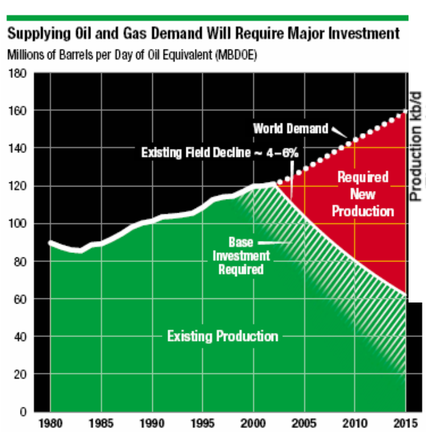
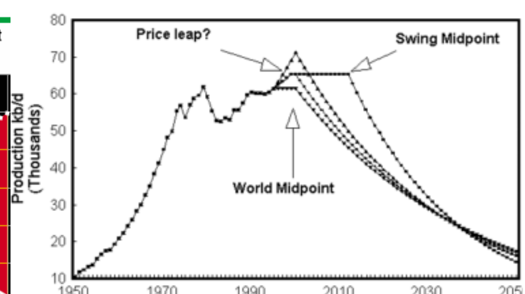
Molecularly Wired Nanostructured Assemblies for Solar Energy Conversion

Thermal
- a. Heating
- b. Electricity

Photoconversion
- a. Photosynthesis
- b. Solar H_2
- c. Photovoltaics
- d. Emerging areas





Graph: World Oil Production 1950-2050
Source: Dr. C.J. Campbell

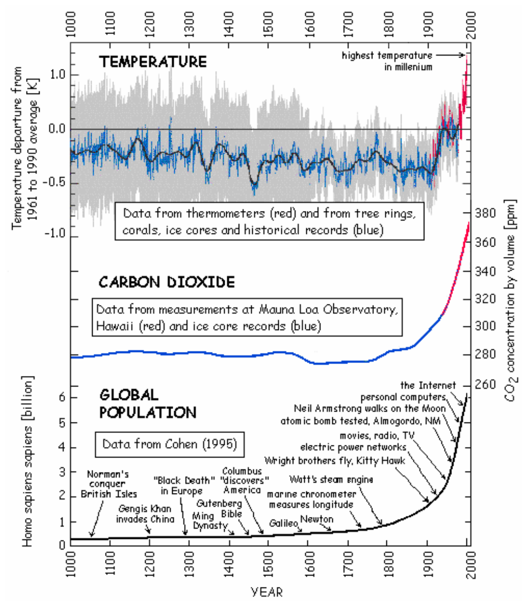
"Understanding depletion is simple. Think of an Irish pub. The glass starts full and ends empty. There are only so many more drinks to closing time. It's the same with oil. We have to find the bar before we can drink what is in it."

Campbell

Global warming over the past millennium

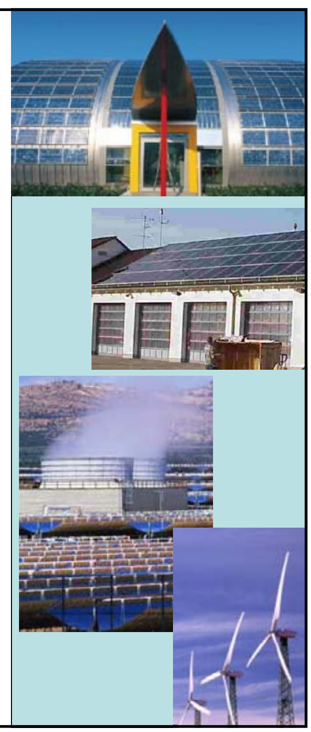
Very rapidly we have entered uncharted territory -– what some call the *anthropocene* climate regime. Over the 20th century, human population quadrupled and energy consumption increased sixteenfold. Near the end of the last century, we crossed a critical threshold, and global warming from the fossil fuel greenhouse became a major, and increasingly dominant, factor in climate change. Global mean surface temperature is higher today than it's been for at least a millennium.

…… Marty Hoffert NYU



The United Nations Framework Convention on Climate Change calls for ''stabilization of greenhouse-gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system . . .''. A standard baseline scenario that assumes no policy intervention to limit greenhouse-gas emissions has 10 TW (10 x 10^{12} watts) of carbon-emission-free power being produced by the year 2050, equivalent to the power provided by all today's energy sources combined.

……………NATURE, VOL 395, 881,1998



Three possible options for meeting the 10 TW- Challenge by 2050

Carbon Neutral Energy (fossil fuel inconjunction with carbon sequestration)

-Need to find secure storage for 25 billion metric tons of CO_2 produced annually (equal to the volume of 12500 km^3 or volume of lake superior!)

Nuclear Power

-Requires construction of a new one-gigawatt-electric (1-GW) nuclear fission plant everyday for the next 50 years

Renewable Energy Sources

- hydroelectric resource 0.5 TW
- from all tides & ocean currents 2 TW
- geothermal integrated over all the land area 12 TW
- globally extractable wind power 2-4 TW
- **solar energy striking the earth 120,000 TW !!!**

The Silver Lining …….

The earth receives more energy from the sun in just one hour than the world uses in a whole year.

Cumulative solar energy production accounts for less than 0.01% of total Global Primary Energy demand.

Solar Energy demand has grown at about 25% per annum over the past 15 years (hydrocarbon energy demand typically grows between 0-2% per annum). Worldwide photovoltaic installations increased by 927 MW in 2004, up from 574 MW installed during the previous year.

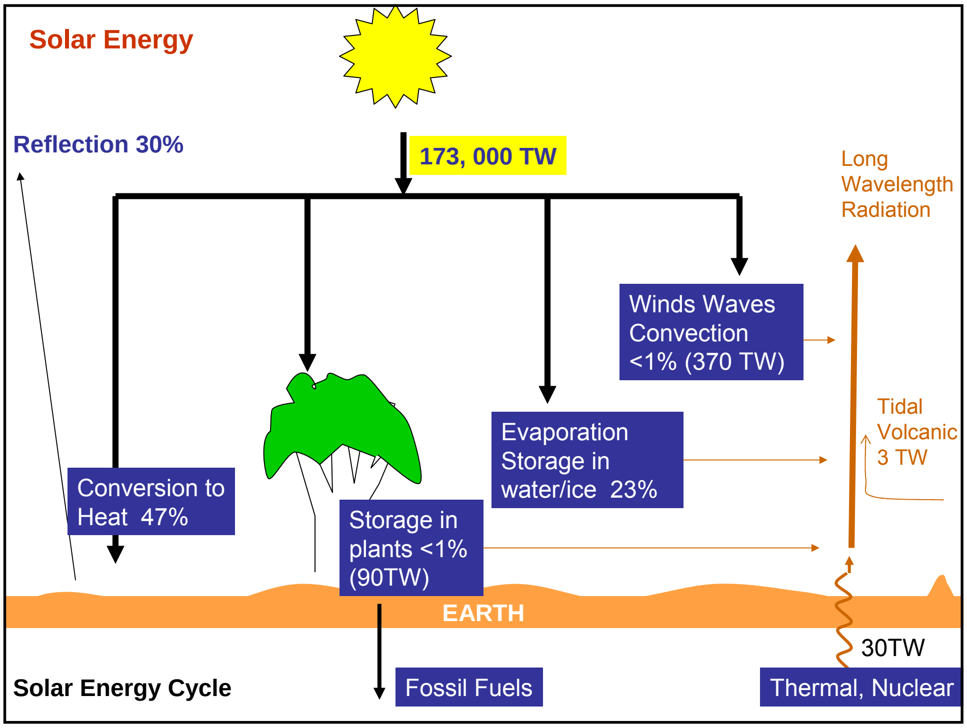
An average crystalline silicon cell solar module has an efficiency of 15%, an average thin film cell solar module has an efficiency of 6%. (*Thin film manufacturing costs potentially are lower, though.)*

Solar Energy (photovoltaic) prices have declined on average 4% per annum over the past 15 years.

For the Fiscal Year 2002, the Japanese solar roof top program received applications from 42,838 households.

Without incentive programs, solar energy costs (in an average sunny climate) range between 22-40 cents/kWh for very large PV systems. (installation costs $8-$10 with no government incentives)

Japan has taken over from the United States as the largest net exporter of PV cells and modules. Around 50 % of the world's solar cell production was manufactured in Japan in 2003. United States accounted for 12%.



Solar Energy Potential

- Theoretical: 1.2×10^5 TW solar energy potential
  (1.76×10^5 TW striking Earth; 0.30 Global mean albedo)

- Practical: $\approx$ 600 TW solar energy potential
  (50 TW - 1500 TW depending on land fraction etc.; WEA 2000)
  Onshore electricity generation potential of $\approx$60 TW (10% conversion efficiency):
- *Photosynthesis*: 90 TW

PV Land Area Requirements

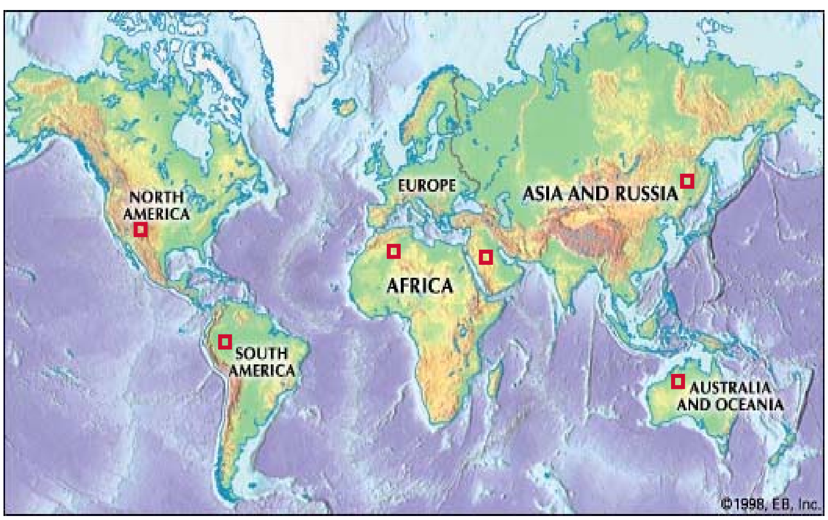
- U.S. Land Area: $9.1x10^{12}$ m^2 (incl. Alaska)
- Average Insolation: 200 W/m^2
- 2000 U.S. Primary Power Consumption: 99 Quads=3.3 TW
- 1999 U.S. Electricity Consumption = 0.4 TW
- Hence:
  $3.3x10^{12}$ W/($2x10^2$ W/m^2 x 10% Efficiency) = $1.6x10^{11}$ m^2
  Requires $1.6x10^{11}$ m^2/ $9.1x10^{12}$ m^2 = 1.7% of Land

PV Land Area Requirements

- $1.2x10^5$ TW of solar energy potential globally
- Generating $2x10^1$ TW with 10% efficient solar farms requires
  $2x10^2/1.2x10^5$ = 0.16% of Globe = $8x10^{11}$ m^2 (i.e., 8.8 % of U.S.A)
- Generating $1.2x10^1$ TW (1998 Global Primary Power) requires
  $1.2x10^2/1.2x10^5$= 0.10% of Globe = $5x10^{11}$ m^2 (i.e., 5.5% of U.S.A.)

PV Land Area Requirements

PV Land Area Requirements



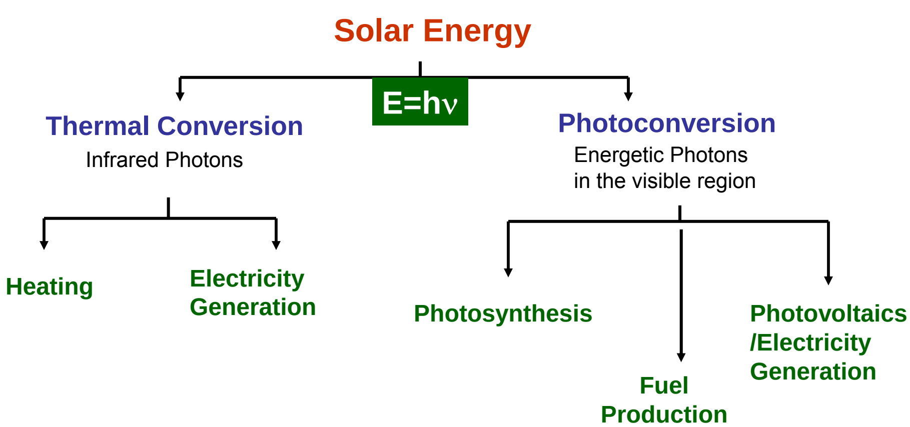
6 Boxes at 3.3 TW Each

U.S. Single Family Housing Roof Area

- $7x10^7$ detached single family homes in U.S.
  ≈2000 sq ft/roof = 44ft x 44 ft
  = 13 m x 13 m = 180 m^2/home
  = $1.2x10^{10}$ m^2 total roof area 2000

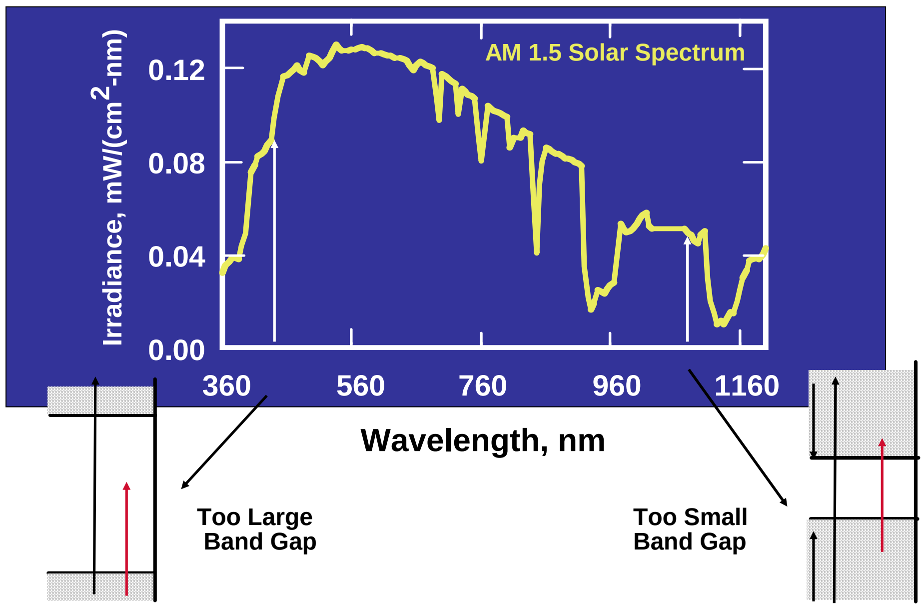
- Hence can (only) supply 0.25 TW, or ≈1/10th of U.S. Primary Energy Consumption

(U.S. Electricity Consumption = 0.4 TW)



E = hc/λ = 119627/λ (kJ/mole) Or E= 1240/λ

Optimum Absorption Threshold



Ia. Thermal Conversion: Solar Heating

- Roughly equal global energy use in each major sector: transportation, residential, transformation, industrial
- World market: 1.6 TW space heating; 0.3 TW hot water; 1.3 TW process heat (solar crop drying: ≈ 0.05 TW)
- Temporal mismatch between source and demand requires storage
- (ΔS) yields high heat production costs: (\$0.03-\$0.20)/kW-hr
- High-T solar thermal: currently lowest cost solar electric source (\$0.12-0.18/kW-hr); potential to be competitive with fossil energy in long term, but needs large areas in sunbelt
- Solar-to-electric efficiency 18-20% (research in thermochemical fuels: hydrogen, syn gas, metals)

1b. Thermal Conversion: Electricity Generation

Concentrating solar power (CSP) focuses on three types of CSP technologies: trough systems, dish/engine systems, and power towers.

These technologies are used in CSP plants that use different kinds of mirror configurations to convert the sun's energy into high-temperature heat. The heat energy is then used to generate electricity in a steam generator.

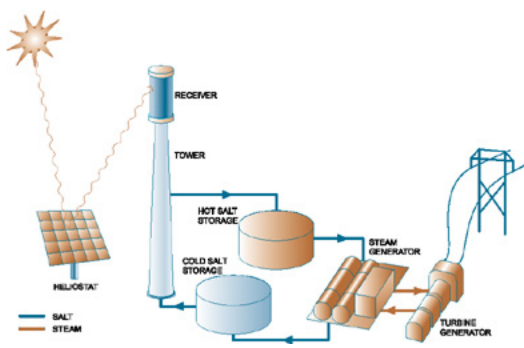
CSP's relatively low cost and ability to deliver power during periods of peak demand—*when and where we need it*—mean that CSP can be a major contributor to the nation's future needs for distributed sources of energy.

At the **National Solar Thermal Test Facility** (NSTTF), built at Sandia National Laboratories in Albuquerque in 1976, the 63-meter tall tower has 222 computer-controlled heliostats that can direct the sun into any of four test bays to produce a total thermal capacity of 5 megawatts.

Solar thermal power plant. (Mojave Desert in Kramer Junction, California) This is one of nine such plants built in the 1980s. During operation, oil in the receiver tubes collects the concentrated solar energy as heat and is pumped to a power block (in background) for generating electricity.

Solar dish-engine system. The dish, a concentrator, collects the energy coming directly from the sun and concentrates it on a small area. A thermal receiver absorbs the concentrated beam of solar energy, converts it to heat, and transfers the heat to the engine/generator. (Credit: Sandia National Laboratories)

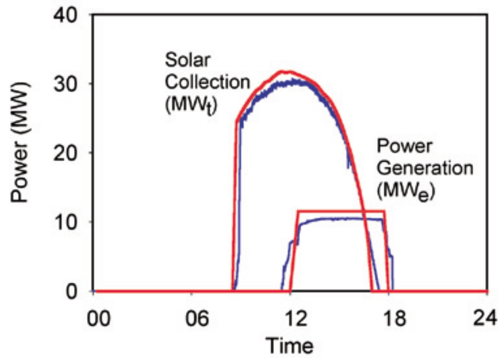
Solar Two, a 10-megawatt central receiver power tower that operated in Daggett, CA. This facility demonstrated the feasibility of power-tower systems, a solar-thermal electric or concentrating solar power technology. In 1988, **the final year of operation**, the system could be dispatched 96% of the time.



Molten-Salt Power Tower Technology

In a molten-salt power tower, sun-tracking heliostats can concentrate solar energy up to 1000 times onto a central, tower-mounted receiver. Molten nitrate salt, which is a clear liquid with properties like water at temperatures above its 240˚C melting point, is pumped from a large storage tank to the receiver, where it is heated in tubes to temperatures of 565 ˚C. The salt is then returned to a second large storage tank, where it remains until needed by the utility for power generation. At that time, the salt is pumped through a steam generator to produce the steam to power a conventional, high-efficiency steam turbine to produce electricity. The salt at 285ƒC then returns to the first storage tank to be used in the cycle again. http://www.energylan.sandia.gov/

10-megawatt Solar Two power tower pilot plant near Barstow, California



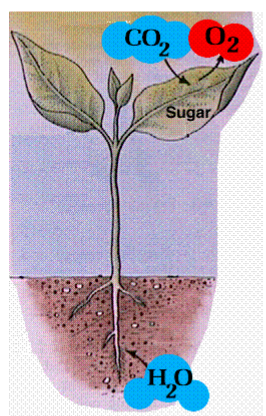
Predicted (red) and actual (blue) solar energy collection and power generation.

Over one 30-day period, Solar Two produced 1633 megawatt-hours, exceeding its one-month performance goal of 1500 megawatt-hours of power production. The plant also produced a record gross turbine power output of 11.6 megawatts Successfully completed operations in April 1999

http://www.energylan.sandia.gov/sunlab/Snapshot/STFUTURE.HTM

2a. Photosynthesis

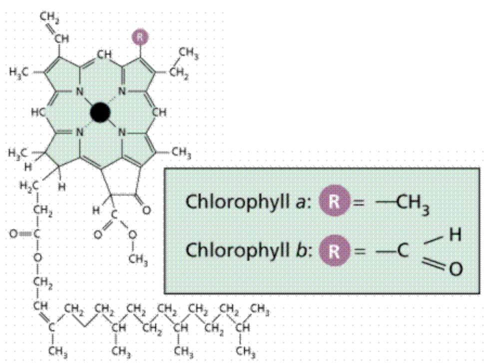
Photosynthesis is the process by which plants, some bacteria, and some protistans use the energy from sunlight to produce sugar, which cellular respiration converts into ATP, the "fuel" used by all living things. The conversion of unusable sunlight energy into usable chemical energy, is associated with the actions of the green pigment chlorophyll. Most of the time, the photosynthetic process uses water and releases the oxygen that we absolutely must have to stay alive.

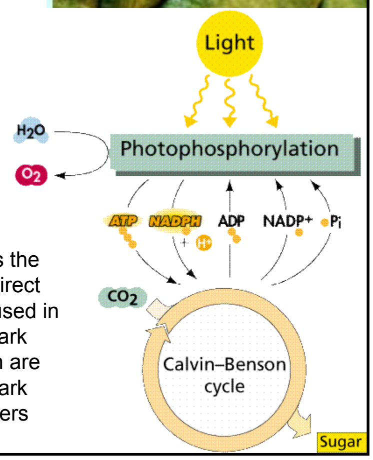


$6H_2O + 6CO_2$ ----------> $C_6H_{12}O_6 + 6O_2$

http://www.emc.maricopa.edu/faculty/farabee/BIOBK/BioBookPS.html

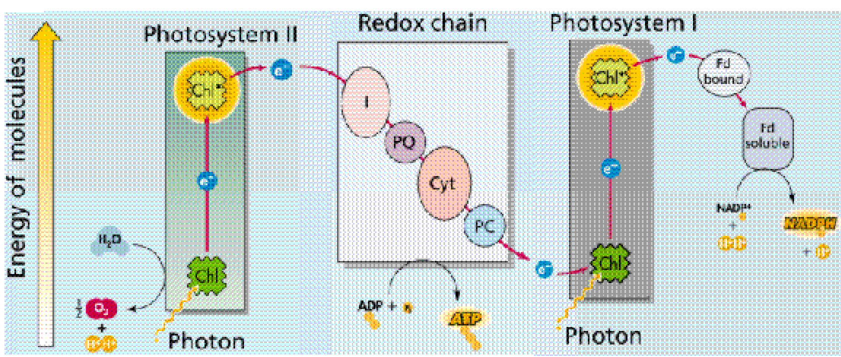
2a. Photosynthesis

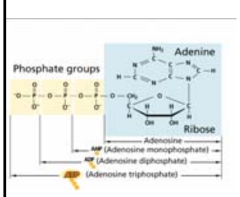




Photosynthesis is a two stage process. The first process is the Light Dependent Process (Light Reactions), requires the direct energy of light to make energy carrier molecules that are used in the second process. The Light Independent Process (or Dark Reactions) occurs when the products of the Light Reaction are used to form C-C covalent bonds of carbohydrates. The Dark Reactions can usually occur in the dark, if the energy carriers from the light process are present.

2a. Photosynthesis





adenosine diphosphate (ADP)

adenosine triphosphate (ATP)

nicotine adenine dinucleotide phosphate (NADP+)

NADPH

Hydrogen Production

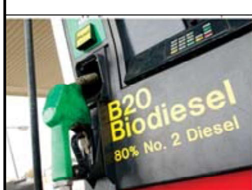
Water molecules can be split into hydrogen and oxygen atoms using algae, one-celled organisms that thrive in water. The green alga *Chlamydomonas reinhardtii* can produce hydrogen and oxygen from water under certain conditions.

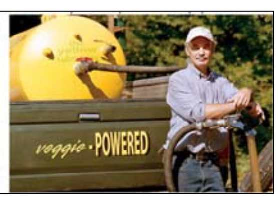
These algae normally grow new cells by photosynthesis, using carbon dioxide from the air in the presence of sunlight. But after placing the aquatic organisms in a large flask of water illuminated by lamps, the ORNL researchers "trick" the algae by depriving them of carbon dioxide and oxygen. As a result, a normally dormant gene becomes activated, leading to the synthesis of the enzyme **hydrogenase**.

The algae use this enzyme to produce both hydrogen and oxygen from water. The relative amounts of oxygen and hydrogen that evolve in the flask are measured by sweeping the gases over hydrogen and oxygen sensors, whose electrical conductivity increases with rising gas concentration.

http://www.ornl.gov/info/ornlreview/v33_2_00/hydrogen.htm

Alternative Fuels





Biodiesel fuel use is on the rise.
- Made from natural, renewable sources (veg oils, animal fats).
- Can be used as pure fuel or blended with petroleum

Ethanol is renewable, but currently more expensive than gasoline.
- Critics argue that it takes more energy to produce a gallon of ethanol than you will obtain from burning it.
- Conflict of Interest: National Corn Growers vs. American Petroleum Institute

Two opposing views

Cornell ecologist, David Pimentel study finds that producing ethanol and biodiesel from corn and other crops is not worth the energy -corn requires 29 percent more fossil energy than the fuel produced.

http://www.news.cornell.edu/stories/July05/ethanol.toocostly.ssl.html

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Ethanol can replace gasoline with significant energy savings, comparable impact on greenhouse gases (Jan 26, 2006) Daniel M. Kammen, UC Berkeley

http://www.berkeley.edu/news/media/releases/2006/01/26_ethanol.shtml

Despite the uncertainty, it appears that ethanol made from corn is a little better – may be 10 or 15 percent - than gasoline in terms of greenhouse gas production

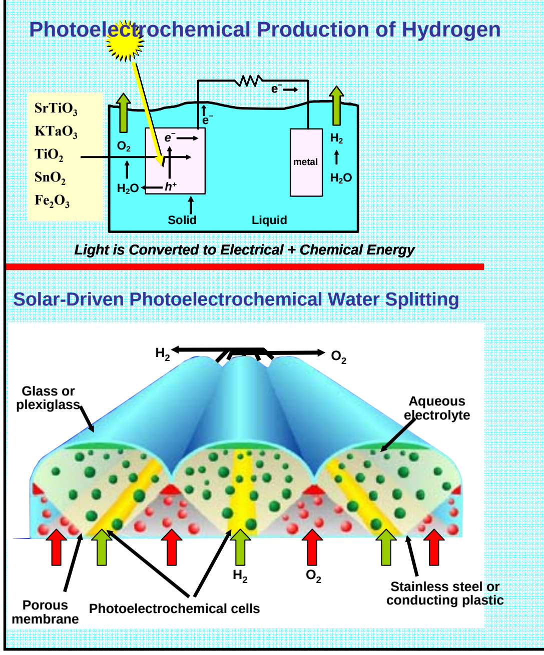
SCIENCE, 27 JANUARY 2006 VOL 311 506-508

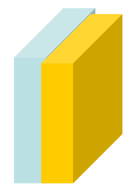
This analysis takes into account energy gain from coproducts

Net Energy Summary *** - adjusted for comparability**	Patzek	Pimentel	Shapouri	Graboski	de Oliviera	Wang	Farrell Science paper 2006
Input energy (kJ/mL)	27	27	21	21	20	19	21
Reported HV of ethanol (MJ/L)	21	21	21	21	21	21.2	21
Coproduct credits (kJ/mL)	4.1	1.9	7.3	4.1	4.1	4.0	4.1
Coproducts as % of total energy	15%	7%	36%	19%	20%	21%	20%
Output Energy (MJ/L)	25	23	29	25	25	25.2	25
Net energy value, NEV (kJ/mL)	-1.6	-3.7	8.0	3.9	4.8	6.1	4.5
Net energy ratio	0.94	0.86	1.4	1.2	1.2	1.3	1.2

Source: Farrell et al SCIENCE, 2006, 311, 506   http://rael.berkeley.edu/EBAMM/EBAMM_1_0.xls

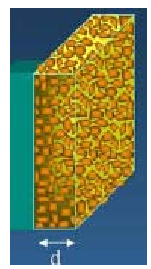
2b. Photoelectrochemical Hydrogen Production





Low surface area
Higher cost
Higher efficiency

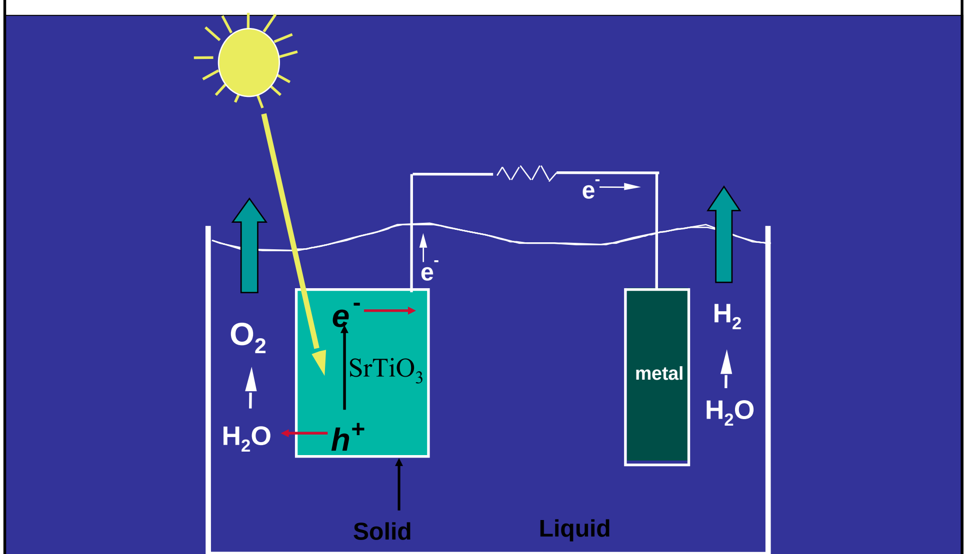
Single Crystal Semiconductor



High surface area
Low cost
Low efficiency

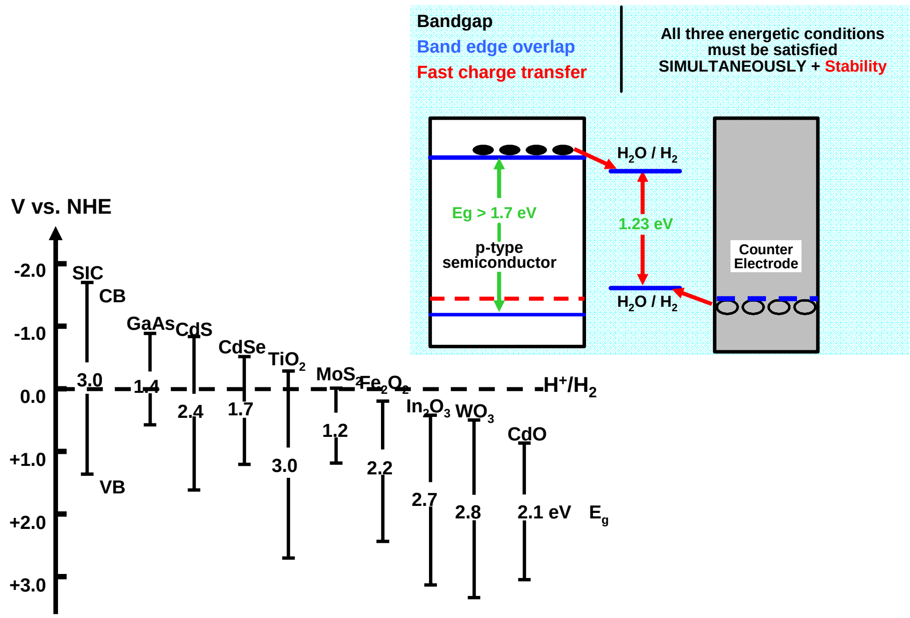
Polycrystalline or nanostructured films

Photoelectrochemical Cell

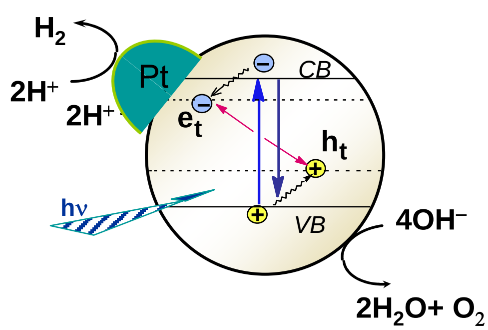


Light is Converted to Electrical+Chemical Energy

Band Edge and Energetic Considerations



Semiconductor (e.g., TiO_2) nanoparticles for hydrogen production



Hydrogen Evolution rates for various Photocatalysts (μl/hr)	
Pt/TiO_2	7.7
Pd/TiO_2	6.7
Rh/TiO_2	2.8
Ru/TiO_2	0.2
Sn/TiO_2	0.2
Ni/TiO_2	0.1
TiO_2	<0.1

Toshima, J. Phys. Chem. **1985,** *89,* 1902

2c Photoelectric Effect

The energy of the absorbed light is transferred to electrons in the atoms of the PV cell. With their newfound energy, these electrons escape from their normal positions in the atoms of the semiconductor PV material and become part of the electrical flow, or current, in an electrical circuit.

http://www1.eere.energy.gov/solar/multimedia.html

Timeline

1839

Edmond Becquerel discovered the process of using sunlight to produce an electric current in a solid material. But it took more than another century to truly understand this process. Scientists eventually learned that the photoelectric or photovoltaic (PV) effect caused certain materials to convert light energy into electrical energy at the atomic level.

1905

Albert Einstein publishes his paper on the photoelectric effect, along with a paper on his theory of relativity.
-Nobel Prize was awarded for this discovery in 1921

1954

Photovoltaic technology is born in the United States when Daryl Chapin, Calvin Fuller, and Gerald Pearson develop the silicon photovoltaic (or PV) cell at Bell Labs—the first solar cell capable of generating enough power from the sun to run everyday electrical equipment. Bell Telephone Laboratories then produces a silicon solar cell with 6% efficiency and later, 11% efficiency. See the California Solar Center for more information.

http://www.eere.energy.gov

Timeline

1964

NASA launches the first Nimbus spacecraft—a satellite powered by a 470-watt photovoltaic array. See NASA's Nimbus Program for more information.

1970

Exxon Corporation & Dr. Elliot Berman designs a significantly less costly solar cell, bringing the price down from $100 per watt to $20 per watt. Solar cells begin powering navigation warning lights and horns on offshore gas and oil rigs, and railroad crossings.

1980

ARCO Solar becomes the first company to produce more than 1 megawatt (a thousand kilowatts) of photovoltaic modules in one year.

1993

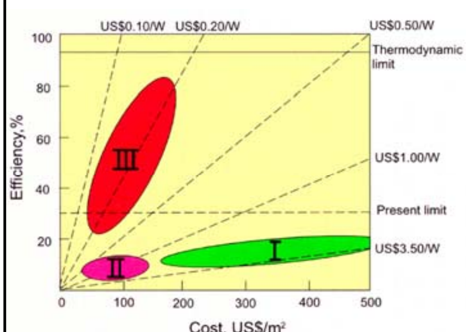
Pacific Gas & Electric installs the first grid-supported photovoltaic system in Kerman, California. The 500-kilowatt system is the first "distributed power" PV installation.

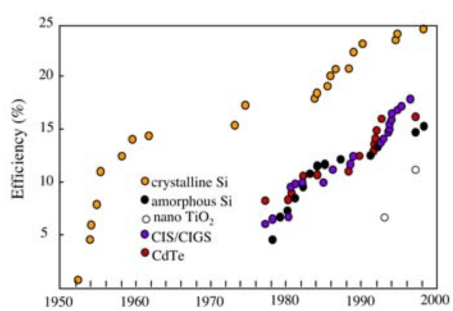
2001

Home Depot begins selling residential solar power systems in three stores in San Diego, California. A year later it expands sales to 61 stores nationwide.

In Spring 2002, largest solar electric system in the US began operating a top the Santa Rita Jail in Dublin, California. This solar installation, helps Alameda County reduce and stabilize energy costs.

Efficiency of Solar Cells

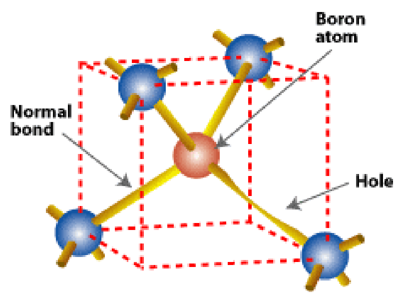


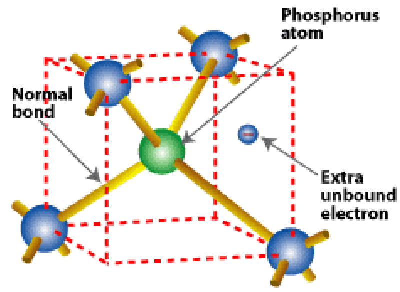


Efficiency Compared with Cost Per Unit Area of PV Devices (The diagonal lines show installed 2001 price of modules per peak-watt. The theoretical limit for Shockley-Queisser devices [present limit] is 32
Third generation devices [shown in red] may exceed this limit by using multiple absorbers, hot carrier effects, or photocurrent doubling via impact ionization. The latter two phenomena are associated with quantum size effects in semiconductors and are being studied in semiconductor nanocrystals).

L. Kazmerski, *Solar-Electric Power: A 2001 Device Overview*, National Center for Photovoltaics, National Renewable Energy Laboratory, Golden, CO (2001).
M. Green, *Annual Report, Third Generation Photovoltaics*, University of New South Wales, Sydney, Australia (2000).

n-and p-type Silicon





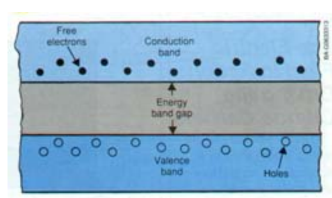
Doping with B or Ga leaves excess holes

Doping with P or As leaves excess electrons

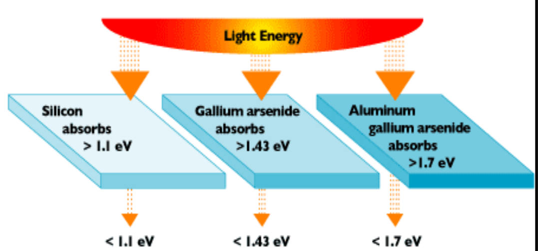
Introduction of an atom of another element into the silicon crystal to alter its electrical properties. The "dopant," which is the introduced element, has either three or five valence electrons

In a crystalline silicon cell, we need to contact p-type silicon with n-type silicon to create the built-in electrical field.

When photons of sun light strike a PV cell, only the photons with a certain level of energy are able to free electrons from their atomic bonds to produce an electric current. This level of energy, known as the band-gap energy, is the amount of energy required to move an outer-shell electron from the valence band (or level) to the conduction band (or level). It is different for each material and for different atomic structures of the same material.



For crystalline silicon, the band-gap energy is 1.1 electron-volts (eV). An electron-volt is equal to the energy an electron acquires when it passes through a potential of 1 volt in a vacuum. Other PV cell materials have band-gap energies ranging from 1 to 3.3 eV.

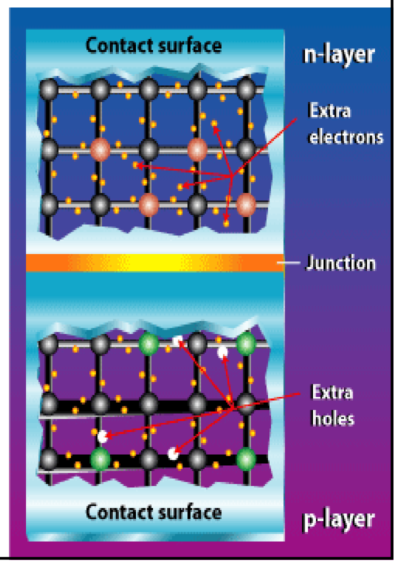


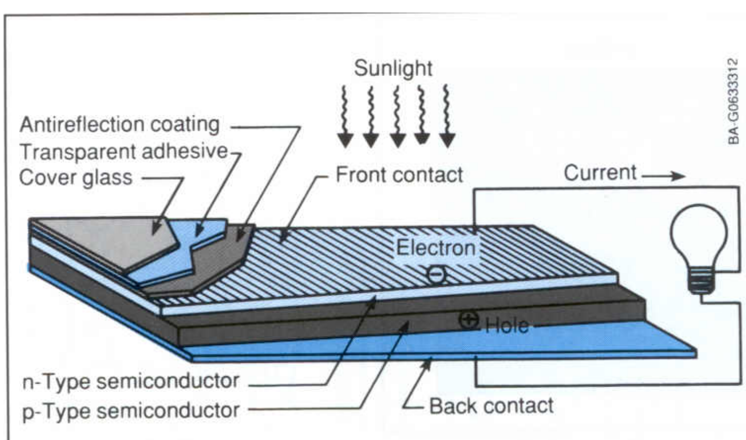
Determine the wavelength of light required for bandgap excitation.

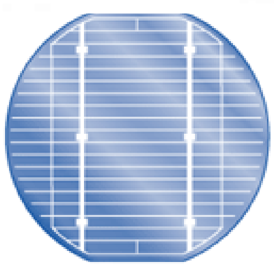
Principle of PV operation

When n- and p-type silicon come into contact, excess electrons move from the n-type side to the p-type side. The result is a buildup of positive charge along the n-type side of the interface and a buildup of negative charge along the p-type side.

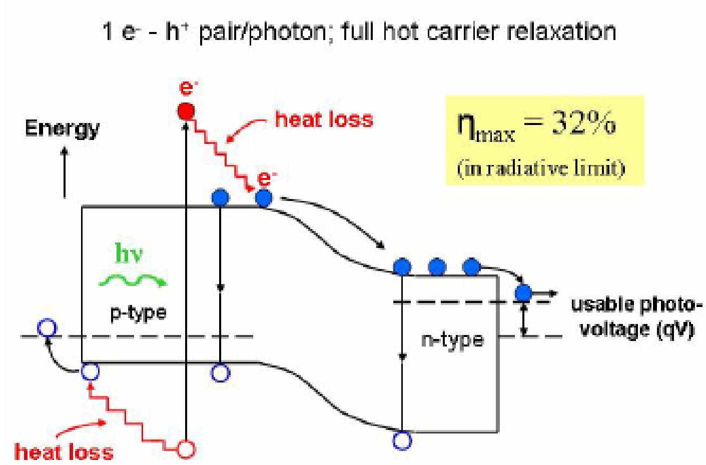
Because of the flow of electrons and holes, the two semiconductors behave like a battery, creating an electric field at the surface where they meet—what we call the **p/n junction**. The electrical field causes the electrons to move from the semiconductor toward the negative surface, where they become available to the electrical circuit. At the same time, the holes move in the opposite direction, toward the positive surface, where they await incoming electrons.



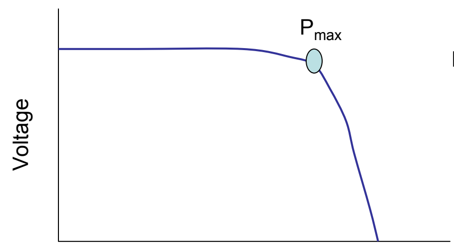




Grid contacts on the top surface of a typical cell are designed to have many thin, conductive fingers spreading to every part of the cell's surface.



The power from an electrical device such as a PV cell is equal to the product of the voltage (V) and the the current (I). Low-band-gap cells have high current but low voltage; high-band-gap cells have high voltage and low current. A compromise is necessary in the design of PV cells. Cells made of materials with band gaps between 1 eV and 1.8 eV can be used efficiently in PV devices.



Power (W)= Current (A) x Voltage (V)

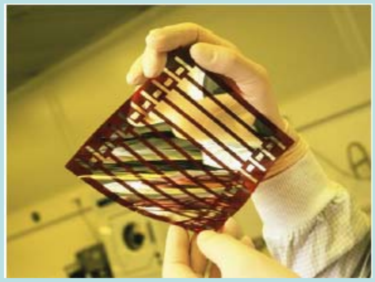
Emerging Areas

THIN Film Solar Cells

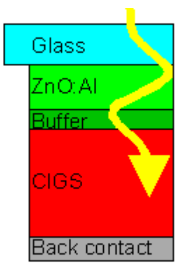
Organic Solar Cells

Dye Sensitized Solar Cells

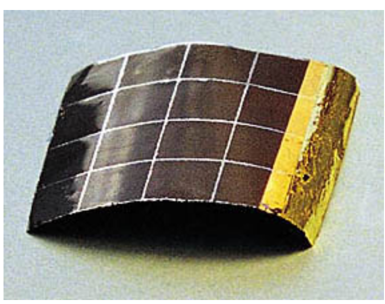
Quantum Dot Solar Cells

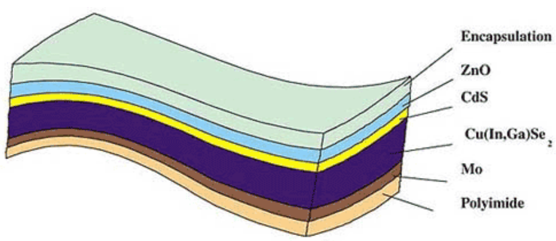


Cu(In,Ga)Se_2 (CIGS) solar cells



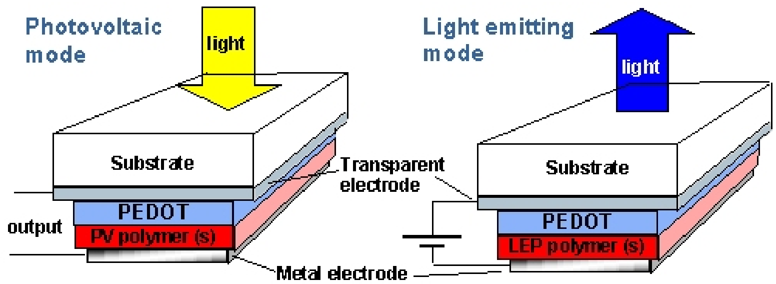
CIGS solar cells are formed by five very thin films on a plate of glass. The picture above shows, schematically, the structure of a solar cell. First the molybdenum back contact (the plus side) is deposited onto the glass plate. On top of that layer, the CIGS film, which absorbs the light, is evaporated. Two very thin films of cadmium sulfide (CdS) and zinc oxide (ZnO) are then put ontop of the CIGS, and the solar cell is completed by a layer of aluminium doped zinc oxide (ZnO:Al).





http://www.tfp.ethz.ch/HESC/HESC.html

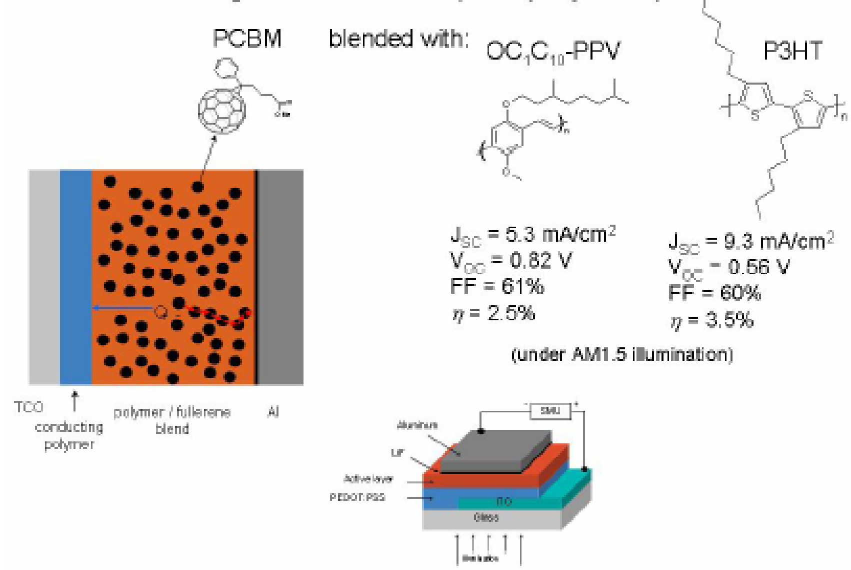
Organic Solar Cells



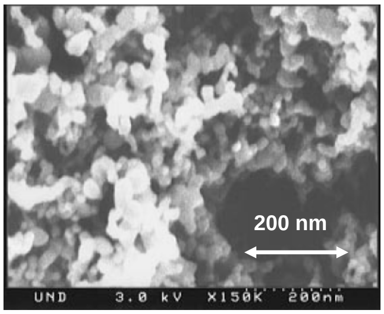
The active polymer layer is sandwiched between two conducting electrodes. One of the electrodes is transparent to let the light in or out depending on the application. An additional conducting polymer layer, called PEDOT, is sometimes used to flatten the transport contact and help inject / carry positive charges in or out of the device.

http://www.cdtltd.co.uk/technology/41.asp

Organic Solar Cell (with polymers)



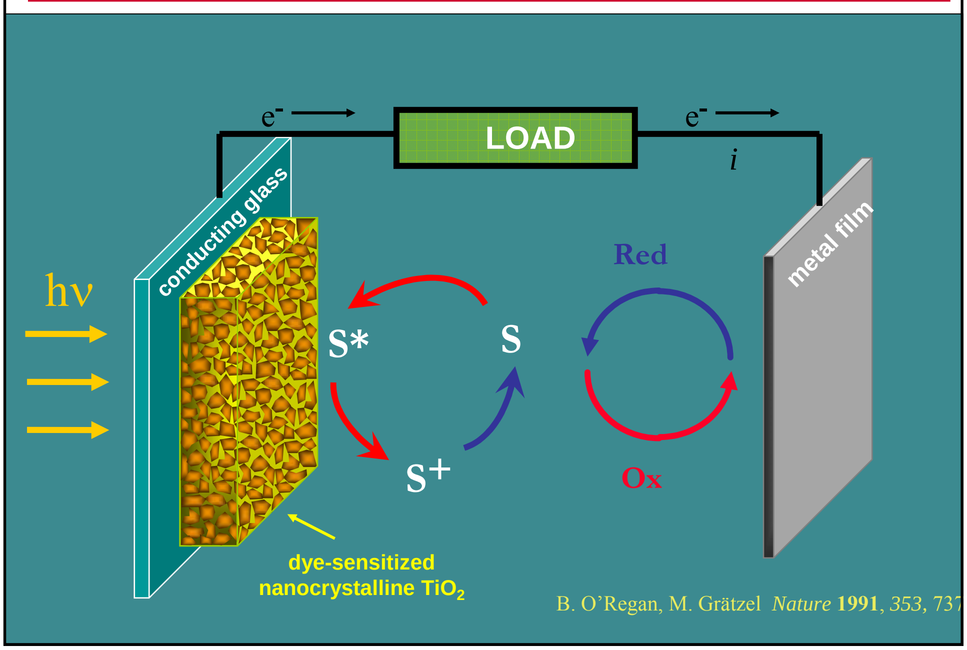
Nanocrystalline Titanium Dioxide



Nanostructured TiO_2 film

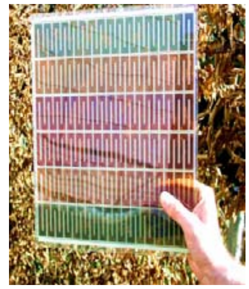
- Particle Size 15-30 nm
- Bandgap 3.2 eV (absorbs only in UV)
- Surface Area
  is larger than single crystal
  ~1000 times
- Commonly prepared in rutile and anatase forms
- Different Electrochemistry
  from single crystal semiconductors

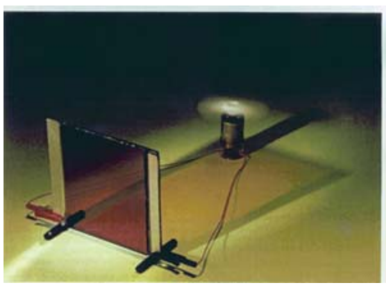
nanocrystalline solar cell



Dye Sensitized Photochemical Solar Cells

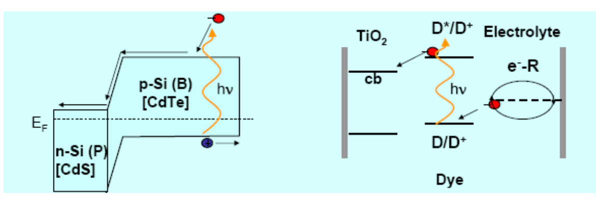
Development of SC nanocluster based cells with more than 10% power conversion efficiency.
Photon-to-photocurrent efficiency up to 100% has been claimed!

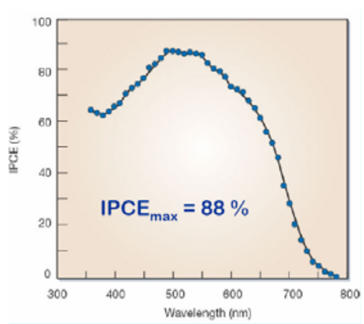


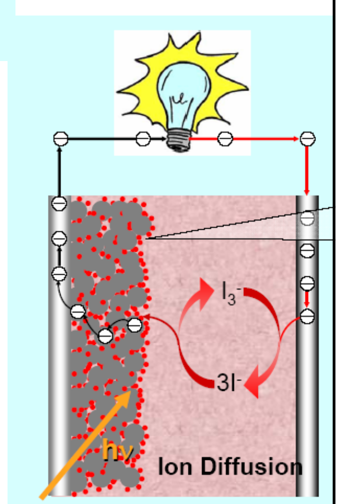


Source: *http://dcwww.epfl.ch/icp/ICP-2/icp-2.html*

Principle of Dye-sensitized Photochemical Solar Cell



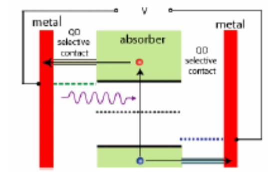




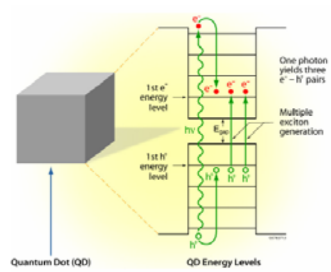
M. Grätzel, Nature 2001, 414, 338−344.
B. O'Regan, M. Grätzel, Nature 1991, 353, 737−740

Quantum Dot Solar Cells

Tunable band edge
  Offers the possibility to harvest light energy over a wide range of visible-ir light with selectivity

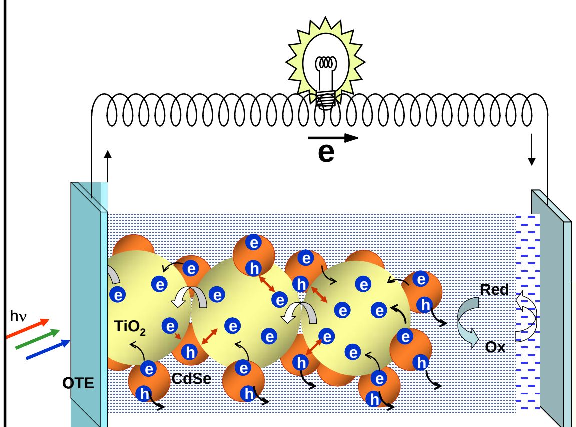


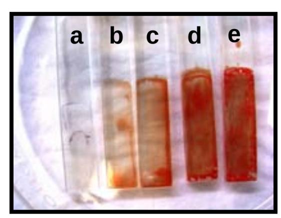
Hot carrier injection from higher excited state
  (minimizing energy loss during thermalization of excited state)

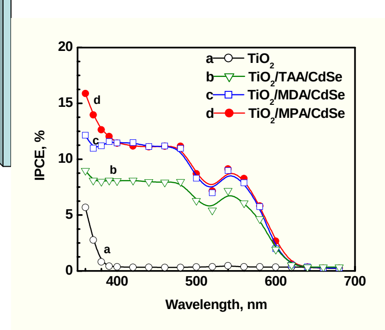


Multiple exciton generation solar cells.
  Impact ionization allows single high energy photons to multiple electron-hole pairs

CdSe Quantum Dot Solar Cells







Robel, Bunker, Kamat J. Am. Chem. Soc. 2006,128, 2385-2393

Photochemical Solar Cells

Each module 24 cm x24 cm
AISIN & TOYOTA

Konarka

Wall-integrated DSC panels (Prototype)