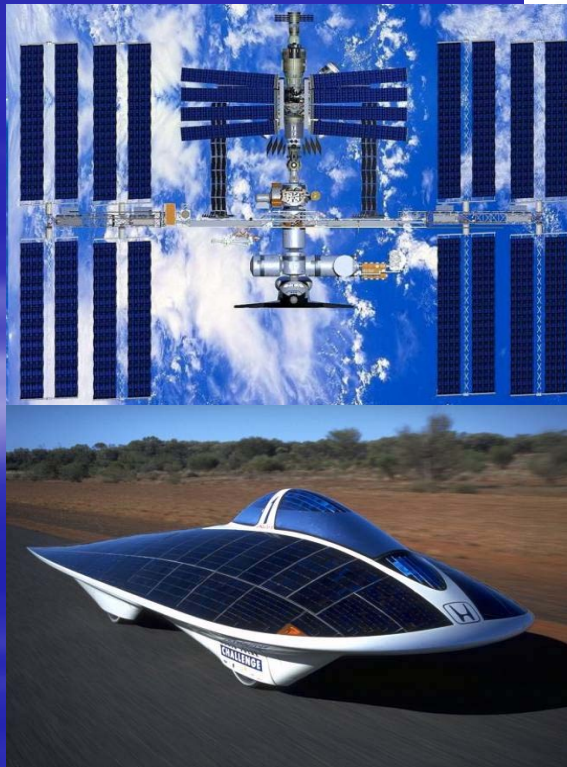
What is a Solar Cell?

- It is also known as Photovoltaic cell (PV cell)
- A device that converts light energy (solar energy) directly to electricity.
- The term solar cell is designated to capture energy from sunlight, whereas PV cell is referred to an unspecified light source.
- It is like a battery because it supplies DC power.
- It is not like a battery because the voltage supplied by the cell changes with changes in the resistance of the load.

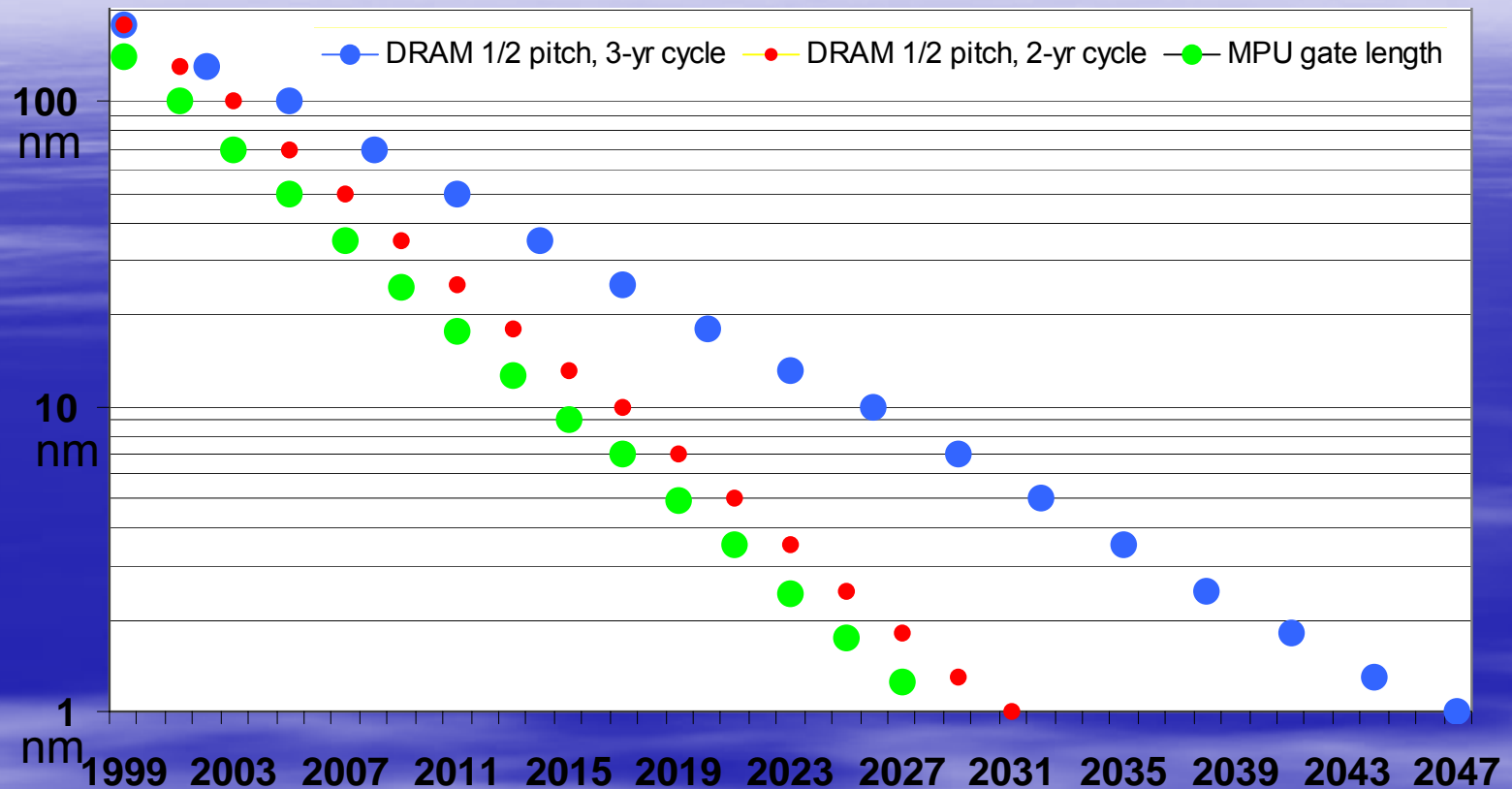


Applications of Solar Cells

- Renewable energy
- Can be powered for remote locations
- It's free, limitless, and environmentally friendly...
- Toys, watches, calculators
- Electric fences
- Remote lighting systems
- Water pumping
- Water treatment
- Emergency power
- Portable power supplies
- Satellites



Moore's Law for semiconductor electronics soon, all microchips will be nanoscale devices

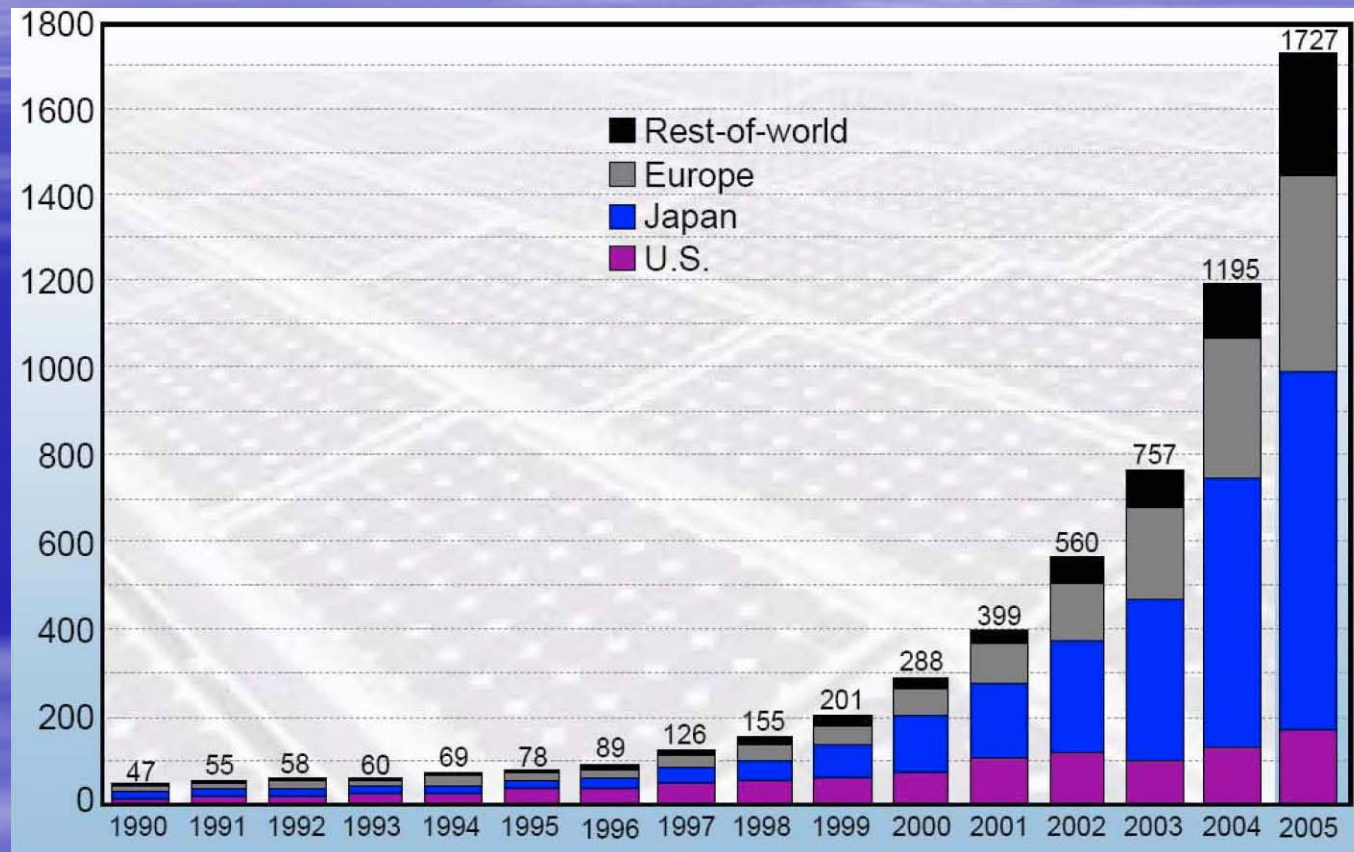


CONCLUSION: Moore's law continues for this decade regarding future size, device performance and cost for semiconductor electronics industry.

We now need to apply Moore's law to set goals for the energy industry.

Example of Moore's law

World PV Cell Production (MW)

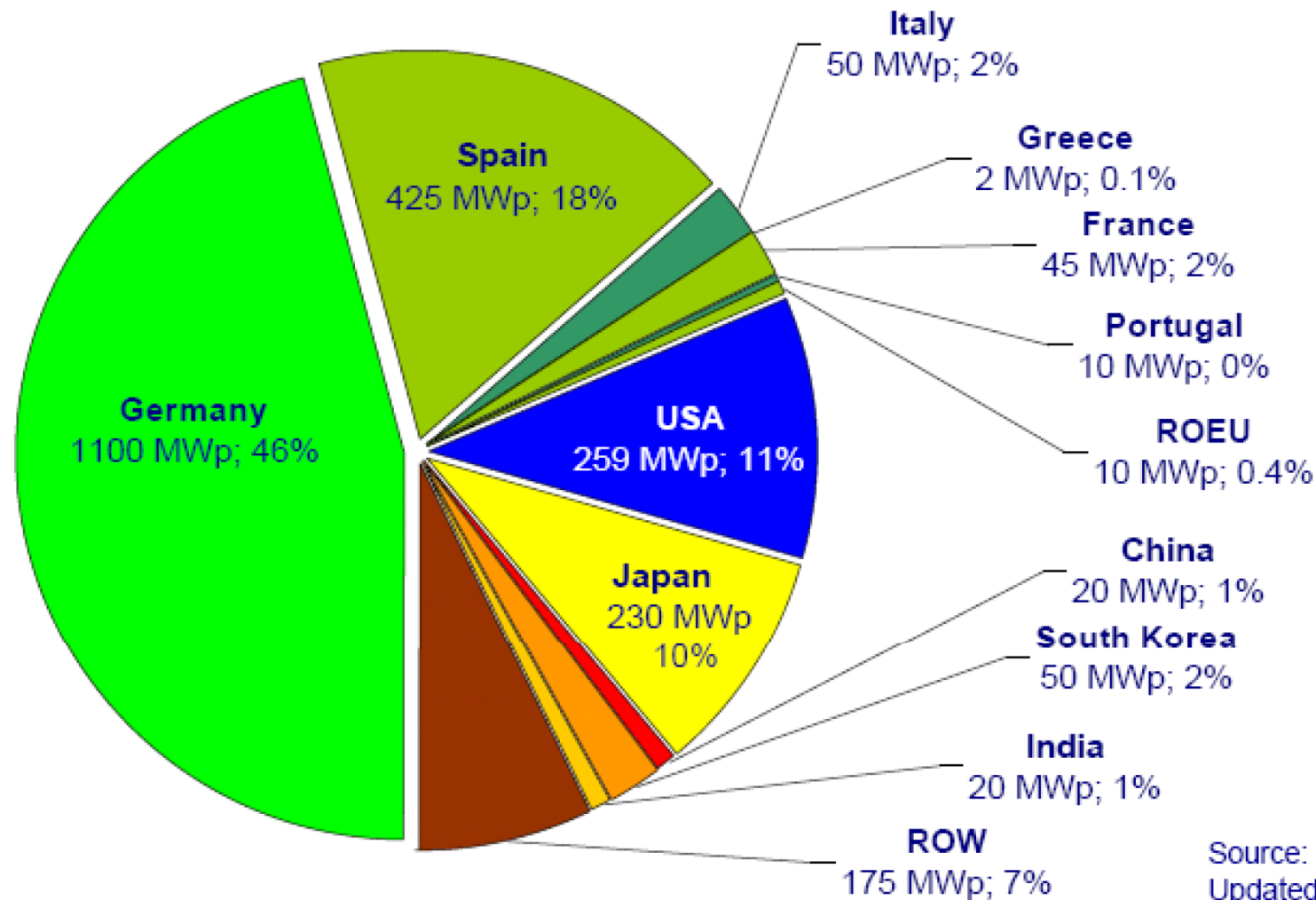


Annual Growth > 30% For the Last Decade

Source: Paul Maycock, PV News, March 2006

Global Solar markets

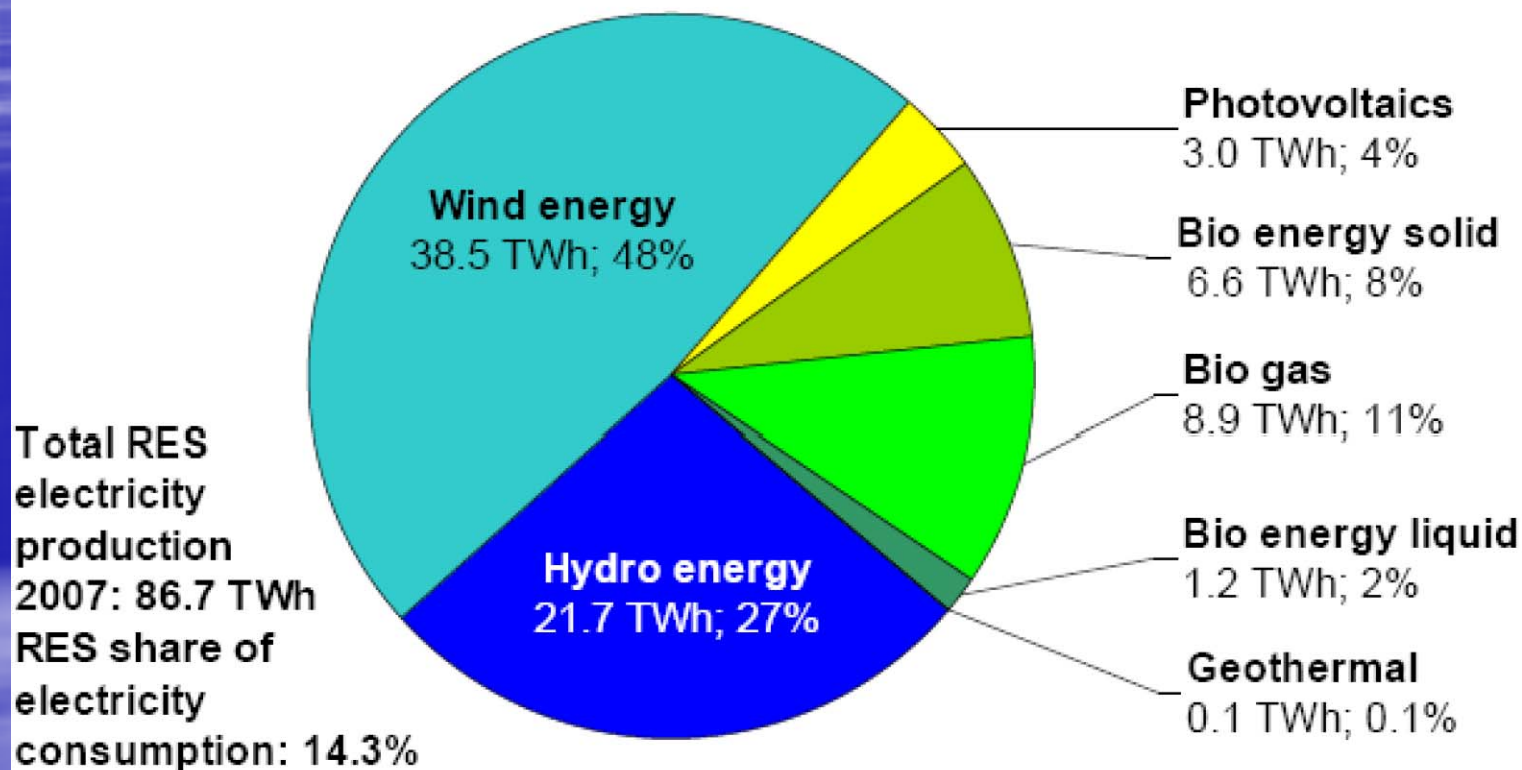
Newly installed PV Power in 2007: 2.4 GWp



Source: EPIA, ASIF, BSW
Updated February 2008

Reduction of environmental impact

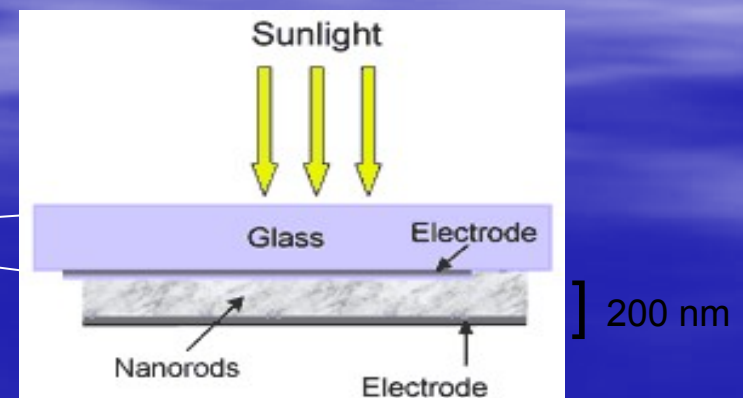
Distribution of Renewable Energy Electricity Production in Germany 2007



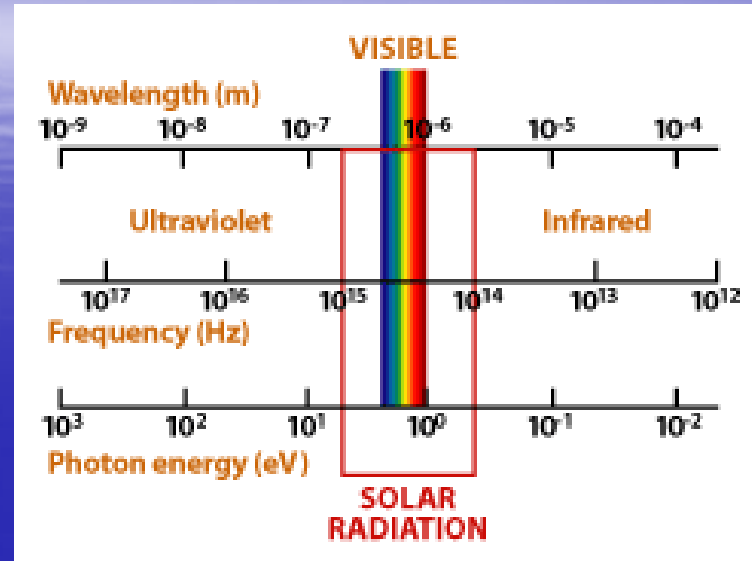
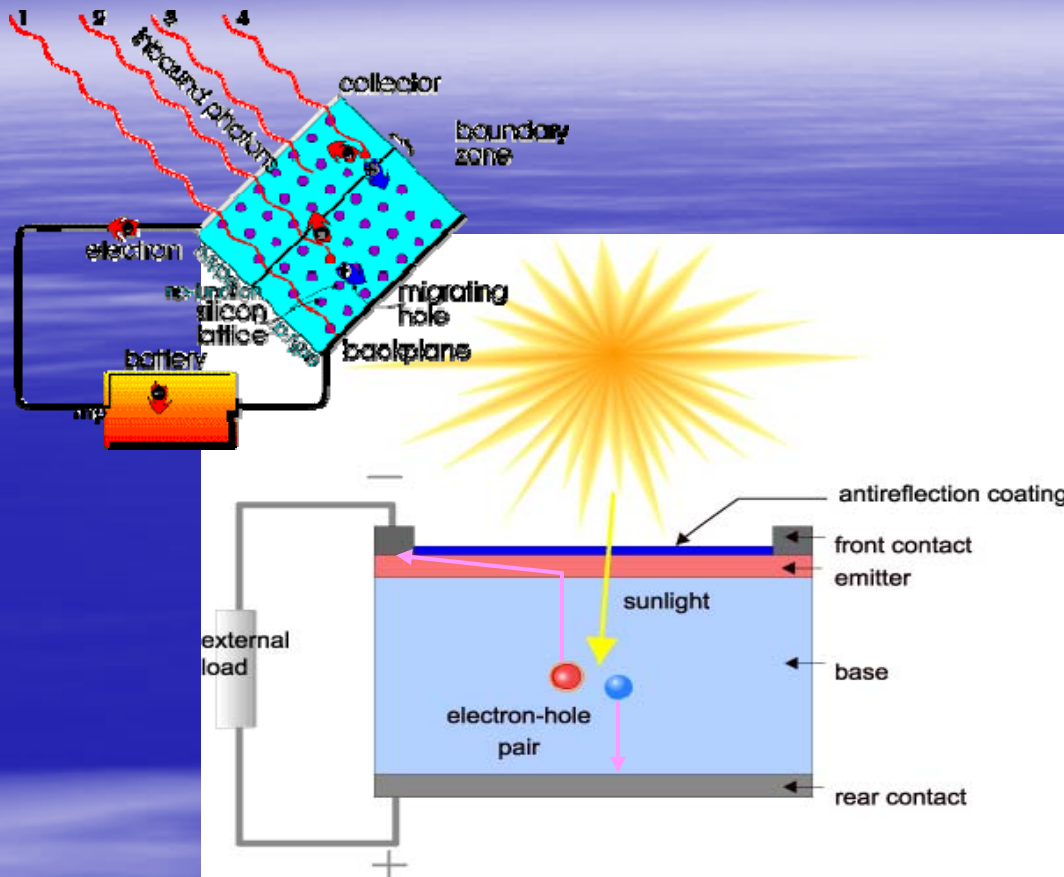
Source: BEE, Jan 2008

Choice of solar technologies:

- Crystalline silicon
- Amorphous silicon
- Cadmium telluride
- Copper indium diselenide CIS family, notably copper indium gallium diselenide CIGS
- Dye sensitised solar cells DSSC
- Organic – polymer or small molecule
- Nano solar cell: silicon nanoparticle ink, carbon nanotube CNT and quantum dots, nanowires
- Inorganic nanorods embedded in semiconducting polymer, sandwiched between two electrodes



How Solar Cells Work: Photovoltaic Effect



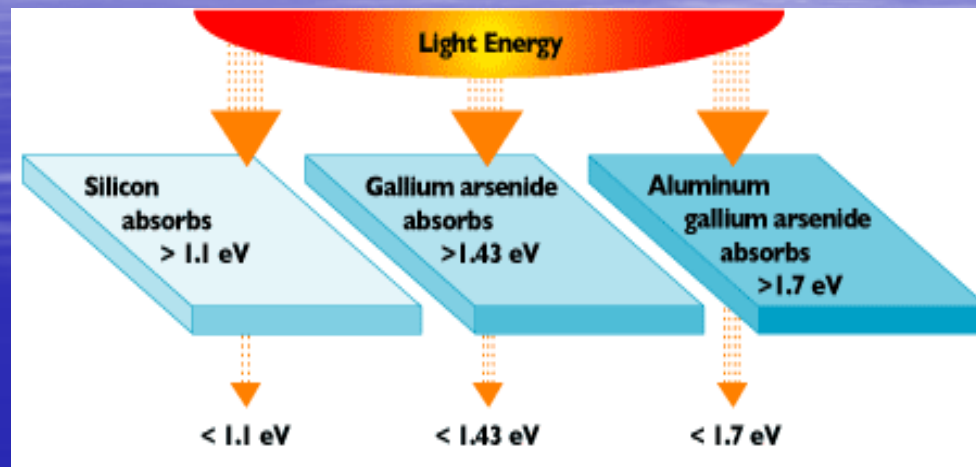
Entire spectrum of sunlight : 0.5 eV ~ 2.9 eV
(Red light : 1.7 eV , Blue light : 2.7 eV)

We need to consider:

- Photon excites valence electron
- Electron-hole pair created
- Electrons & holes “separate”
- Band gap determines what is absorbed

1. Energy source
2. Absorption
3. Transport
4. Collection

How it works

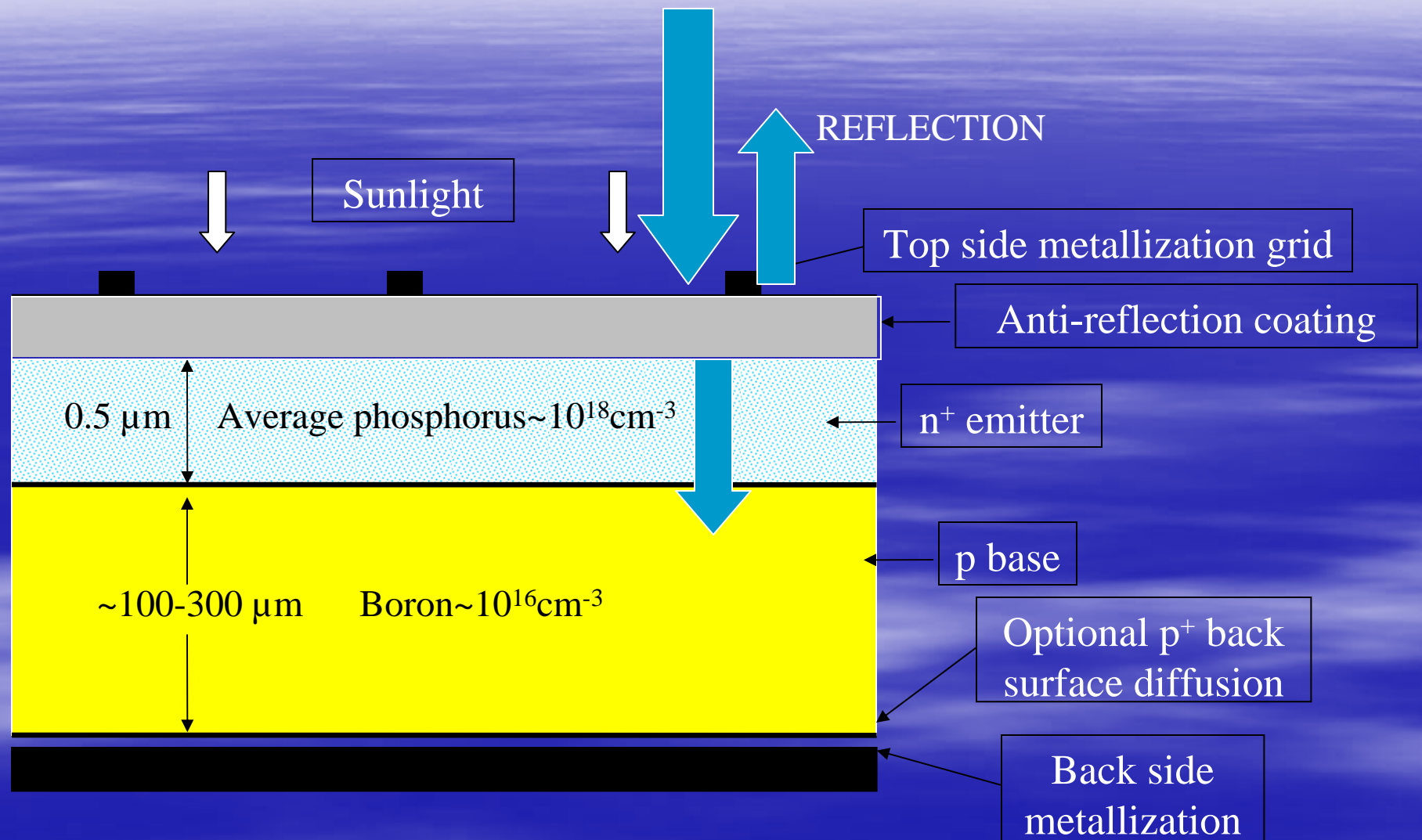


To free an electron, the energy of a photon must be at least as great as the bandgap energy.

$E_{\text{photon}} \geq E_{\text{band gap}}$: absorb to create free electrons.
 $E_{\text{photon}} < E_{\text{band gap}}$: pass through the material.

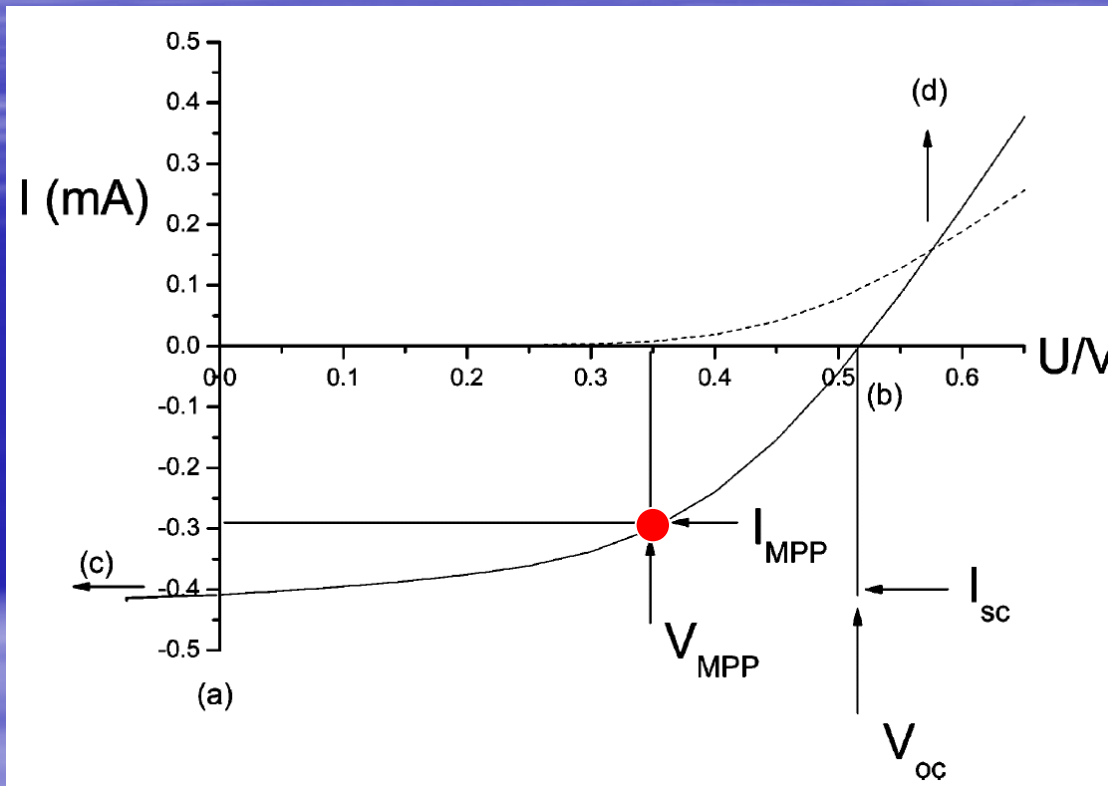
$E_{\text{band gap}}$ of other effective PV semiconductors ranges from 1.0 to 1.6 eV.
In this range, electrons can be freed without creating extra heat.

Typical P-N Junction Silicon Solar Cell Structure



Characterization of a Solar Cell Device

Photovoltaic power conversion efficiency of a solar cell



$$\eta_e = \frac{V_{oc} * I_{sc} * FF}{P_{in}}$$

$$FF = \frac{I_{mpp} * V_{mpp}}{I_{sc} * V_{oc}}$$

Current-voltage (I - V) curves of an organic solar cell (dark, - - -; illuminated, -). The characteristic intersections with the abscissa and ordinate are the open circuit voltage (V_{oc}) and the short circuit current (I_{sc}), respectively. The largest power output (P_{max}) is determined by the point where the product of voltage and current is maximized. Division of P_{max} by the product of I_{sc} and V_{oc} yields the fill factor FF . P_{in} is the incident light power density.

Generation photovoltaic

- 1st: Consists of a large-area, single layer p-n junction diode, which is capable of generating usable electrical energy from light sources with the wavelengths of sunlight. These cells are typically made using a silicon wafer.
- 2nd: Based on the use of thin-film deposits of semiconductors. These devices were initially designed to be high-efficiency, multiple junction photovoltaic cells.
- 3rd: Very different from the previous semiconductor devices as they do not rely on a traditional p-n junction to separate photogenerated charge carriers. These new devices include photoelectrochemical cells, polymer solar cells, and nanocrystal solar cells. Dye-sensitized solar cells are now in production. Examples include Amorphous silicon, Polycrystalline silicon, micro-crystalline silicon, Cadmium telluride, copper indium selenide/sulfide.
- 4th: Composite photovoltaic technology with the use of polymers with nano particles can be mixed together to make a single multispectrum layer. Then the thin multi spectrum layers can be stacked to make multispectrum solar cells more efficient and cheaper based on polymer solar cell and multi junction technology used by NASA on Mars missions.

Comparison of thin film solar cells

Type	Benefit or intended benefit	Efficiency	Challenges	Companies
a-Si	Thin Film, Flexible substrates	8-10%	Constant degradation	Innovalight
	Potential for roll to roll processing		low efficiency	United Solar
	unavailable for mono- or poly-Si.		Not tightly rollable	Mitsubishi
NanoSi	As above with high efficiency	High?		Kovio
CdTe	Fairly high efficiency	9-11%	Cd is toxic	First Solar
	Well proven		Controlled disposal only	Calyxo
	Over \$1 billion of orders		Not tightly rollable	
	Lowest cost/watt over life			
CIGS	High efficiency at low cost	10-14%	Price of indium.	HONDA
	long life		New process/	Global Solar
	transparent		stability	Wurth
	no disposal problems, printable			Nanosolar
DSSC	Tolerant of polarised/	11%	Liquids handling	G24i UK
	low level light-can use heat		Price of ruthenium?	Dyesol
	extreme angle of incoming light		5 year life?	Sony
	Transparent/colors, tightly rollable			
	No disposal problems, printable			
Organic	Potential for lowest cost ?	2-6%	Cost	Konarka
	Large area possible		Efficiency	Plextronics
	Tightly rollable		1 year life?	Heliatek
	No disposal problems,		Narrow spectrum	
	Spray directly onto things?			

Thin Film PV Technologies

➤ nanoparticle Si



➤ CIGS/CIS



➤ CdTe



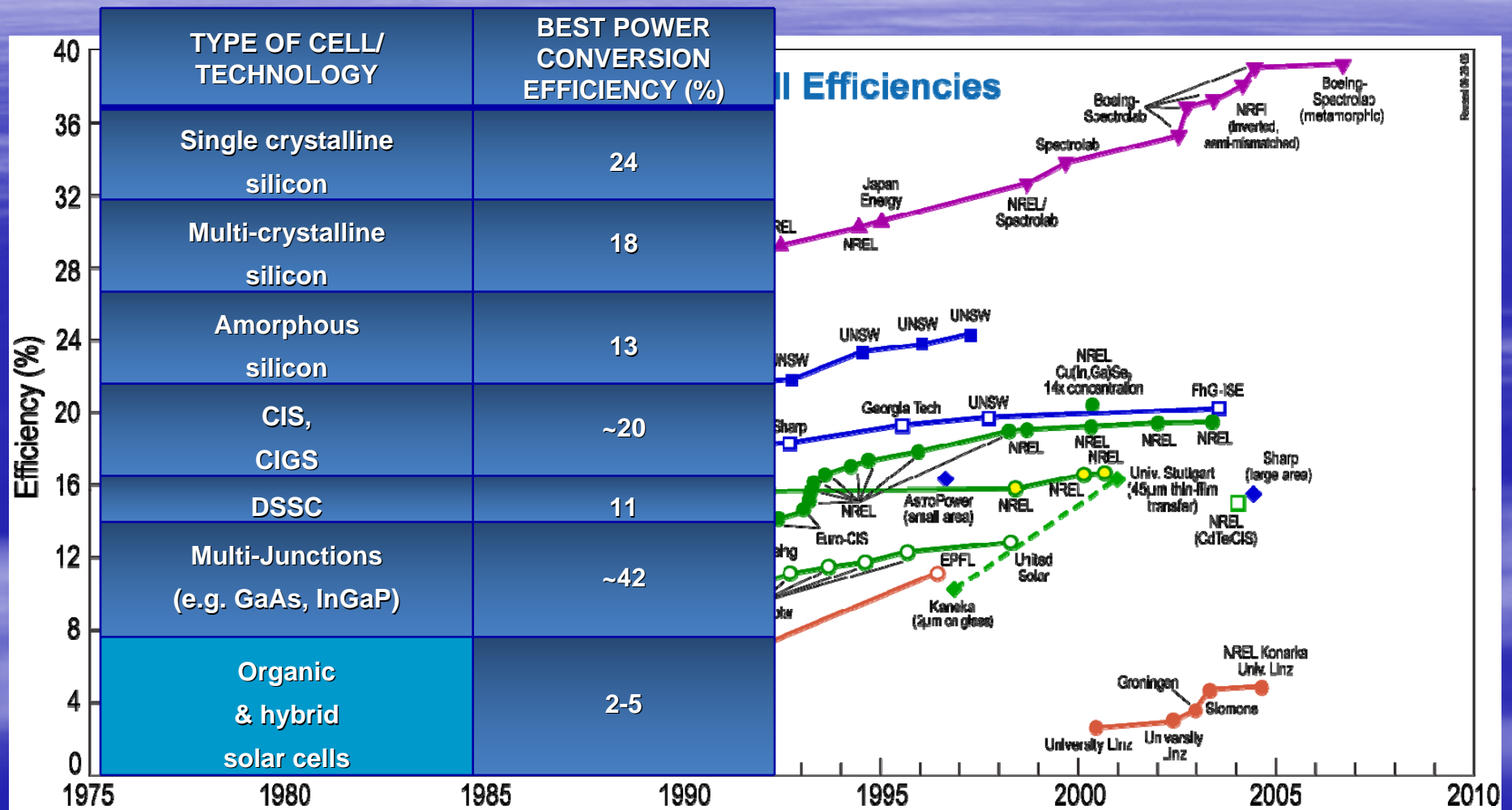
➤ DSSC's



➤ Organic PV



Best Cell Efficiencies

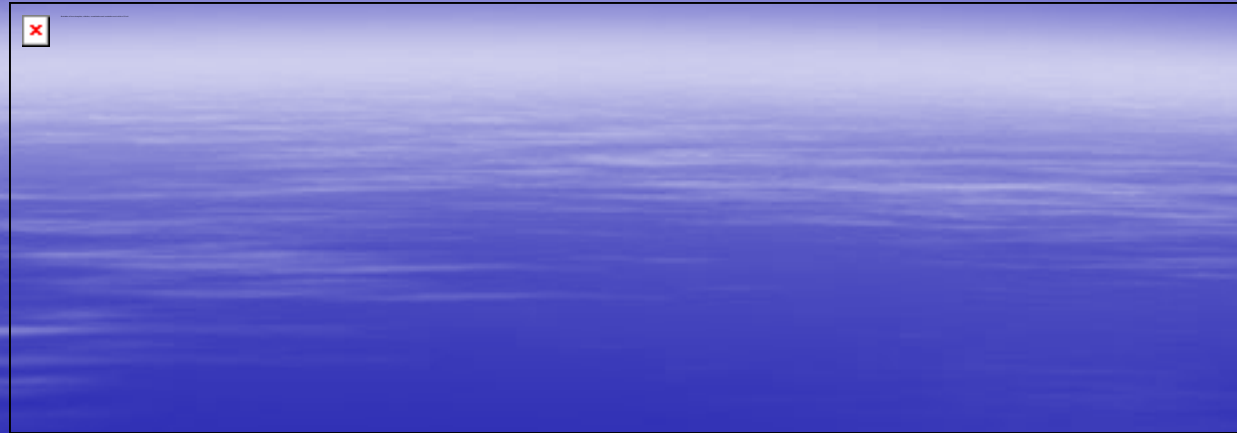
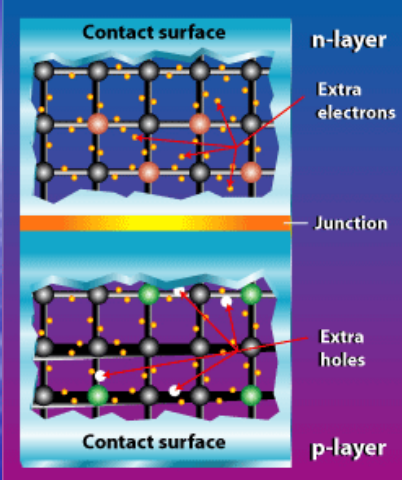


Current Obstacles

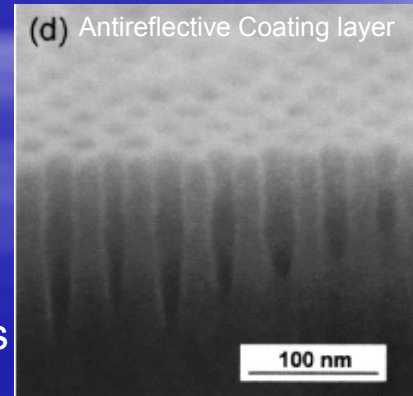
Efficiency vs. cost

- Solar cell efficiencies vary from 6% for amorphous silicon-based solar cells to 42.8% with multiple-junction research lab cells.
- Solar cell energy conversion efficiencies for commercially available *multicrystalline Si* solar cells are around 14-16%.
- The highest efficiency cells have not always been the most economical — for example a **30% efficient multijunction cell** based on exotic materials such as gallium arsenide or indium selenide and produced in low volume might well **cost one hundred times** as much as an **8% efficient** amorphous silicon cell in mass production, while only delivering about four times the electrical power.

To Make an Efficient Solar Cell,



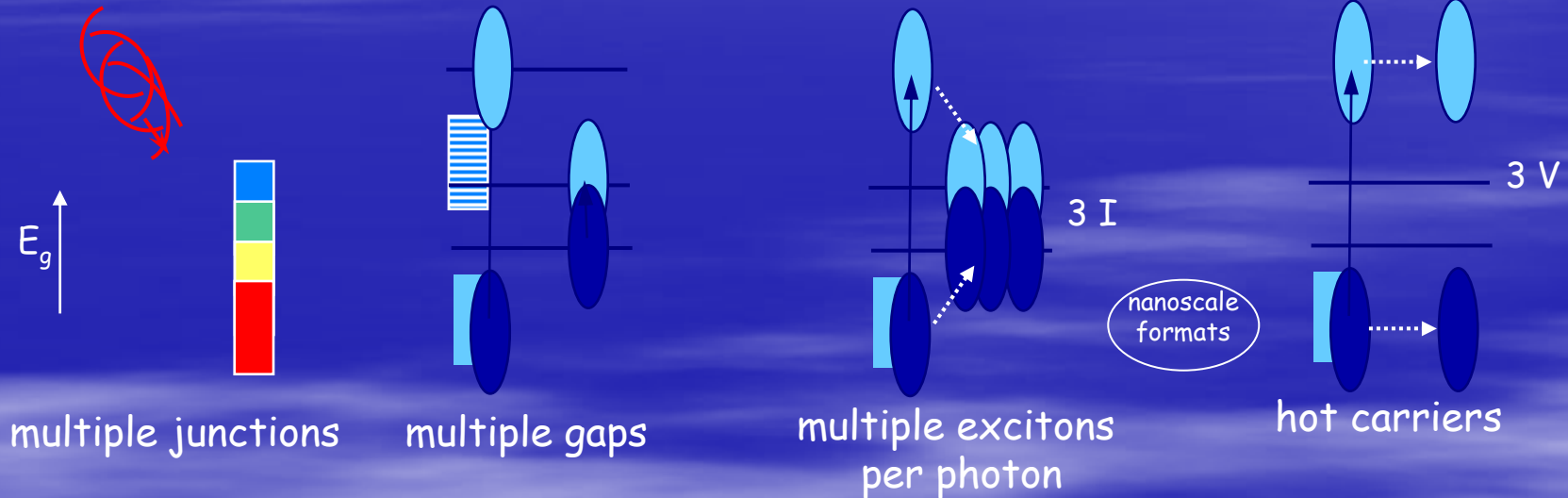
- Tune the p-layer to the properties of incoming photons to absorb as many as possible, and thus, to free up as many electrons as possible.
- Keep the electrons from meeting up with holes and recombining with them before they can escape from the PV cell.
- One designs the material to free the electrons as close to the junction as possible, so that the electric field can help send the free electrons through the conduction layer (the n-layer) and out into the electrical circuit.
- Antireflective Coating
 - ☞ Silicon reflects more than 30% of the light that shines on it.
 - ☞ To improve the conversion efficiency of a solar cell:
 1. Coat the top surface with a thin layer of silicon monoxide (SiO_2).
a single layer : 10% ; a second layer : less than 4%
 2. Texture the top surface: cones and pyramids which capture light rays



Revolutionary Photovoltaics: 50% Efficient Solar Cells

present technology: 32% limit for

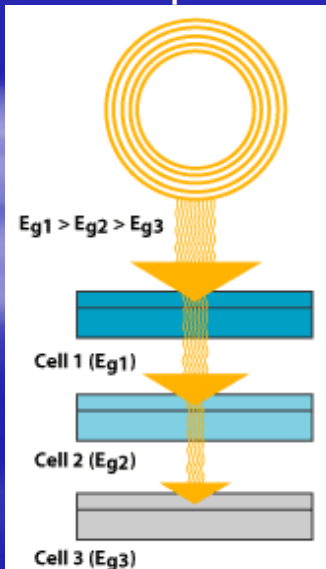
- single junction
- one exciton per photon
- relaxation to band edge



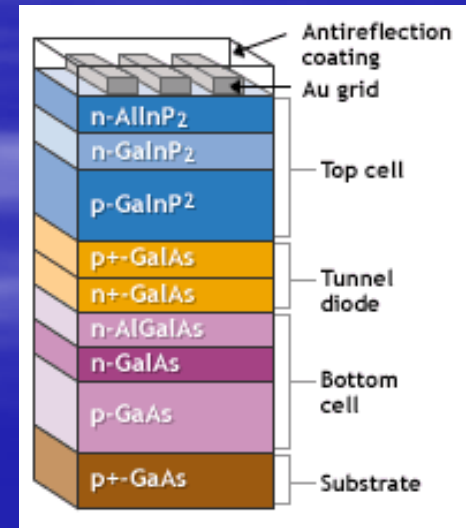
rich variety of new physical phenomena
challenge: understand and implement

Thin Film Solar Cell Junction Structures

- Homo junction : p-n junction of crystalline silicon
- Hetero junction : formed by contacting two different semiconductors—CdS and CuInSe₂
- p-i-n / n-i-p : typically, amorphous silicon thin-film cells use a p-i-n structure, whereas CdTe cells use an n-i-p structure.
- Multi junction : also called a cascade or tandem cell, can achieve a higher total conversion efficiency by capturing a larger portion of the solar spectrum

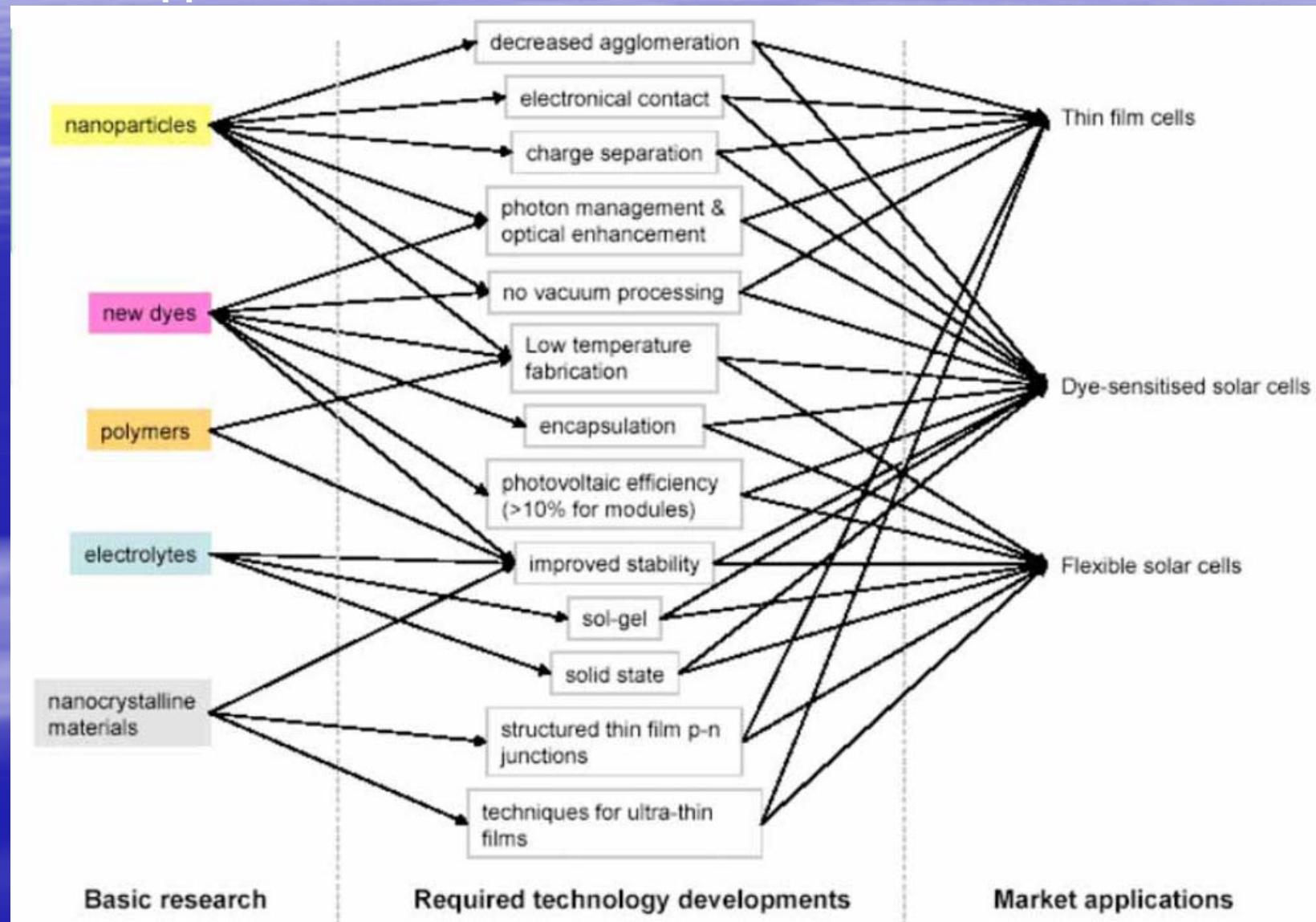


- A multijunction device is a stack of individual single-junction cells in descending order of bandgap (E_g).
- The top cell captures the high-energy photons and passes the rest of the photons on to be absorbed by lower-bandgap cells.



Prospects for Nano-enhanced Solar Cells (Ying Guo)

Basic research underway with the technology developments required to achieve the desired applications.





Solar Cells based on Nanotechnology:

Organic and Hybrid cells

Nano-crystalline TiO_2 Film: Dye-Sensitized Solar Cell (DSSC)

Quantum dot solar cells

Nanowire solar cells

Organic and hybrid solar cells

Why organic solar cells ?

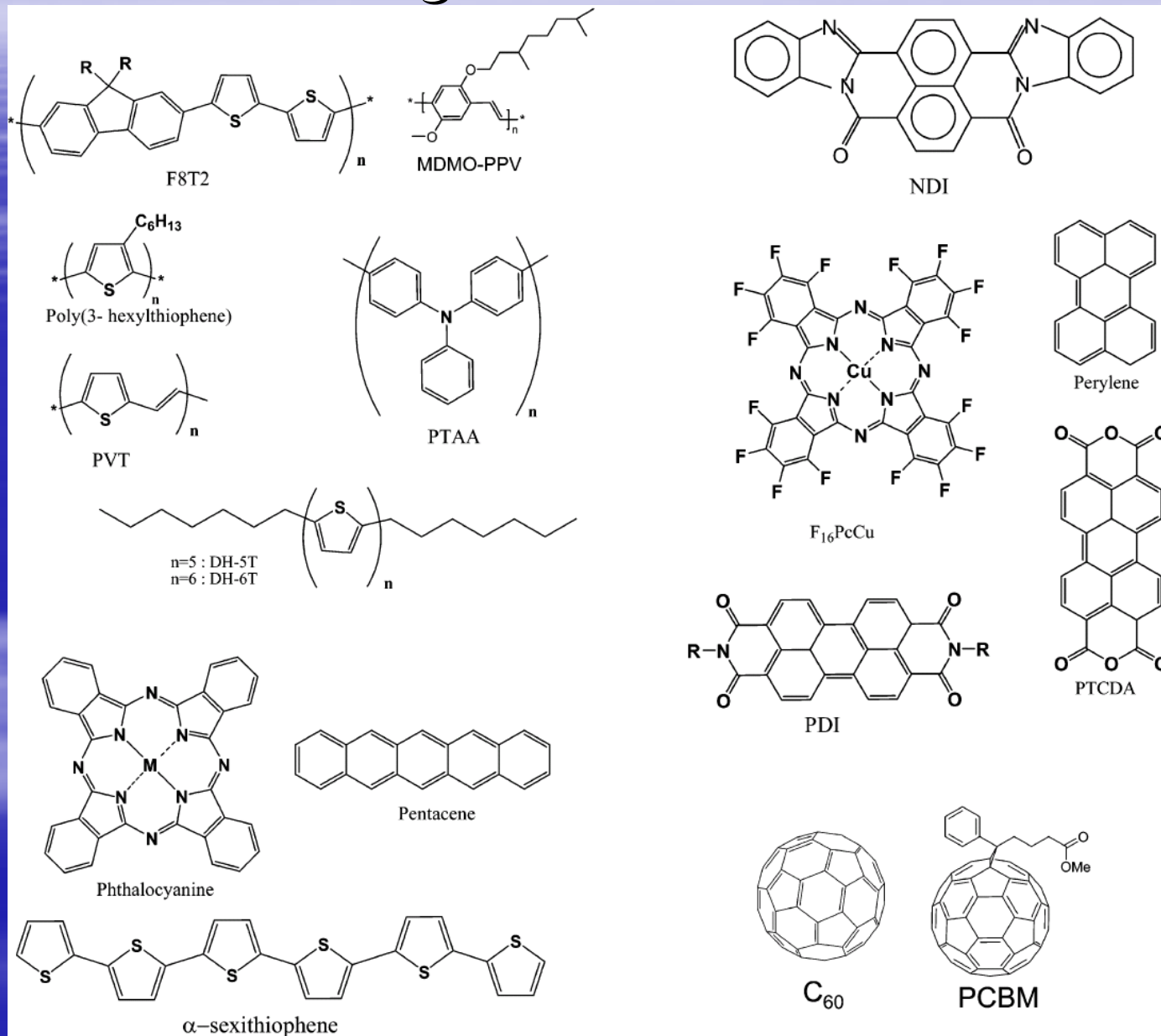
ADVANTAGES

- Easier and cheaper fabrication processes: non-vacuum, low temperature, available at industrial scale.
- Low cost materials (?), low quantity (g/m^2), flexible and cheap substrates (no glass).
- High EQE over the whole sun spectrum.
- High light absorption (100nm are enough to absorb most of the light)

DISADVANTAGES

- Lower carrier mobility than in inorganic semiconductors.
- New devices, a lot of work for optimising morphology and composition.

Examples of organic semiconductors used in organic solar cells



Harald Hoppe, *et al*, J. Mater. Res., **19**, 1924-1945, (2004)

Organic Hetero-Junction Cell

- The first cells were built in the 50' (organic dyes with inorganic semiconductors).
- First organic cells had very low efficiency: $10^{-2}/10^{-3}$ %.
- Due to the very short diffusion length for excitons (about 10nm), only the charges very close to the junction could be efficiently separated and collected by the electrodes.

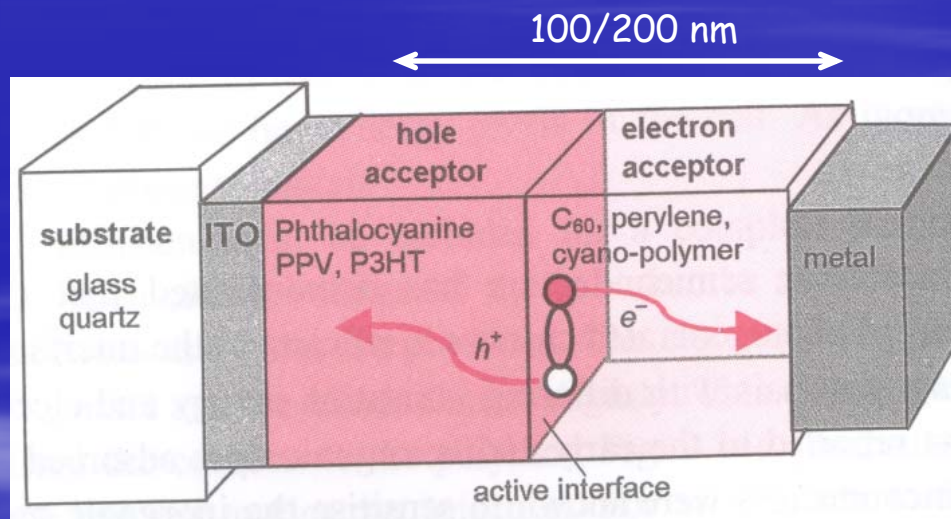
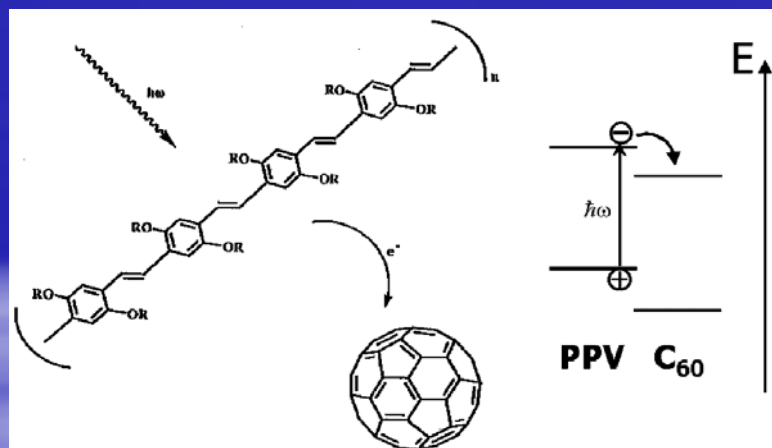
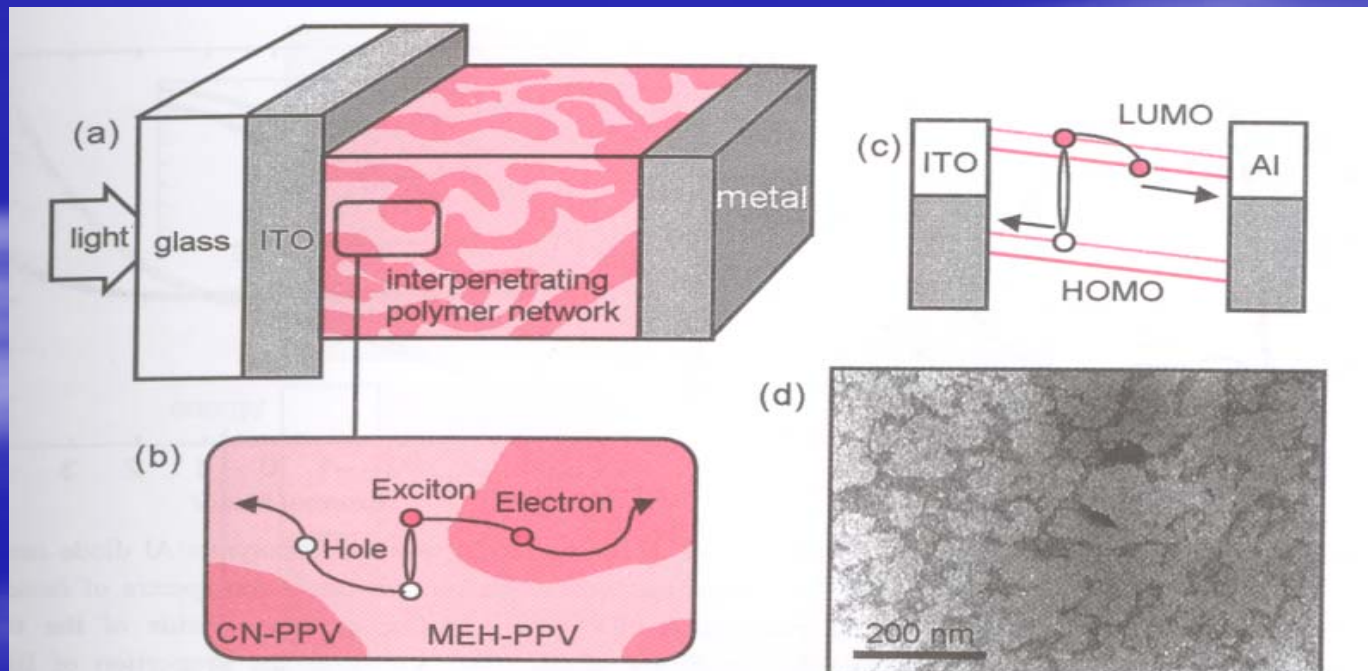


Illustration of the photoinduced charge transfer with a sketch of the energy level. After excitation in the PPV polymer, the electron is transferred to the C₆₀

The Bulk Hetero-Junction

- A composite of two organic semiconductor (n and p) sandwiched between two electrodes with work function matching the energy bands of the composite.
- It can be seen as nanoscale p-n junctions.
- The density of p-n junctions is much higher than in bilayer cells.
- Much larger interfacial area, where charges can be separated.
- Efficiency increased of 2-3 order of magnitude reaching 1%.
- Separate conduction path for electron and holes (like in DSC).



Organic cells can be a cheap alternative to inorganic semiconductor cells: low cost material, cheap fabrication process, good spectral response.

What has to be done?

- Optimising the morphology is the key for better efficiencies.
- Two competing goals: good mixing, partial ordering.

Hybrid cells

BHJ with organic/inorganic semiconductors

ex. P3OT:CdTe, P3HT:CdSe, CuPC:Si, P3HT:TiO₂, P3HT:CIS

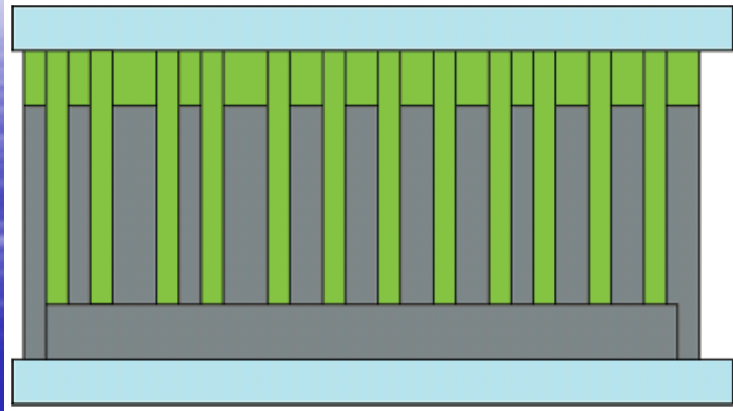
Maximum reported eff. is 2%

ADVANTAGES

Inorganic semiconductors have much higher carrier mobility.

Inorganic semiconductor can be produced in the form of nanocrystal in order to control the ordering of the microstructure

Ideal structure of a bulk heterojunction solar cell



Interspaced with an average length scale:
 $10\text{-}20\text{ nm} \leq \text{Exciton diffusion length}$

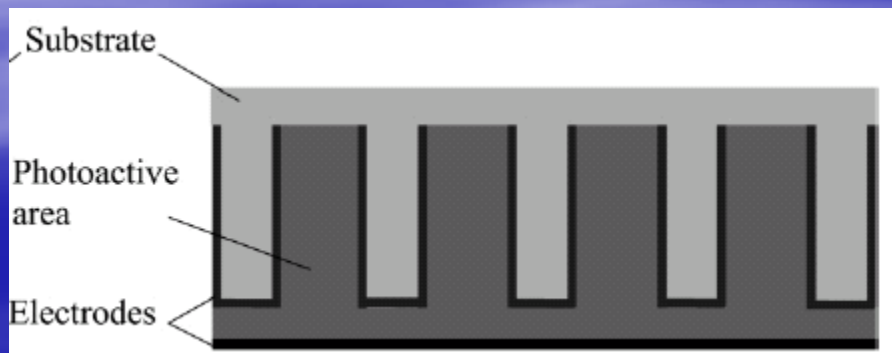
The two phases have to be interdigitated in percolated highways to ensure high mobility charge carrier transport with reduced recombination.

Buried Nanoelectrodes

Diffraction gratings and buried nano-electrodes—architectures for organic solar cells

M.Niggemann, M.Glatthaar, A.Gombert, A.Hinsch, V.Wittwer*

Thin Solid Films **451–452** (2004) 619–623



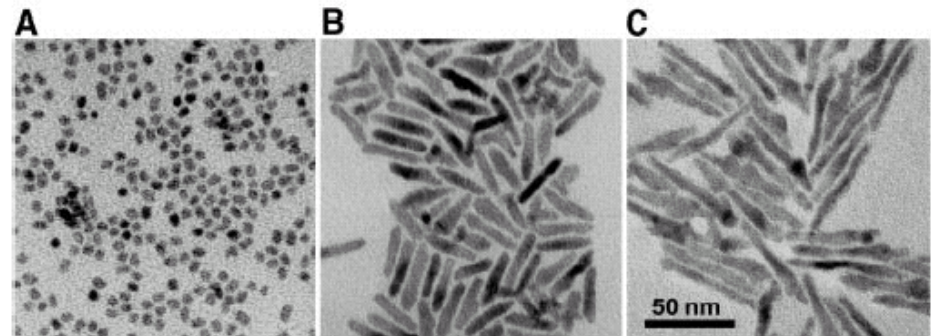
Separate the absorption process from the charge transport in case of different mobility for holes and e^- in the blend

Hybrid cells

Hybrid Nanorod-Polymer Solar Cells

Wendy U. Huynh, Janke J. Dittmer, A. Paul Alivisatos
Science **295** p.2425 (2002)

Fig. 2. Cadmium selenide nanocrystals with aspect ratios ranging from 1 to 10. The samples, shown by transmission electron micrographs (TEMs) at the same scale, have dimensions (A) 7 nm by 7 nm, (B) 7 nm by 30 nm, and (C) 7 nm by 60 nm.



Hybrid solar cells with vertically aligned CdTe nanorods and a conjugated polymer

Yoonmook Kang, Nam-Gyu Park, and Donghwan Kimb
Applied Physics Letters **86**, 113101 (2005)

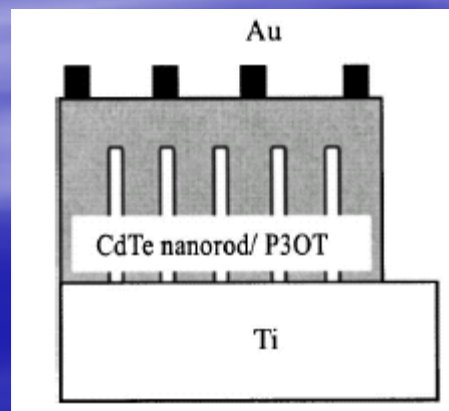
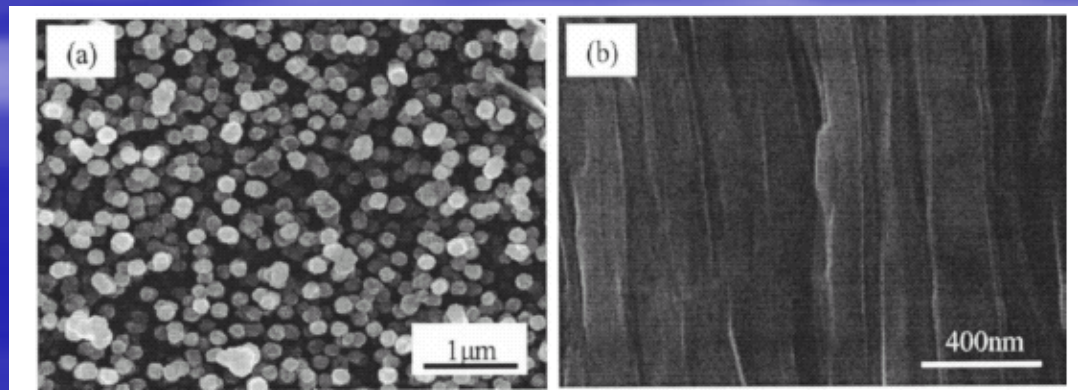
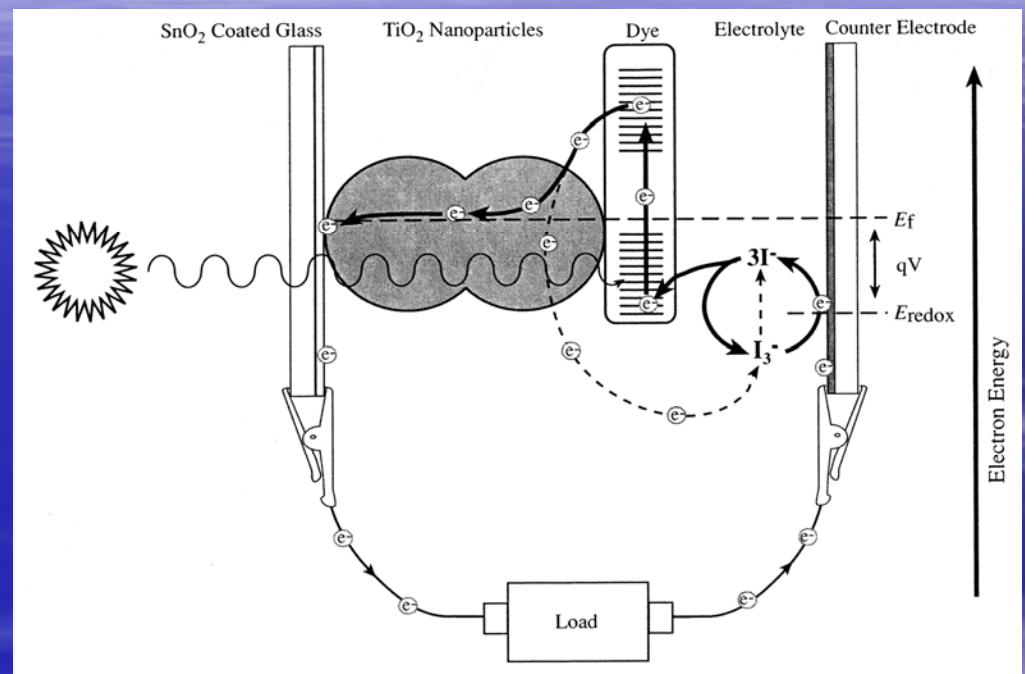
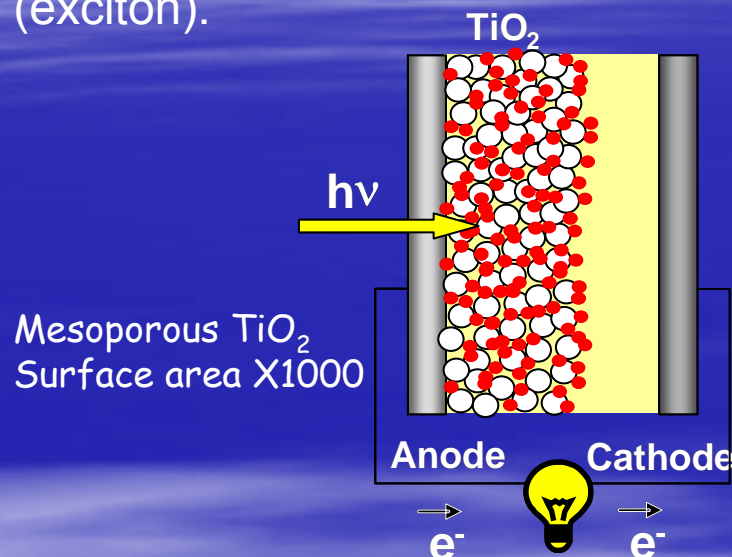


FIG. 2. Scanning electron microscopy images: (a) the top view of the vertical aligned CdTe nanorods; (b) the cross section of the composite layer.



Nano-crystalline TiO₂ Film Dye-Sensitized Solar Cell (DSSC)

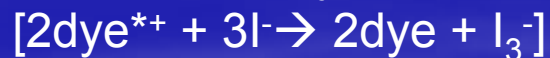
The adsorbed dye molecule absorbs a photon forming an excited state. [dye*]
The excited state of the dye can be thought of as an electron-hole pair (exciton).



The excited dye transfers an electron to the semiconducting TiO₂ (electron injection).

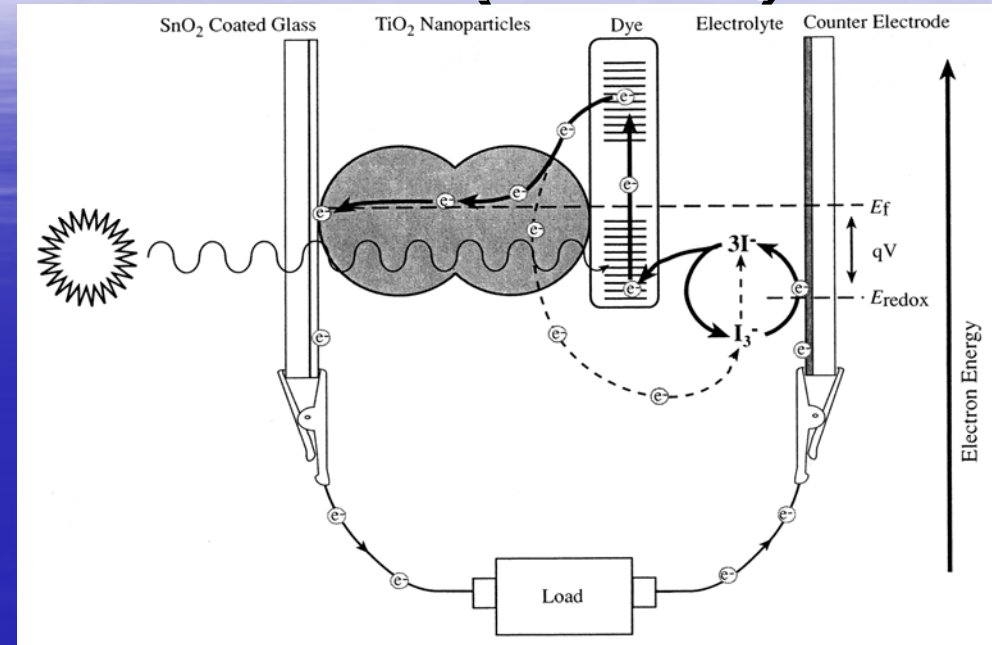
This separates the electron-hole pair leaving the hole on the dye. [dye*⁺]

The hole is filled by an electron from an iodide ion.

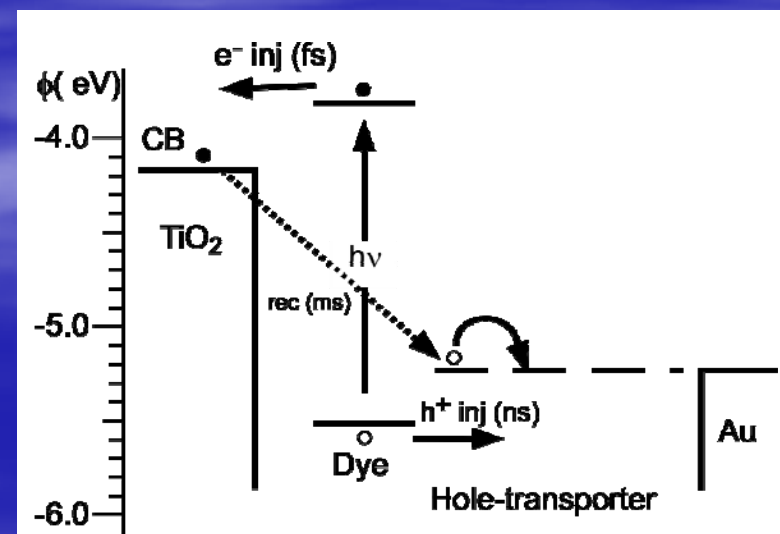


Nano-crystalline TiO₂ Film Dye-Sensitized Solar Cell (DSSC)

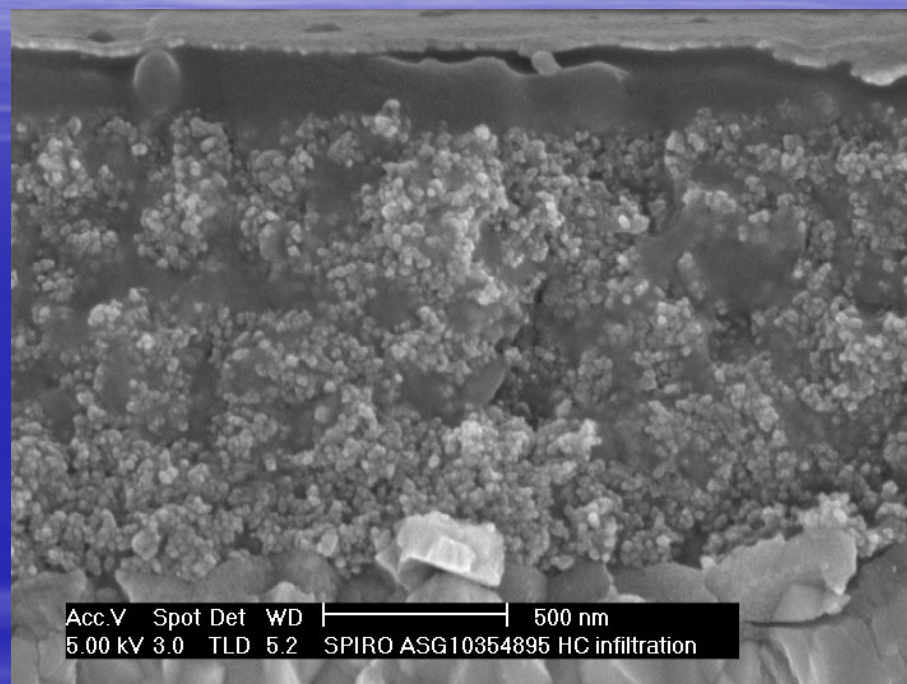
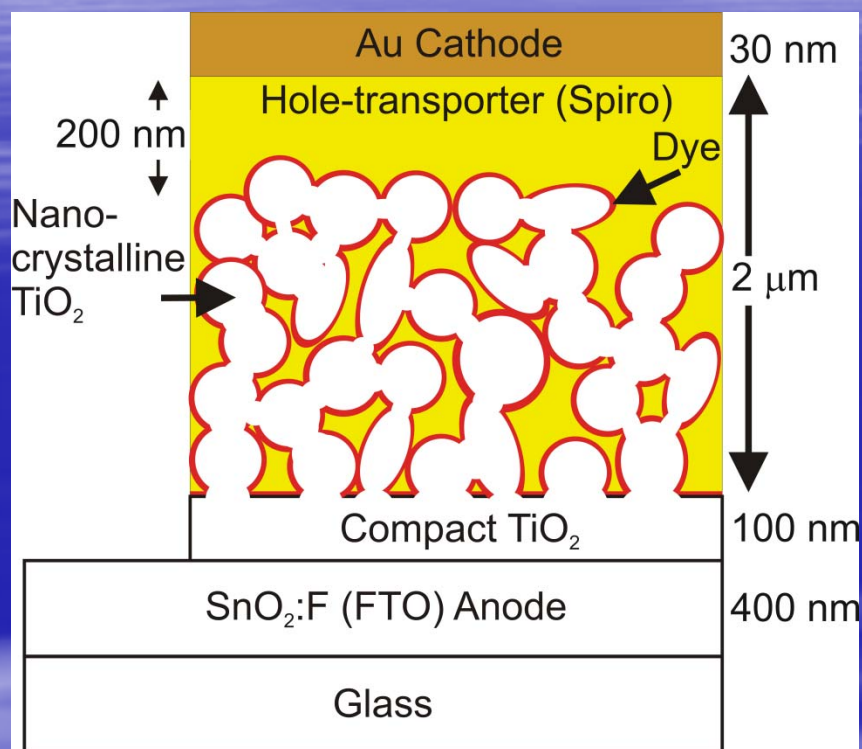
- Electrons are collected from the TiO₂ at the cathode.
- Anode is covered with carbon catalyst and injects electrons into the cell regenerating the iodide.



- Redox mediator is iodide/triiodide (I⁻/I₃⁻)
- The dashed line shows that some electrons are transferred from the TiO₂ to the triiodide and generate iodide. This reaction is an internal short circuit that decreases the efficiency of the cell.

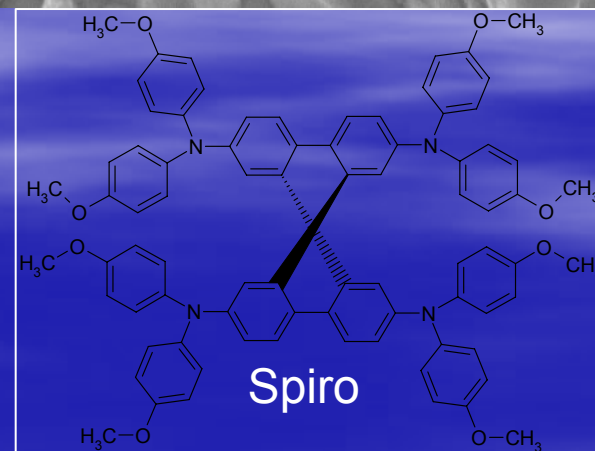
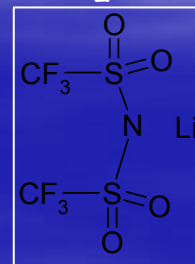


Solid-state dye-sensitized solar cell*



Light absorption in dye, electron transfer to TiO_2 ,
hole transfer to Spiro-MeOTAD.

Additives in HTM: tbp and Lithium TFSI



*Bach, U. et al. Nature 395, 583–585 (1998)

Application of Carbon Nanotubes to Counter Electrodes of Dye-sensitized Solar Cells

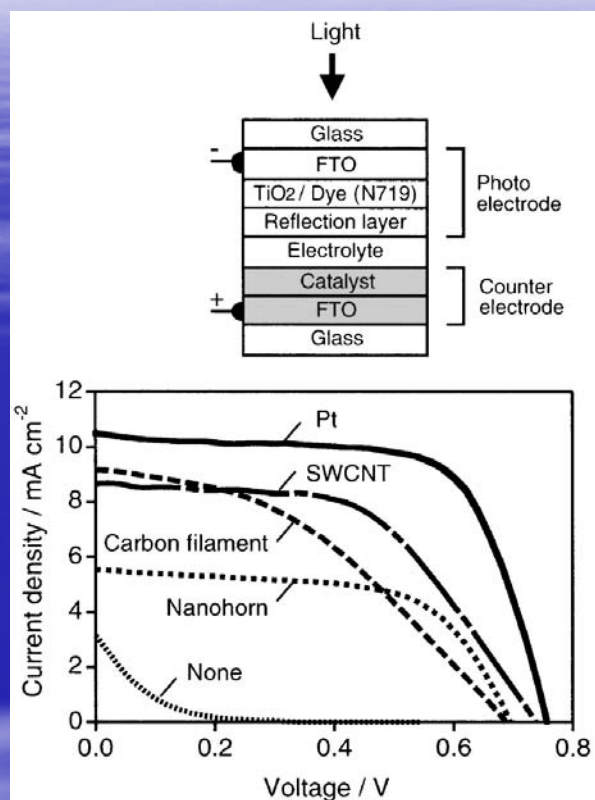


Table 1. Conversion efficiency (η) of the cells and specific surface area (S) of carbon materials

Catalyst	$\eta/\%$	$S/\text{m}^2 \text{ g}^{-1}$
SWCNT	3.5	764
Carbon filament	2.5	350
Nanohorn	2.4	300
Pt	5.4	—
None	0.1	—

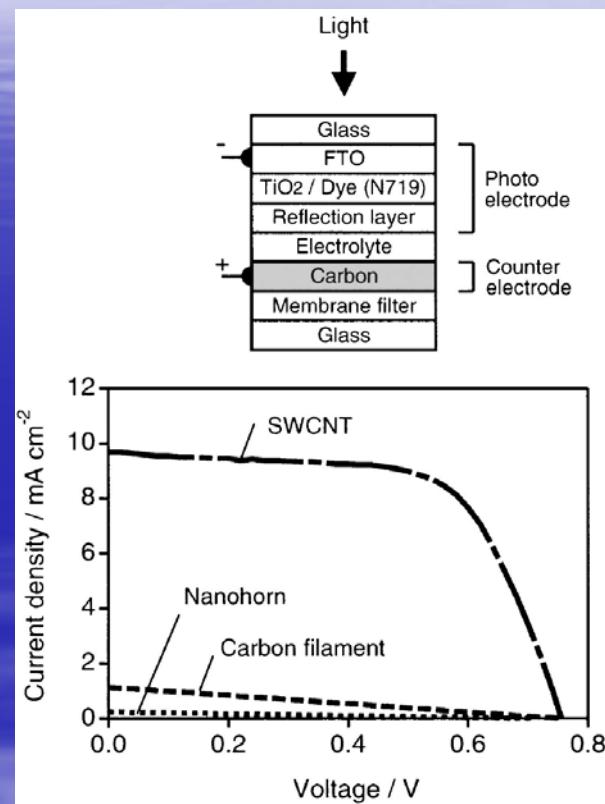


Table 2. Conversion efficiency (η) of the cells and sheet resistance (R) of carbon electrodes

Electrode	$\eta/\%$	$R/\Omega \text{ square}^{-1}$
SWCNT	4.5	1.8
Carbon filament	0.2	990
Nanohorn	0.04	> 1000

Key Step – Charge Separation

- Charge must be rapidly separated to prevent back reaction.
- Dye sensitized solar cell, the excited dye transfers an electron to the TiO_2 and a hole to the electrolyte.
- In the PN junction in Si solar cell has a built-in electric field that tears apart the electron-hole pair formed when a photon is absorbed in the junction.

Basic problems needed to overcome:

1. the high recombination rate at the TiO_2 interface
2. the low conductivity of the hole conductor itself.



Solar Cells based on Nanotechnology:

Quantum dot solar cells
Nanowire solar cells

Strategies for Improvement

(with nanostructures- QDs)

- Capture more sunlight - Tune energy band gaps of materials

“Stacked Architecture”

Potential Advantages:

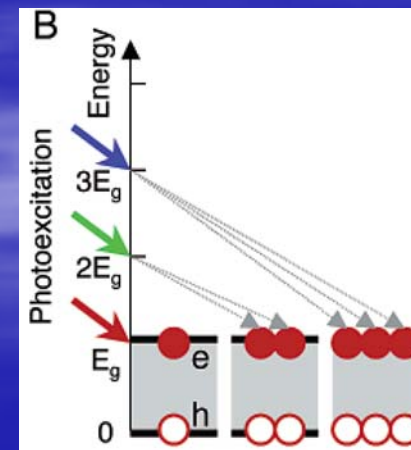
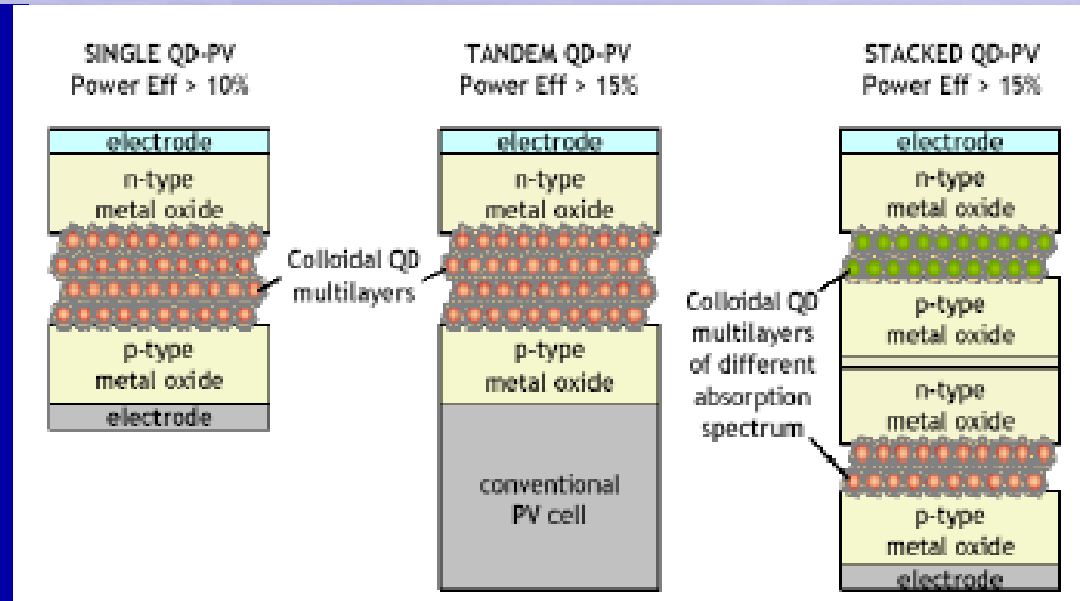
- Cheaper Materials
- Capture more of Solar Spectrum

- Generate more electrons per photon:

“Multiple Exciton Generation”

Potential Advantages:

- Dramatic Efficiency Improvements
- Greater Solar Spectrum



MEG- Multiple Exciton Generation

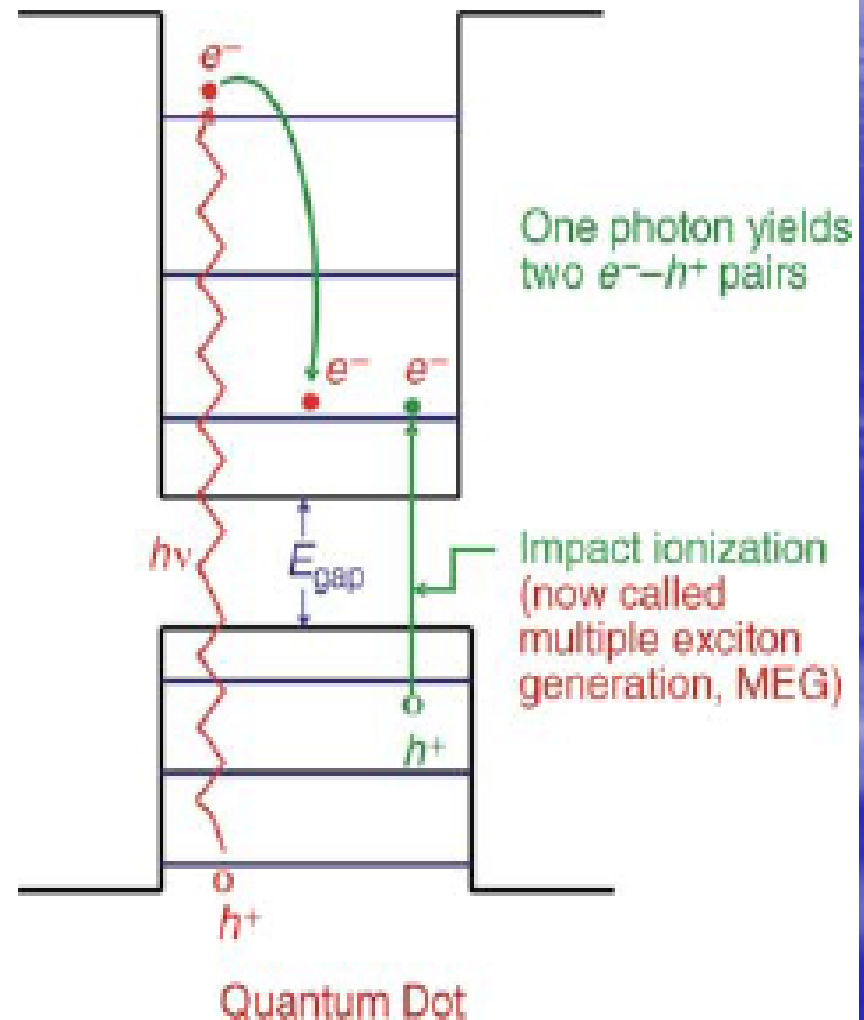
Basic Solar Cell:

1 photon = 1 exciton
(1 electron/ 1 hole + excess energy)

MEG Solar Cell:

1 photon = 2+ excitons
(2+ electron/holes
–reduce heat loss!)

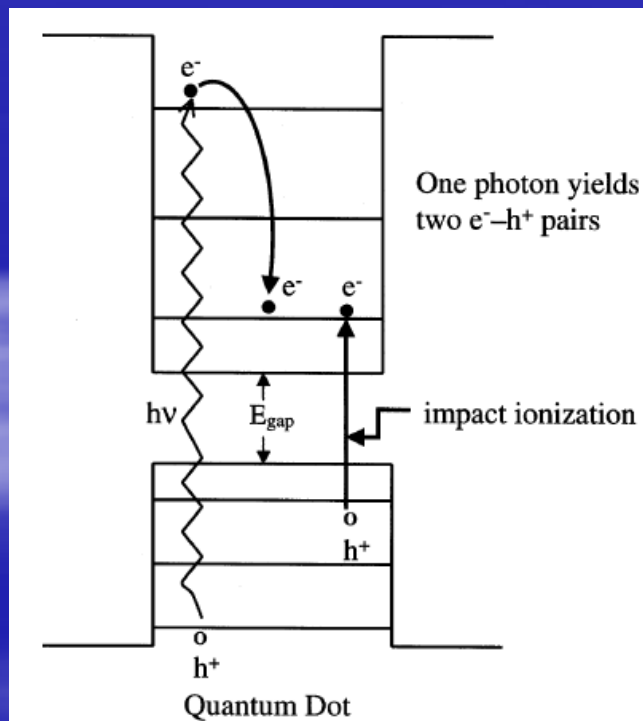
Potential Efficiency Improvement



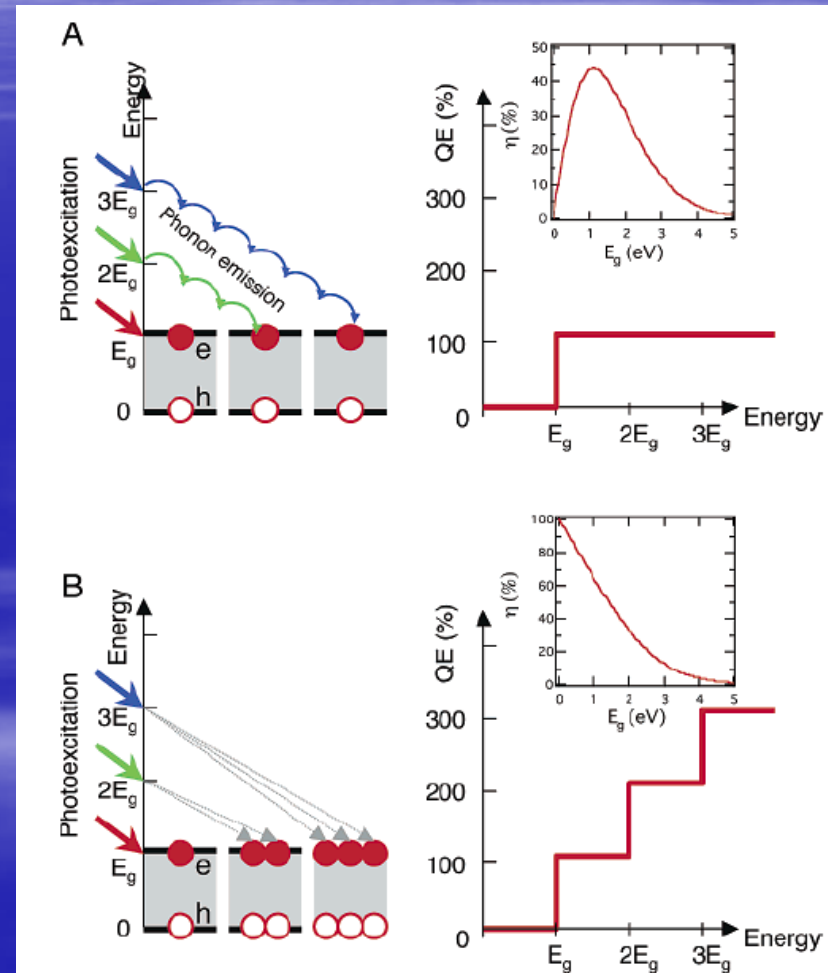
Why Quantum Dots for solar cells?

Thermal relaxation of excited charge carriers can be significantly slowed down.

1. Enhanced photovoltage = collect charges while their hot.
2. Enhanced photocurrent = get more from the hot ones.



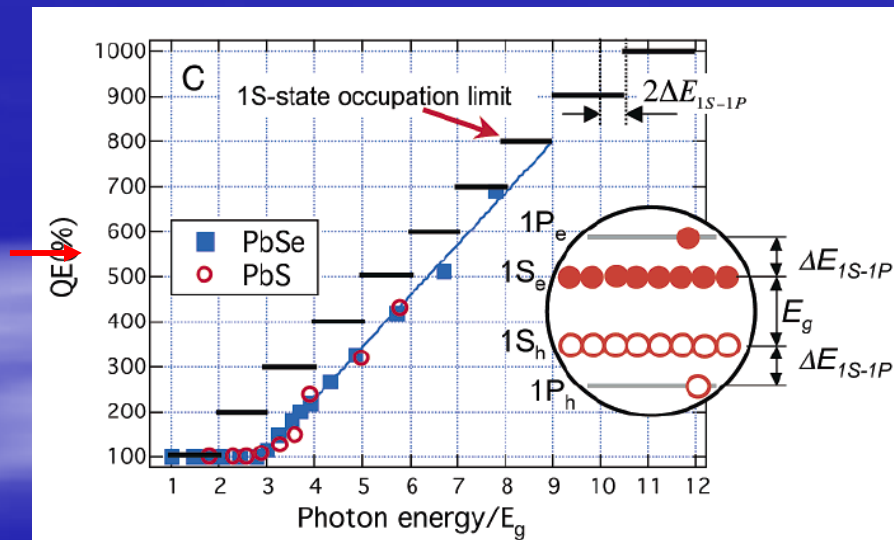
Nozik. Physica E 14 115 (2002)



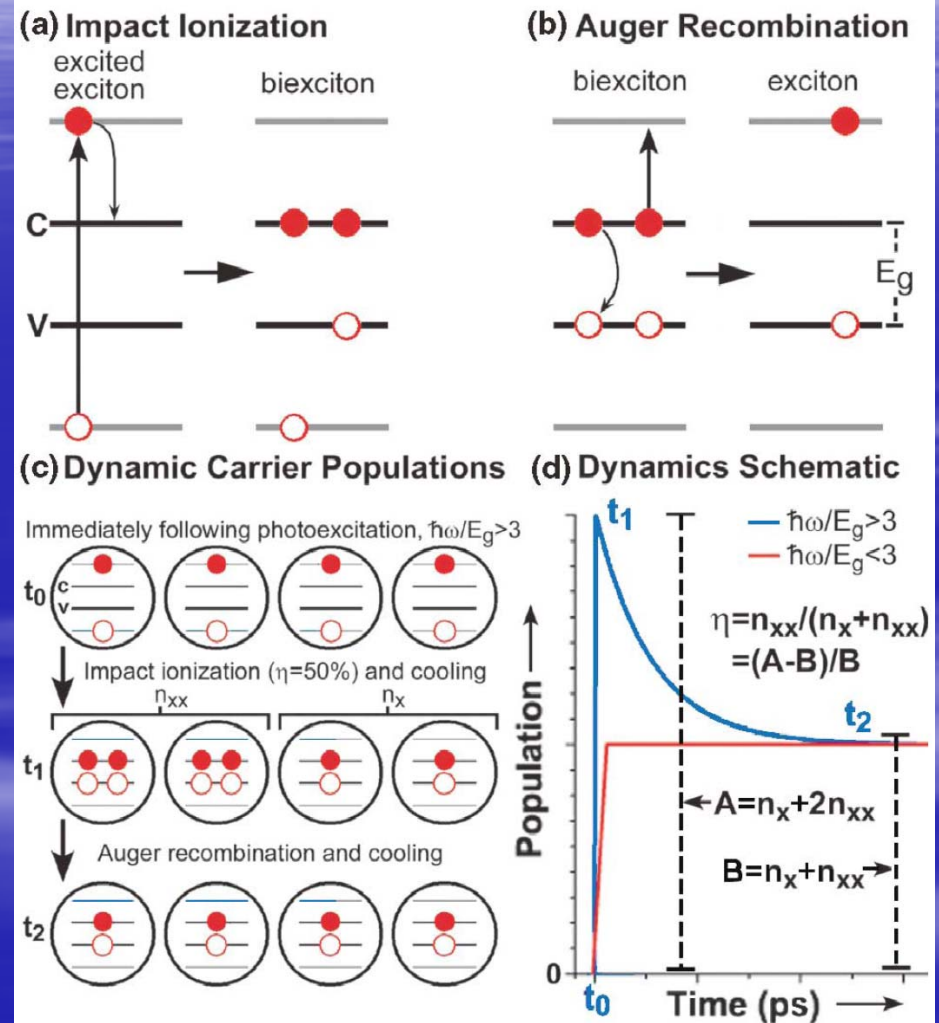
Schaller. Nano Letters 6 424 (2006)

Detection

- Higher photon energy/band gap ratios give higher carrier multiplication efficiencies.
- Onset at $\sim 3E_g$.



Schaller. Nano Letters 6 424 (2006)



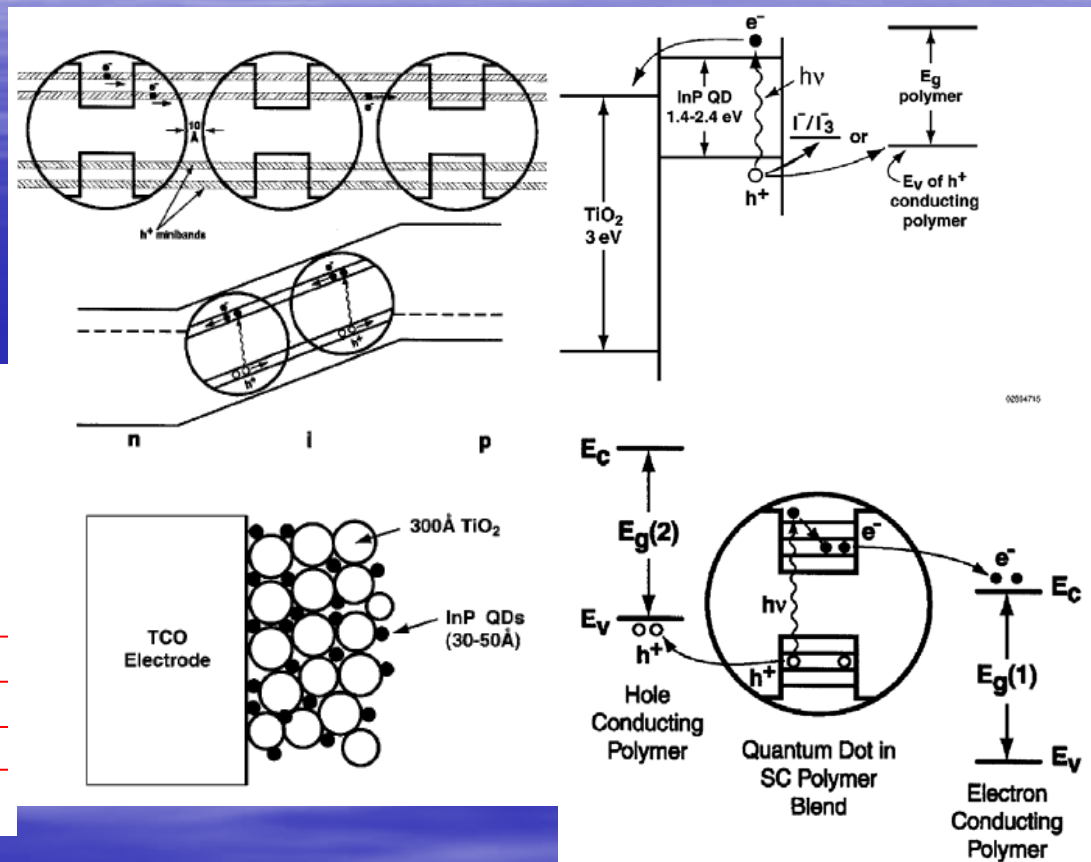
Schaller. PRL 92 186601 (2004)

QD Solar Cells

The Trick:

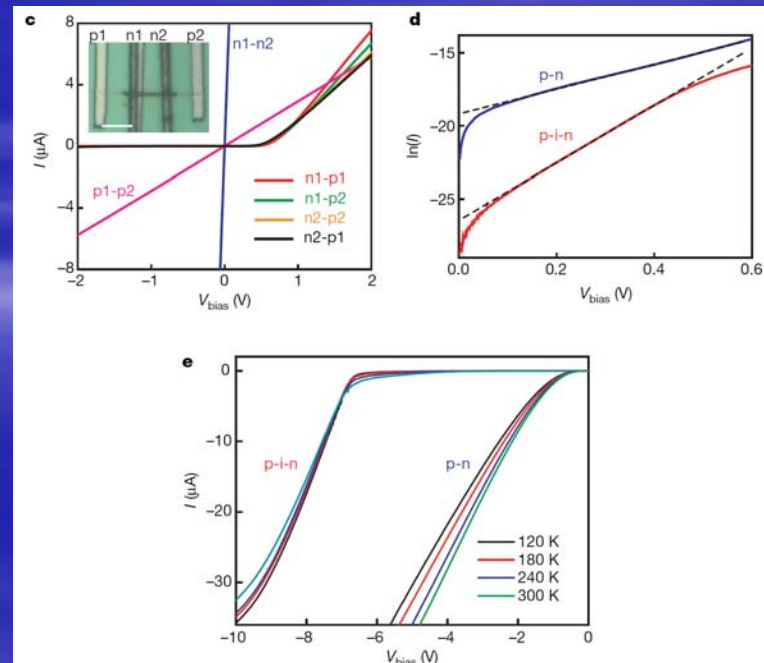
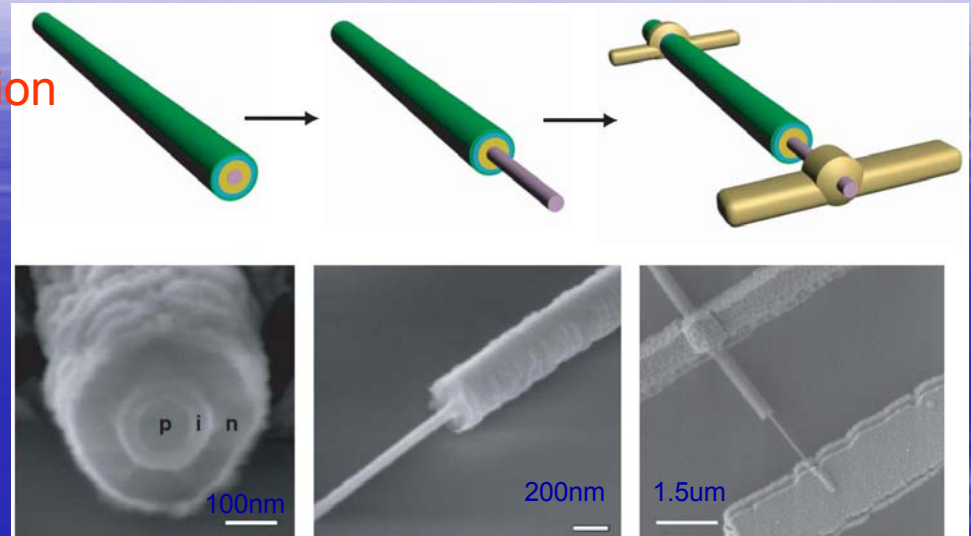
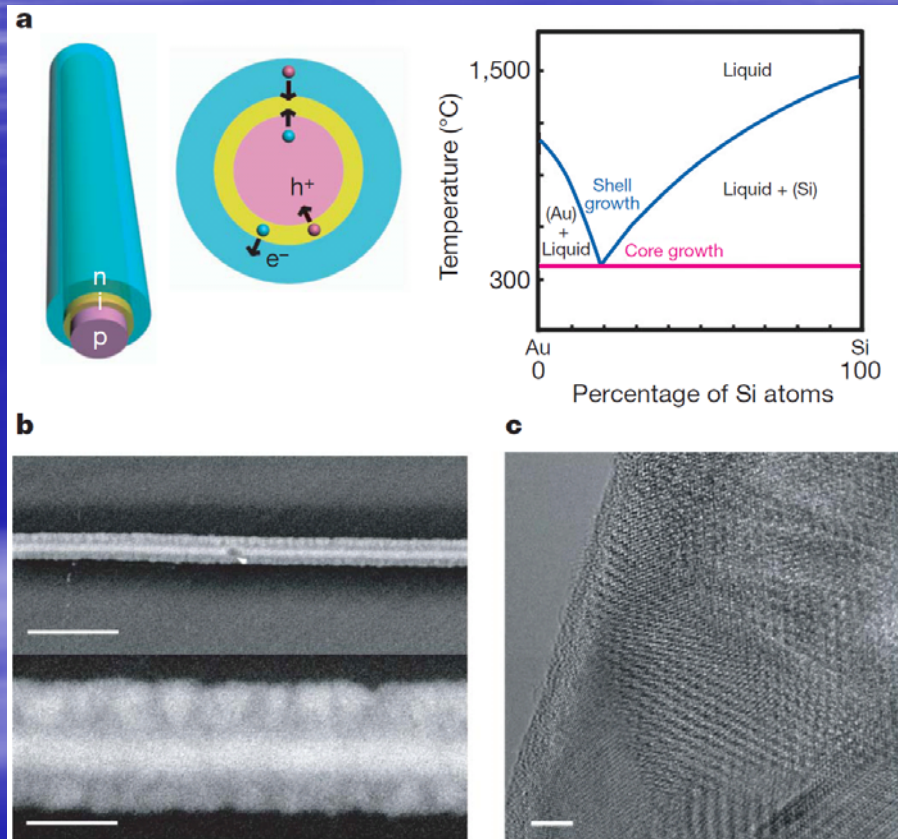
- Have to be able to extract charge carriers produced in quantum dots.

The two fundamental pathways for enhancing the conversion efficiency (increased photovoltage [7,8] or increased photocurrent [9,10] can be accessed, in principle, in three different QD solar cell configurations; these configurations are shown in Fig. 2 and they are described below. However, it is emphasized that these potential high-efficiency configurations are speculative and there is no experimental evidence yet that demonstrates actual enhanced conversion efficiencies in any of these systems.



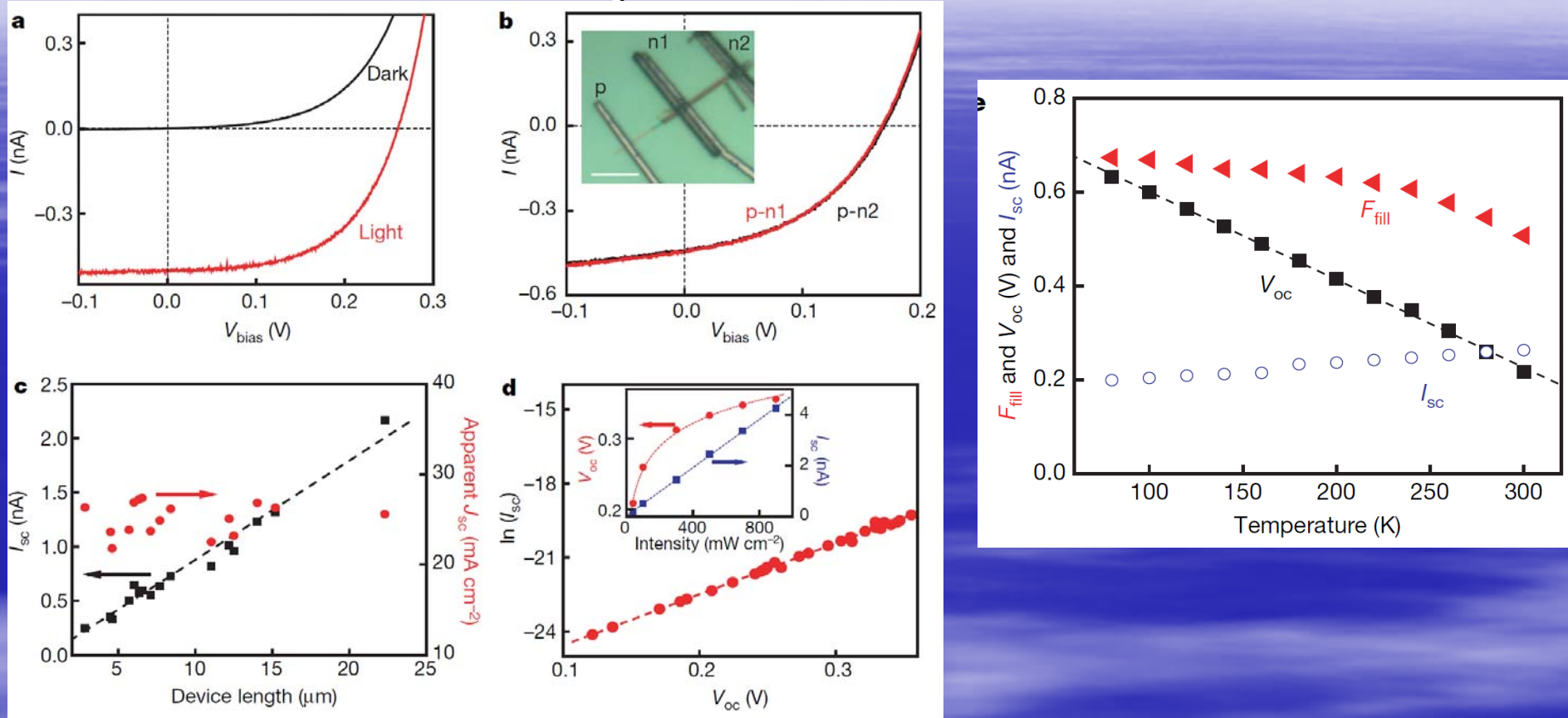
Coaxial silicon nanowires as solar cells and nanoelectronic power sources

Device fabrication and diode characterization



Charles M. Lieber *et al*, Nature **449**, 885 (2007)

Characterization of the p-i-n silicon nanowire photovoltaic device



The overall apparent efficiency of the p-i-n coaxial silicon nanowire photovoltaic elements—3.4% (upper bound) and 2.3% (lower bound)—exceeds reported nanorod/polymer and nanorod/dye systems, and could be increased substantially with improvements in V_{oc} by means of, for example, surface passivation.

Charles M. Lieber *et al*, Nature **449**, 885 (2007)

Application of the p-i-n silicon nanowire photovoltaic device

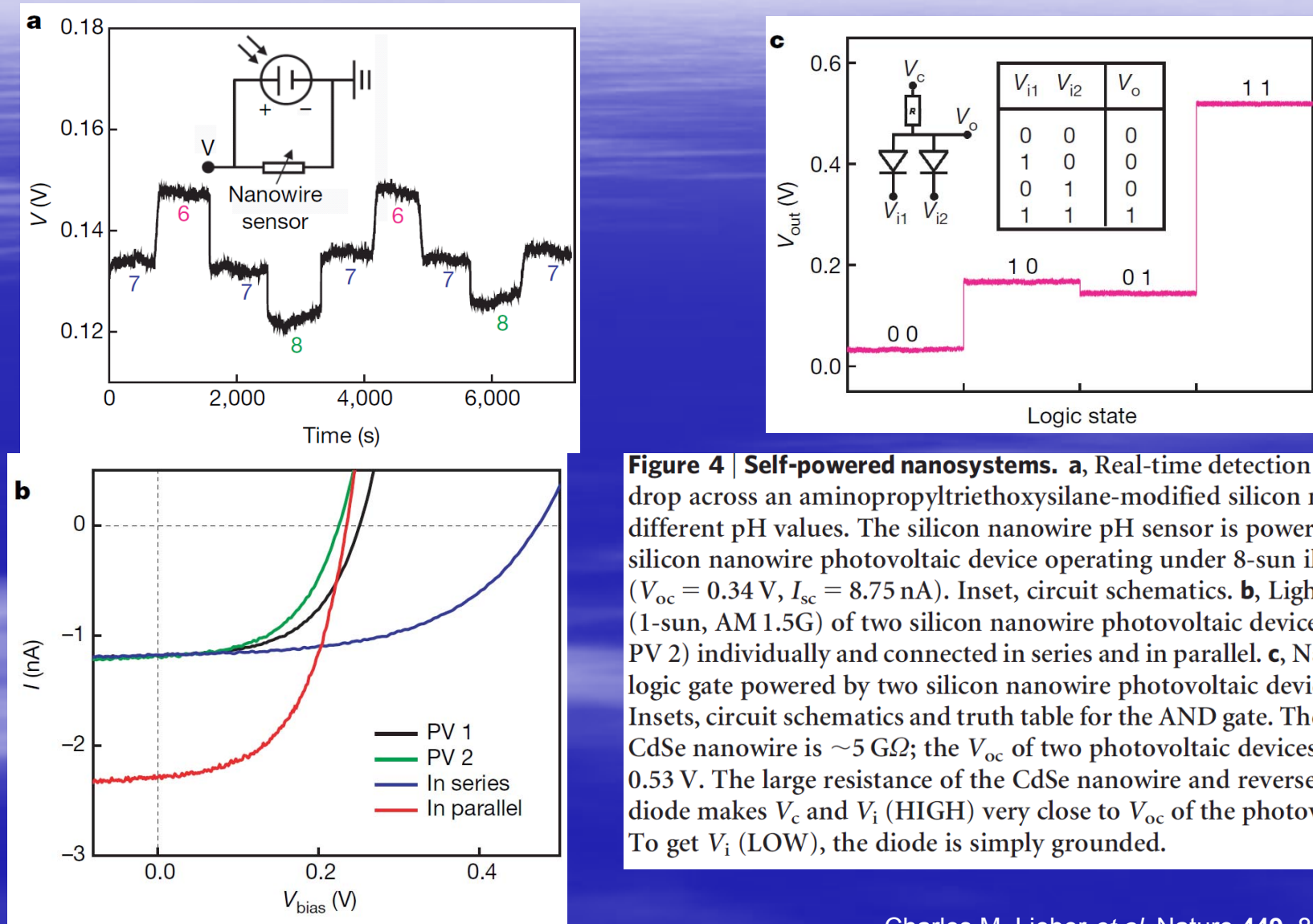
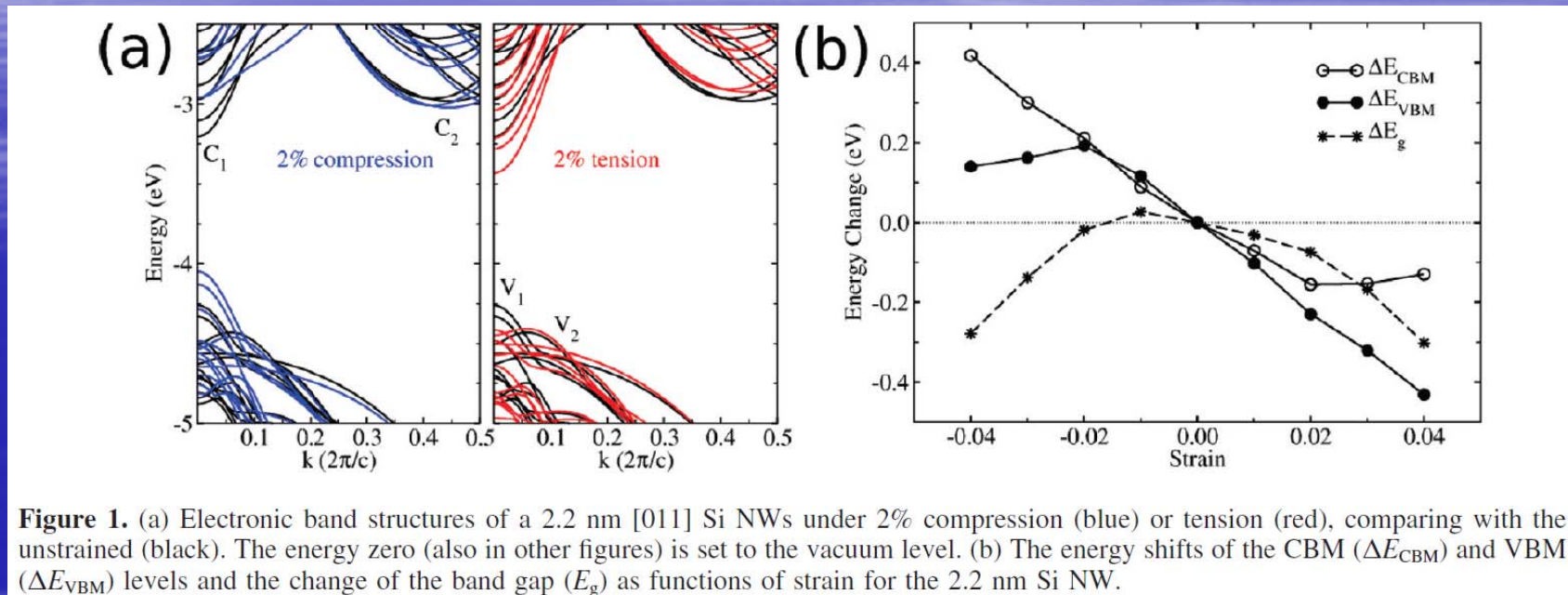


Figure 4 | Self-powered nanosystems. **a**, Real-time detection of the voltage drop across an aminopropyltriethoxysilane-modified silicon nanowire at different pH values. The silicon nanowire pH sensor is powered by a single silicon nanowire photovoltaic device operating under 8-sun illumination ($V_{oc} = 0.34$ V, $I_{sc} = 8.75$ nA). Inset, circuit schematics. **b**, Light I - V curves (1-sun, AM 1.5G) of two silicon nanowire photovoltaic devices (PV 1 and PV 2) individually and connected in series and in parallel. **c**, Nanowire AND logic gate powered by two silicon nanowire photovoltaic devices in series. Insets, circuit schematics and truth table for the AND gate. The resistance of CdSe nanowire is ~ 5 G Ω ; the V_{oc} of two photovoltaic devices in series is 0.53 V. The large resistance of the CdSe nanowire and reverse-biased p-i-n diode makes V_c and V_i (HIGH) very close to V_{oc} of the photovoltaic device. To get V_i (LOW), the diode is simply grounded.

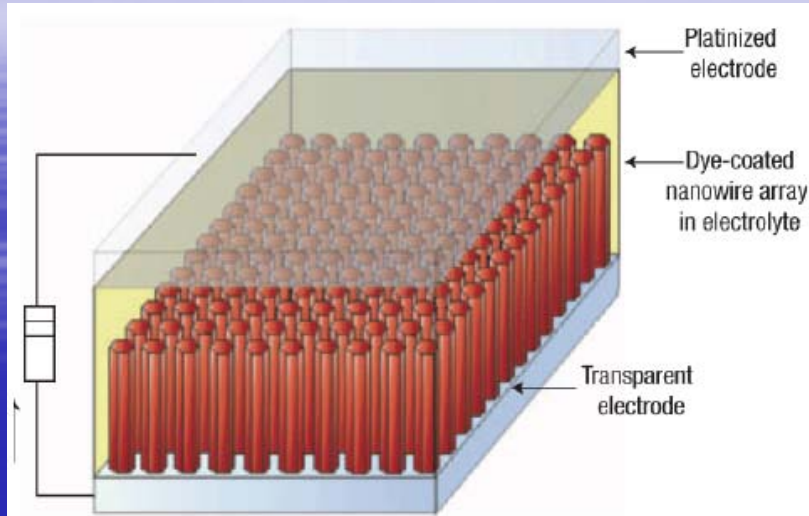
Strained Si Nanowires: Solar cells

Efficient charge separation for solar cells could be achieved by applying strain to silicon nanowires

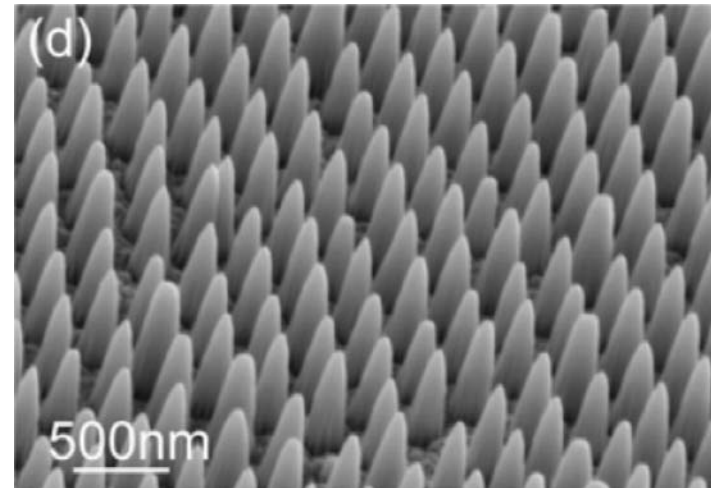


- The added strain in the nanowire changes the structure of energy bands, such that positive and negative charges can be separated into different regions of the nanowire.
- The main potential benefit of silicon nanowire cells over traditional crystalline silicon cells is that the silicon would not need to be doped with other materials.
- This means that nanowire solar cells could be made inexpensively from much lower quality silicon, and without labour-intensive processing.

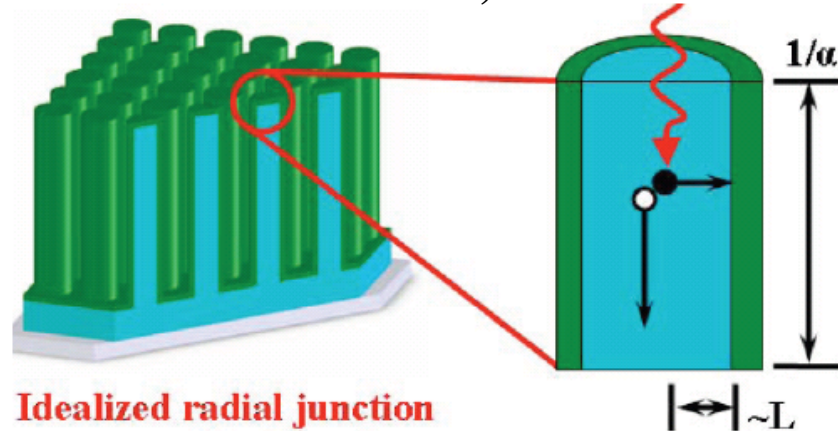
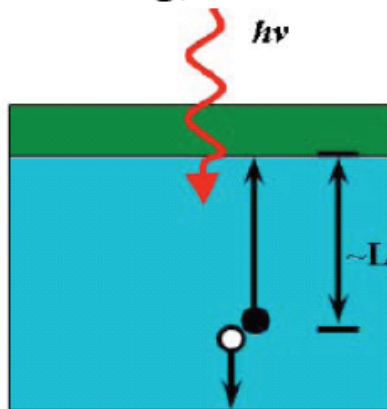
Nanowire applications for solar cells



P. Yang, Nature Materials



Y. Cui, Stanford

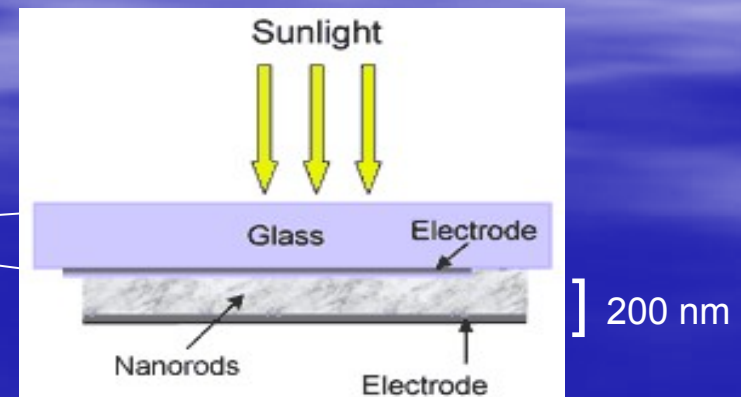


**Idealized radial junction
nanorod solar cell**

Nanowires decouple light absorption and carrier extraction into different directions !
Atwater, Caltech

Choice of solar technologies:

- Crystalline silicon
- Amorphous silicon
- Cadmium telluride
- Copper indium diselenide CIS family, notably copper indium gallium diselenide CIGS
- Dye sensitised solar cells DSSC
- Organic – polymer or small molecule
- Others such as silicon nanoparticle ink, carbon nanotube CNT and quantum dots
- Nano solar cell: Inorganic nanorods embedded in semiconducting polymer, sandwiched between two electrodes



Summary

- A mix of future sustainable energy conversion technologies will be needed
- New materials and nanoscience discoveries are necessary to its development
- Strong interplay between basic and applied sciences is a key to success
- Interdisciplinary approaches, and coupling theory/experiment are vital
- Working with industry at all stages is a key factor
- The challenges and constraints are global and complementary among different countries
- International collaboration and networking must be encouraged and supported