Molecular photonics

Lecture 11.

Solar Energy Conversion

World energy statistics and projections

Quantity	Definition	Units	2001	2050	2100
N	Population	B persons	6.145	9.4	10.4
GDP	GDP	T $/yr	46	140	284
GDP/N	Per capita GDP	$/(person-yr)	7,470	14,850	27,320
$\dot{E}$/GDP	Energy intensity	W/($/yr)	0.294	0.20	0.15
$\dot{E}$	Energy consumption rate	TW/yr	13.5	27.6	43.0
C/E	Carbon intensity	KgC/(W·yr)	0.49	0.40	0.31
$\dot{C}$	Carbon emission rate	GtC/yr	6.57	11.0	13.3
$\dot{C}$	Equivalent CO_2 emission rate	$GtCO_2$/yr	24.07	40.3	48.8

Nathan S. Lewis and Daniel G. Nocera
Powering the planet: Chemical challenges in solar energy utilization
PNAS **2006,** *103*, 15729

Problems

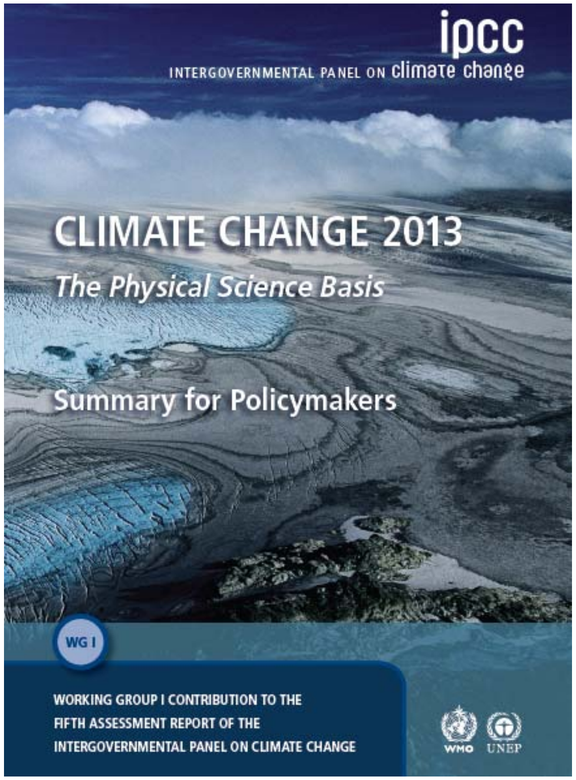
- Environment – pollution and global warming (greenhouse effect)
- Security - fossil fuel sources are in problematic countries
- Unsustainable (exhaustible)
- Unpredictable costs
- Primitive chemistry

Global Warming


APRIL 28, 2008
Obama's Working-Class Woes
Why More Women Are Choosing C-Sections
Can Richard Branson Save the Airline Industry?
TIME
SPECIAL ENVIRONMENT ISSUE
How to Win The War On Global Warming
BY BRYAN WALSH
www.time.com


The Economist
Iraq, the war and the constitution
PAGES 22-24
America's unhappy borders
PAGES 13 AND 31
Brother Roger, Taizé's melodic monk
OBITUARY, PAGE 70
Yum! Brands' finger lickin' growth
PAGES 60-62
AUGUST 27TH–SEPTEMBER 2ND 2005
The oiloholics
CHINA

ipcc INTERGOVERNMENTAL PANEL ON climate change WMO UNEP



Warming of the climate system is unequivocal, and since the 1950s, many of the observed changes are unprecedented over decades to millennia. The atmosphere and ocean have warmed, the amounts of snow and ice have diminished, sea level has risen, and the concentrations of greenhouse gases have increased

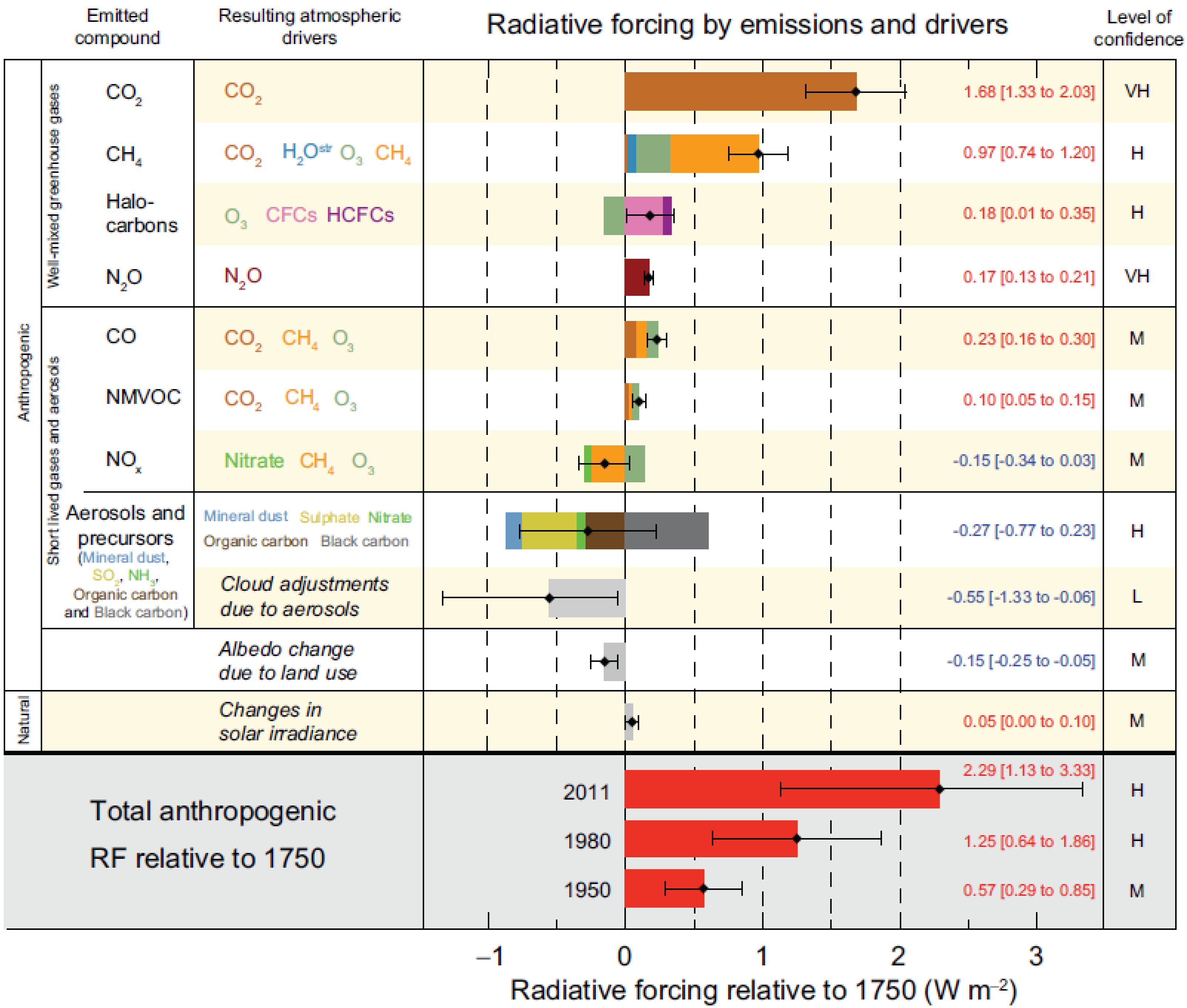
Human influence has been detected in warming of the atmosphere and the ocean, in changes in the global water cycle, in reductions in snow and ice, in global mean sea level rise, and in changes in some climate extremes (see Figure SPM.6 and Table SPM.1). This evidence for human influence has grown since AR4. It is *extremely likely* that human influence has been the dominant cause of the observed warming since the mid-20th century

Continued emissions of greenhouse gases will cause further warming and changes in all components of the climate system. Limiting climate change will require substantial and sustained reductions of greenhouse gas emissions.

The global warming controversy

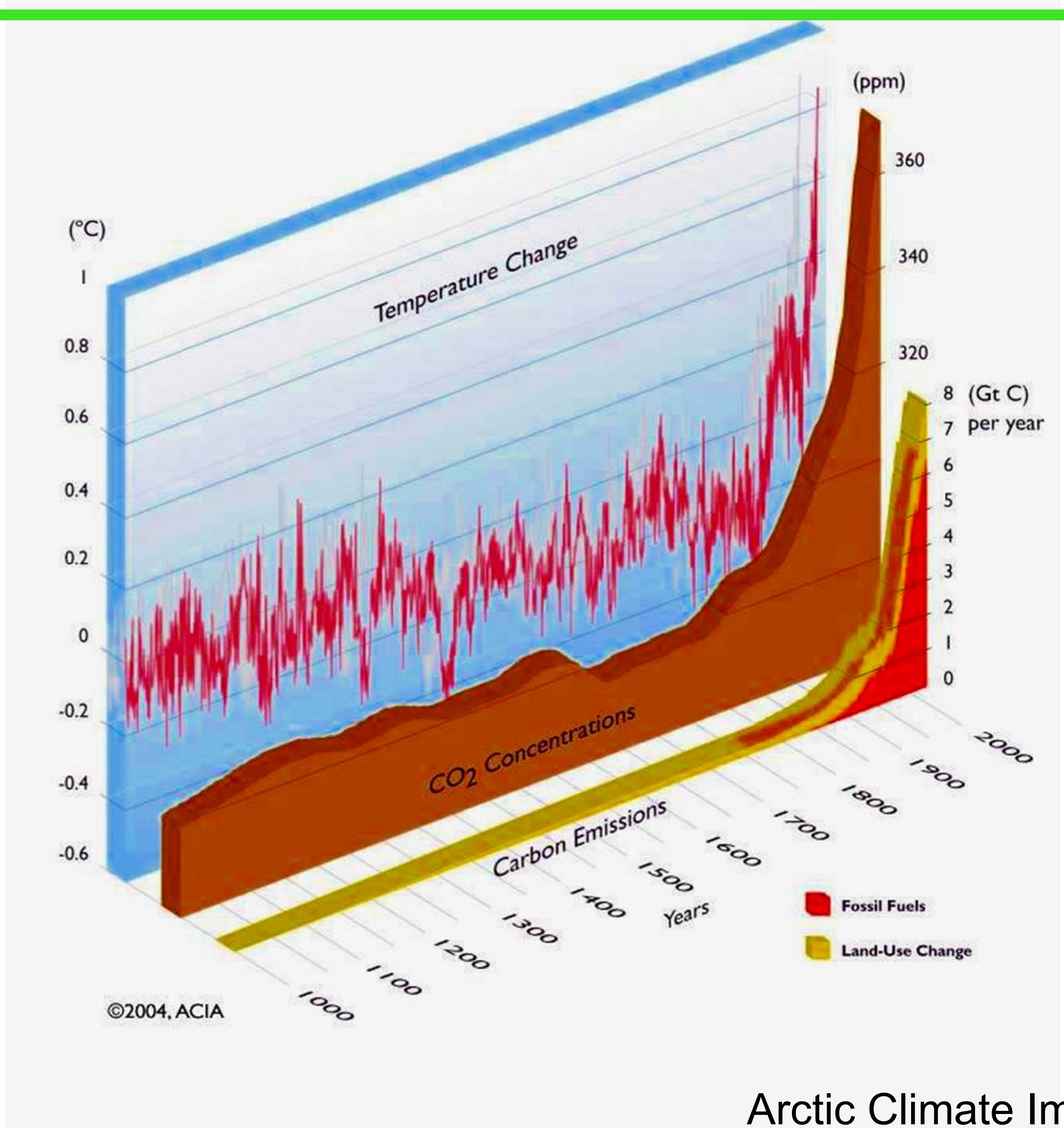
The global warming controversy is a variety of disputes regarding the nature, causes, and consequences of global warming. The disputed issues include the causes of increased global average air temperature, especially since the mid-20th century, whether this warming trend is unprecedented or within normal climatic variations, whether humankind has contributed significantly to it, and whether the increase is wholly or partially an artifact of poor measurements. Additional disputes concern estimates of climate sensitivity, predictions of additional warming, and what the consequences of global warming will be.

The controversy is significantly more pronounced in the popular media than in the scientific literature, where there is a strong consensus that global surface temperatures have increased in recent decades and that the trend is caused mainly by human-induced emissions of greenhouse gases.



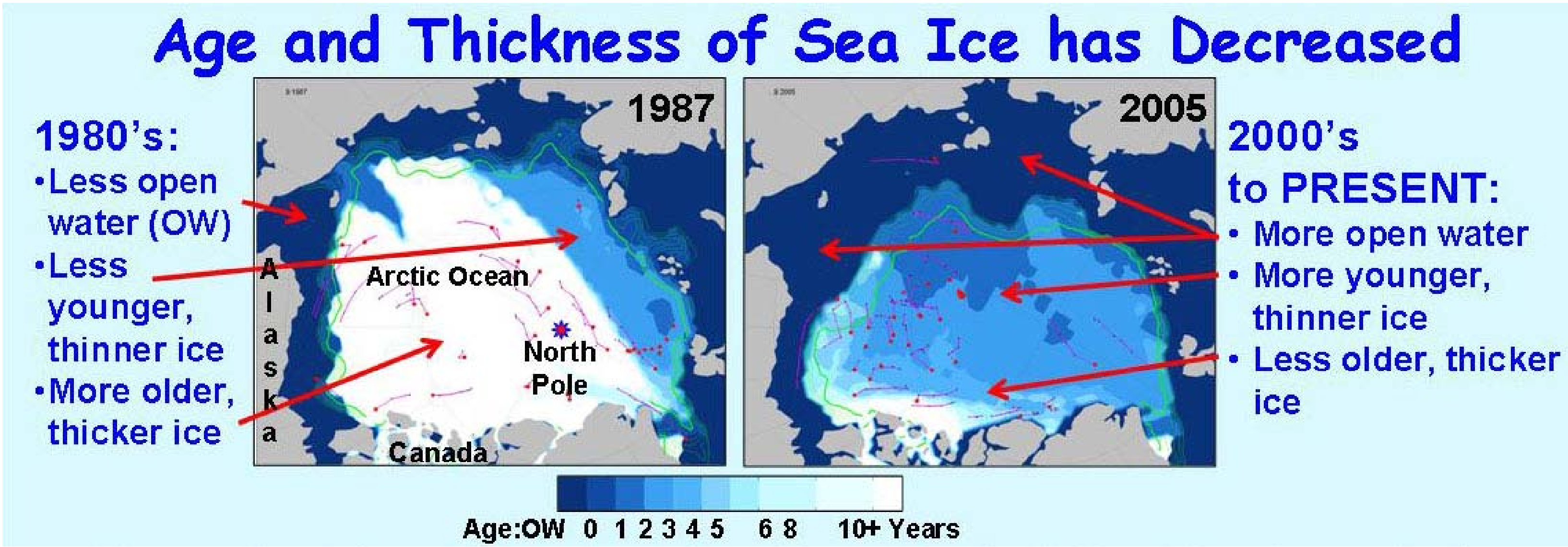
Emitted compound
Resulting atmospheric drivers
Radiative forcing by emissions and drivers
Level of confidence
Anthropogenic
Well-mixed greenhouse gases
CO_2
CO_2
1.68 [1.33 to 2.03]
VH
CH_4
CO_2 H_2O^{str} O_3 CH_4
0.97 [0.74 to 1.20]
H
Halo-carbons
O_3 CFCs HCFCs
0.18 [0.01 to 0.35]
H
N_2O
N_2O
0.17 [0.13 to 0.21]
VH
Short lived gases and aerosols
CO
CO_2 CH_4 O_3
0.23 [0.16 to 0.30]
M
NMVOC
CO_2 CH_4 O_3
0.10 [0.05 to 0.15]
M
NO_x
Nitrate CH_4 O_3
-0.15 [-0.34 to 0.03]
M
Aerosols and precursors (Mineral dust, SO_2, NH_3, Organic carbon and Black carbon)
Mineral dust Sulphate Nitrate Organic carbon Black carbon
-0.27 [-0.77 to 0.23]
H
Cloud adjustments due to aerosols
-0.55 [-1.33 to -0.06]
L
Albedo change due to land use
-0.15 [-0.25 to -0.05]
M
Natural
Changes in solar irradiance
0.05 [0.00 to 0.10]
M
Total anthropogenic RF relative to 1750
2011
2.29 [1.13 to 3.33]
H
1980
1.25 [0.64 to 1.86]
H
1950
0.57 [0.29 to 0.85]
M
–1
0
1
2
3
Radiative forcing relative to 1750 (W m^{-2})

Closer to the present. 1000 years of global CO_2, carbon and temperature change.



Arctic Climate Impact Assessment

Arctic Sea Ice



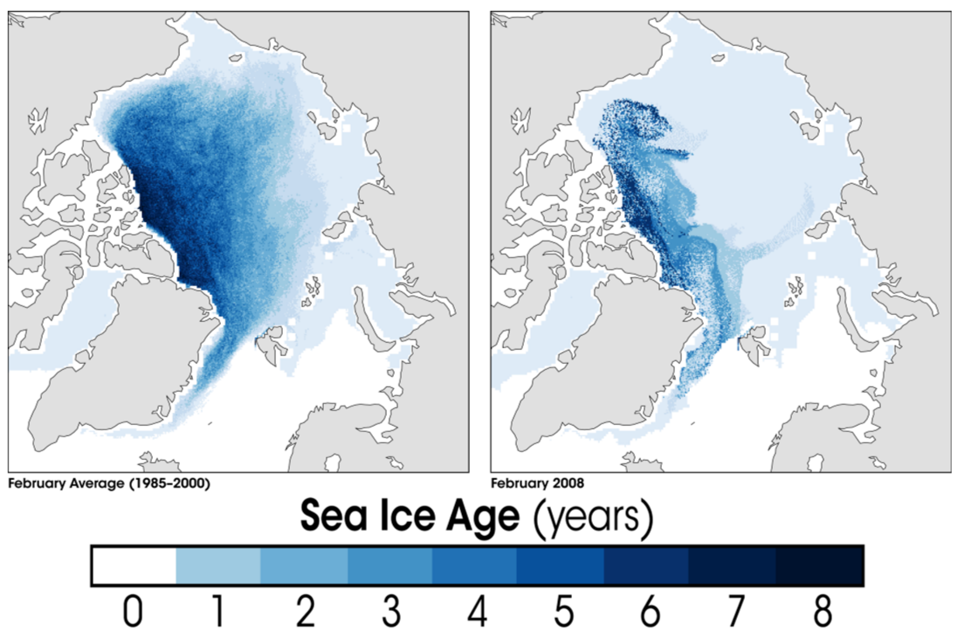
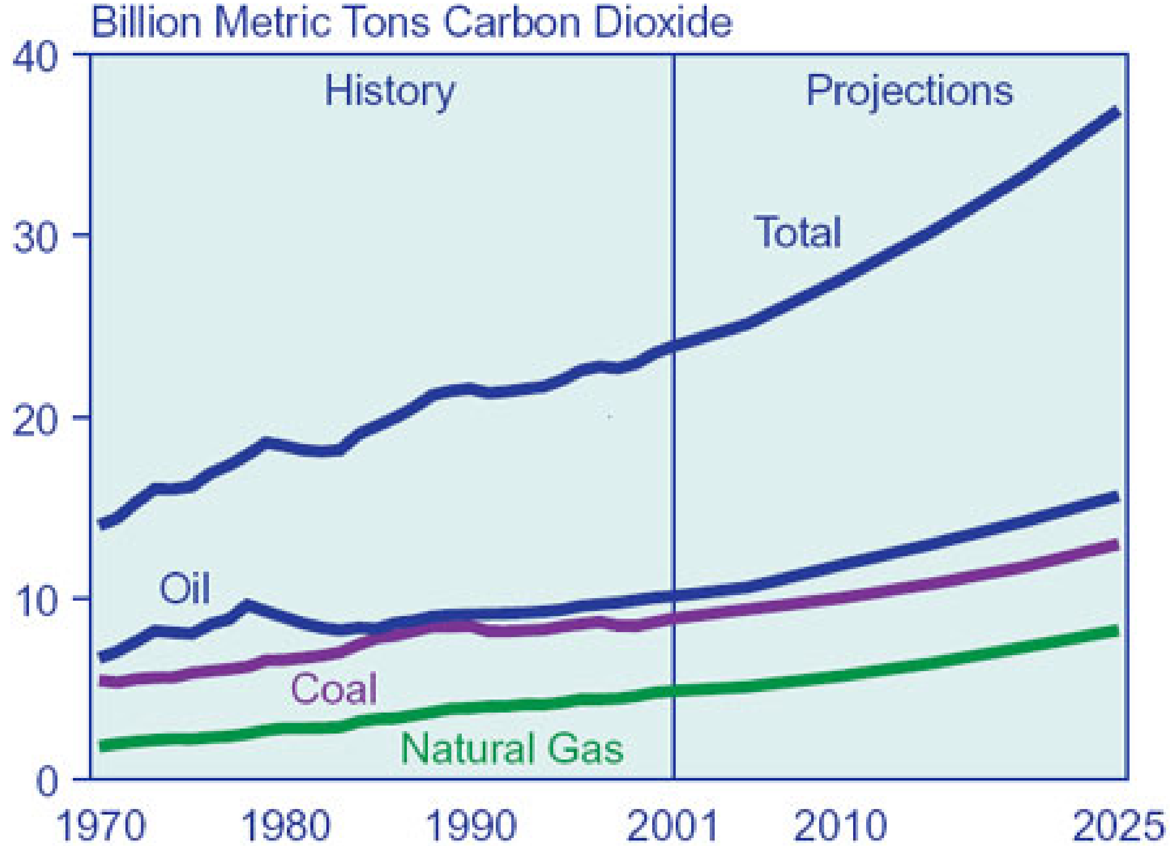
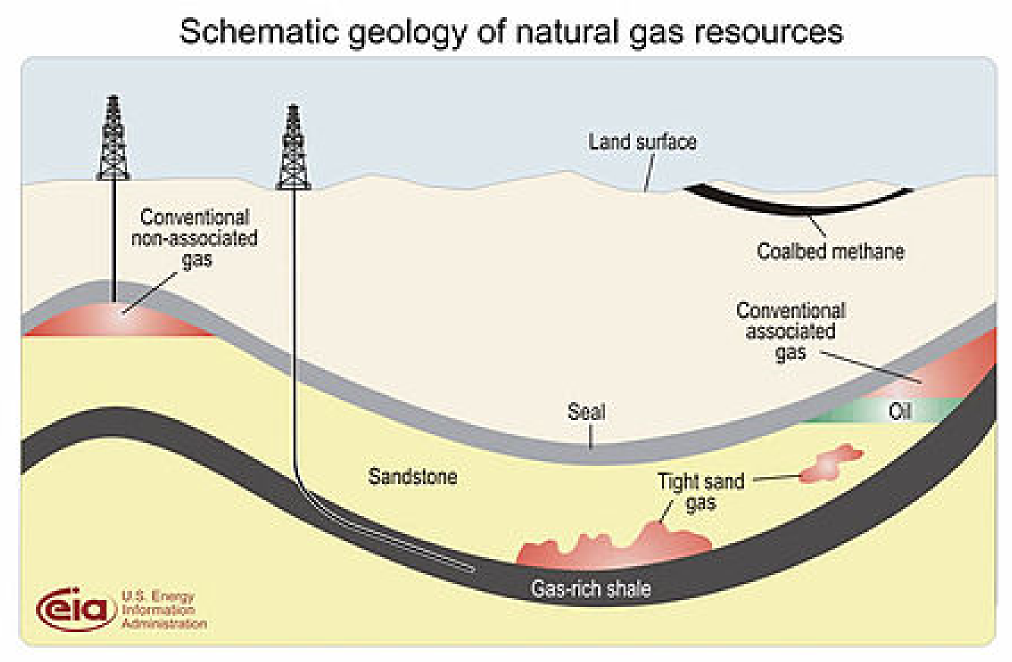


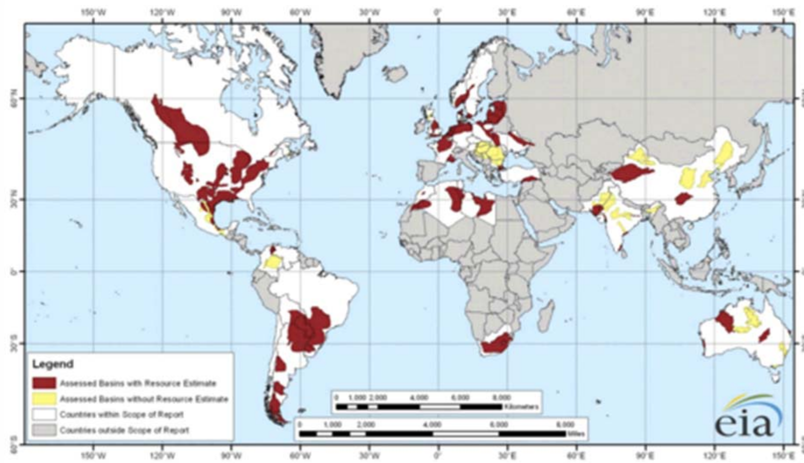
Figure 17. World Energy-Related Carbon Dioxide Emissions by Fuel Type, 1970-2025

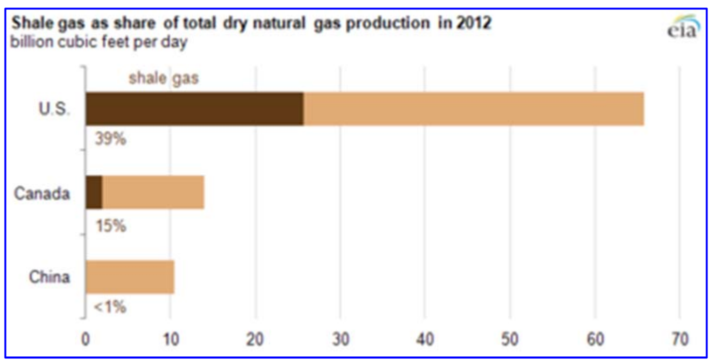


Sources: **History:** Energy Information Administration (EIA), *International Energy Annual 2001*, DOE/EIA-0219(2001) (Washington, DC, February 2003), web site www.eia.doe.gov/iea/. **Projections:** EIA, System for the Analysis of Global Energy Markets (2004).

Shale gas/oil







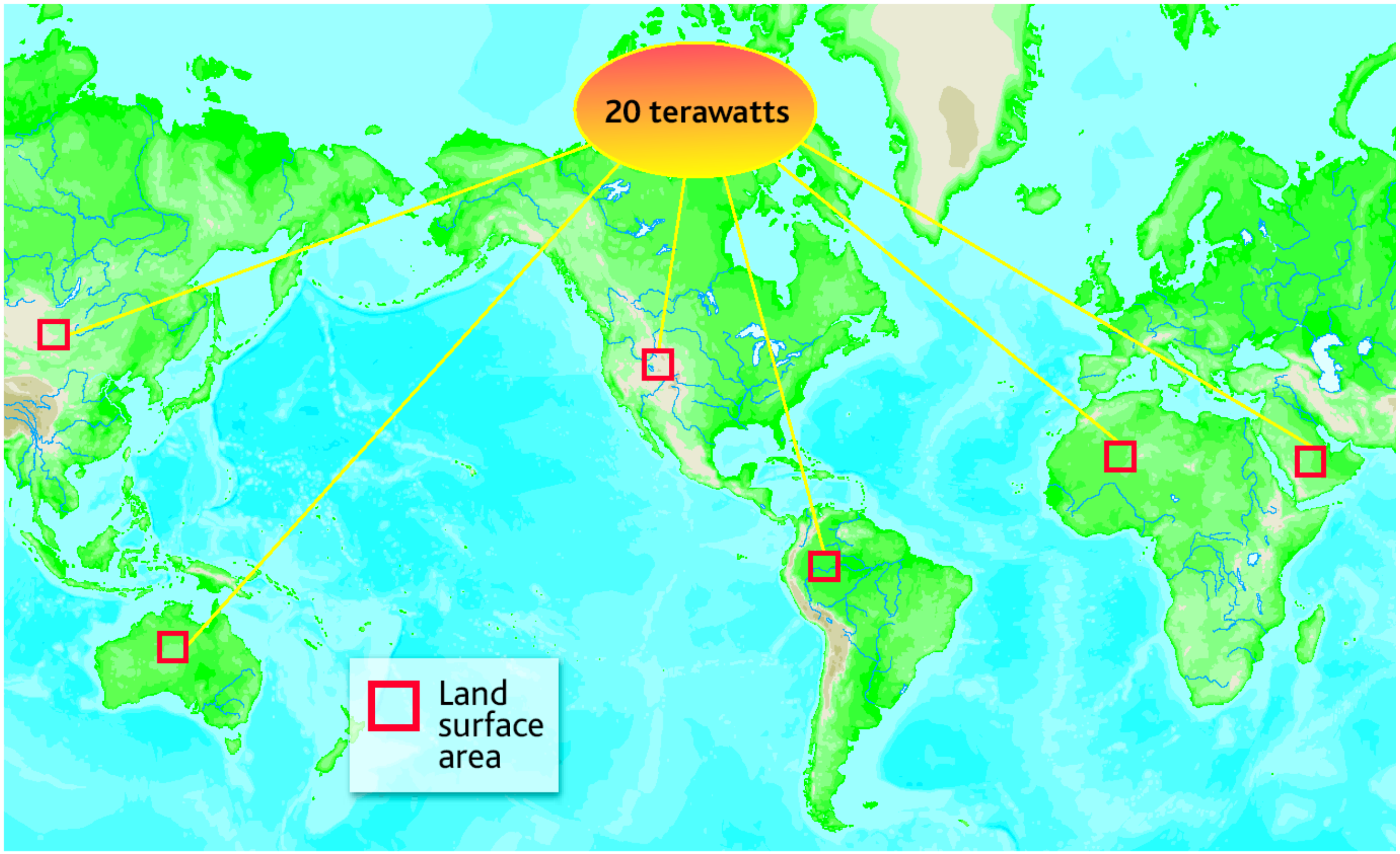
As of 2013, the US, Canada, and China are the only countries producing shale gas in commercial quantities. The US and Canada are the only countries where shale gas is a significant part of the gas supply.

Solutions: carbon-neutral energy sources

- Nuclear
- Solar

Sunlight is by far the most abundant global carbon-neutral energy resource. More solar energy strikes the surface of the earth in one hour than is obtained from all of the fossil fuels consumed globally in a year.

Solar energy conversion

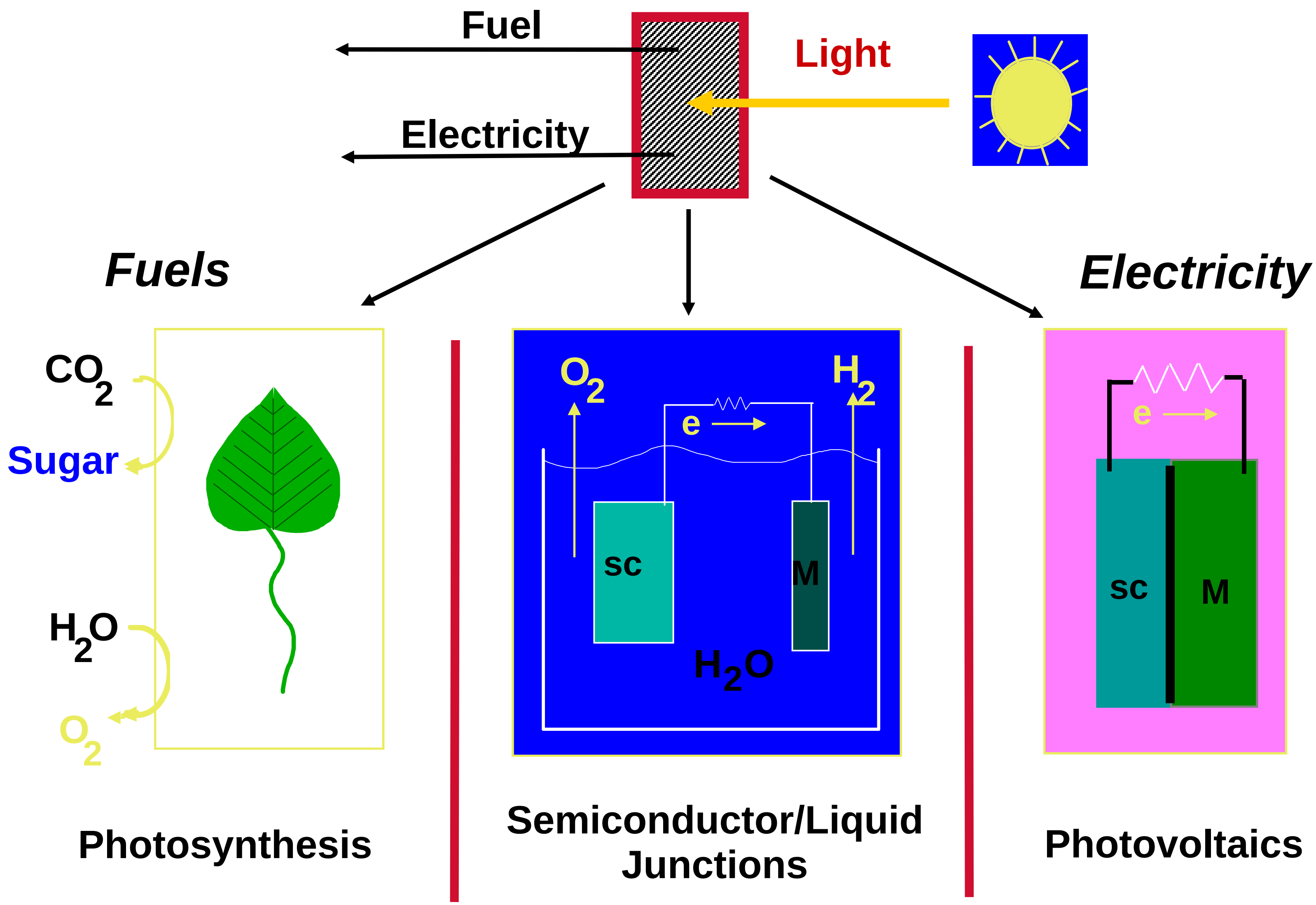


Global need. This map shows the amount of land needed to generate 20 TW with 10% efficient solar cells.

Conversion strategies - Solar

- Light to electricity – solar cells. Currently commercial technology (Si).
- Light to fuel – chemical solar energy conversion. Utilized in photosynthesis.

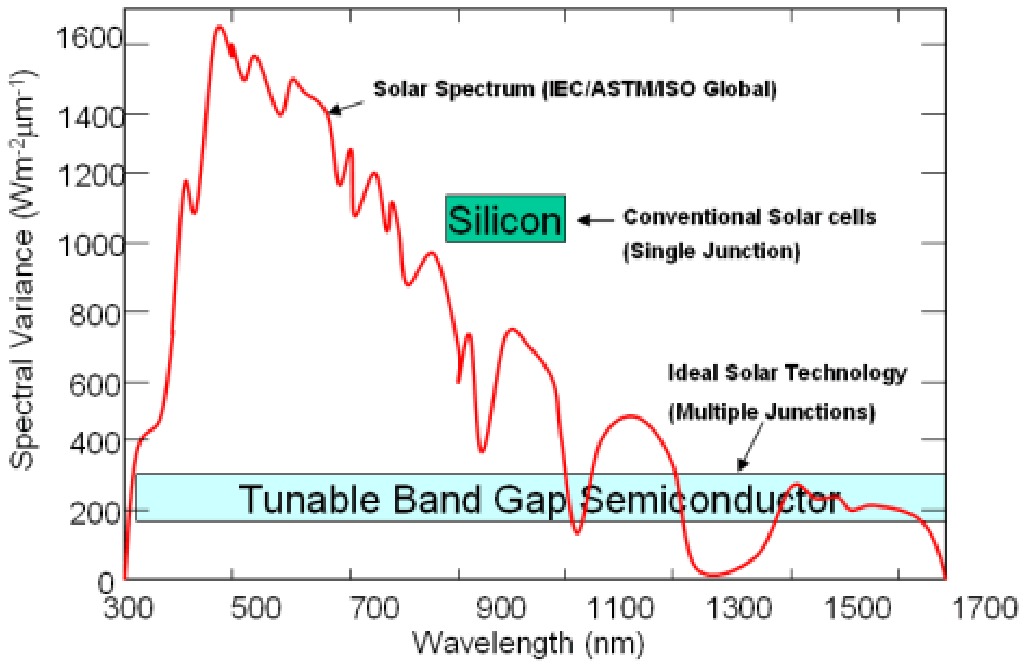
Energy Conversion Strategies

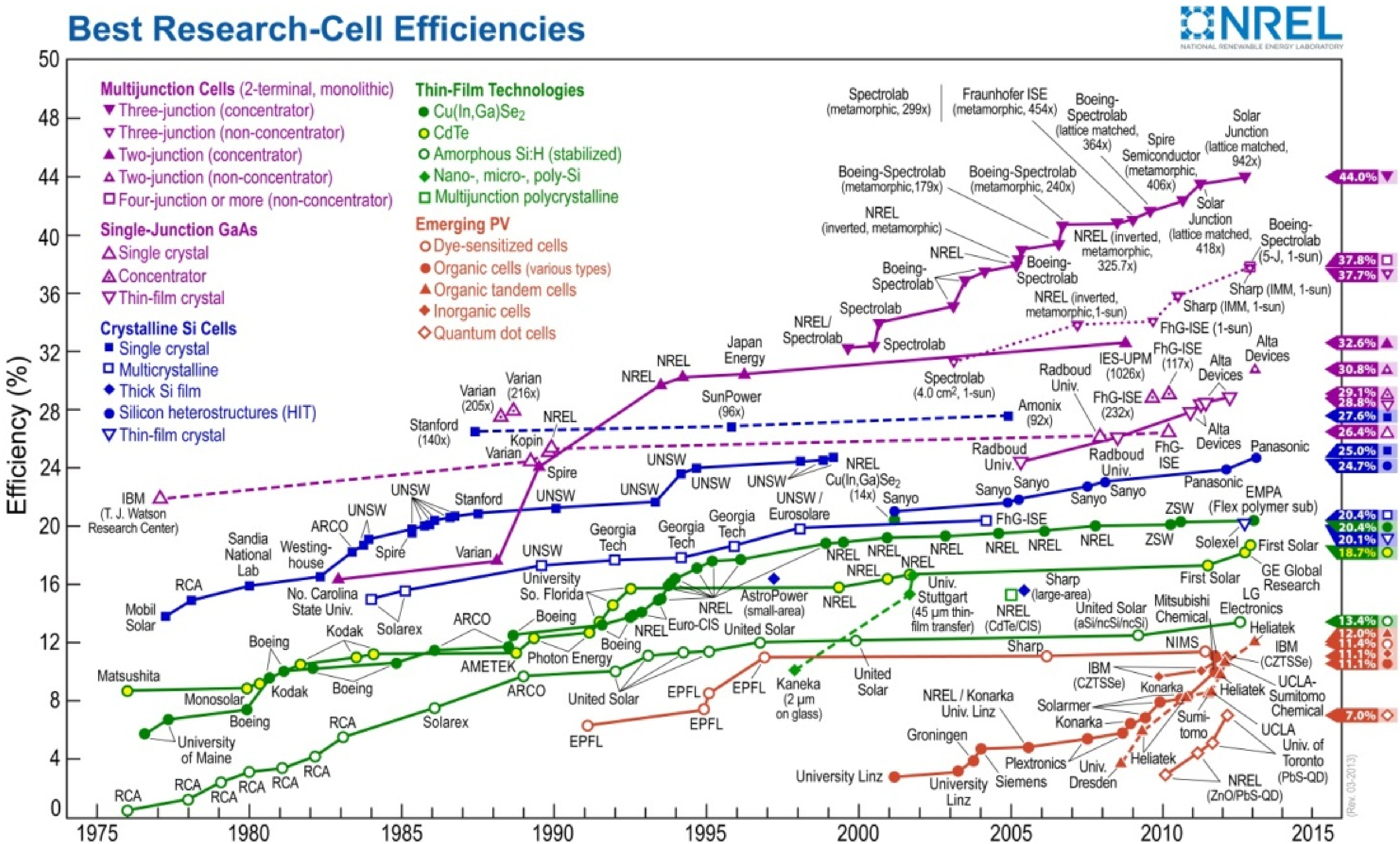


Solar cells

- Semiconductor (silicon, GaAs, etc.)
- Organic
- Nanocrystalline dye-sensitized (Grätzel)
- Quantum dot

SPECTRAL COMPOSITION OF SOLAR RADIATION & USEFUL SOLAR CELL OPTICAL RANGES

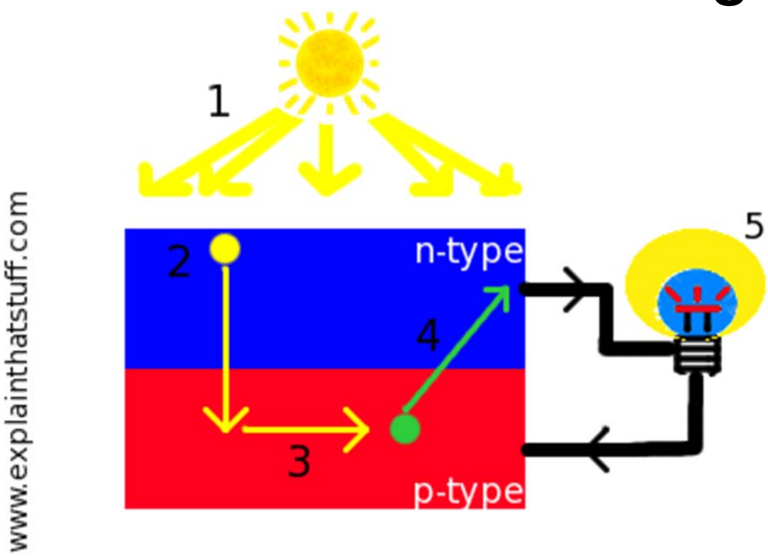


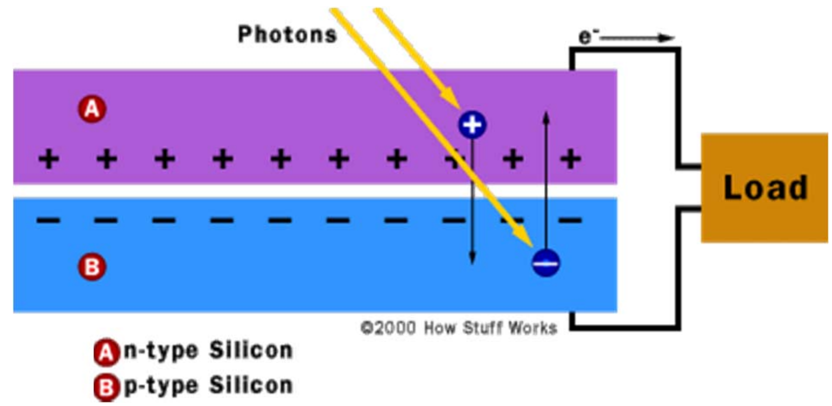


Best Research-Cell Efficiencies
NREL
NATIONAL RENEWABLE ENERGY LABORATORY
Efficiency (%)
Multijunction Cells (2-terminal, monolithic)
Three-junction (concentrator)
Three-junction (non-concentrator)
Two-junction (concentrator)
Two-junction (non-concentrator)
Four-junction or more (non-concentrator)
Single-Junction GaAs
Single crystal
Concentrator
Thin-film crystal
Crystalline Si Cells
Single crystal
Multicrystalline
Thick Si film
Silicon heterostructures (HIT)
Thin-film crystal
Thin-Film Technologies
Cu(In,Ga)Se2
CdTe
Amorphous Si:H (stabilized)
Nano-, micro-, poly-Si
Multijunction polycrystalline
Emerging PV
Dye-sensitized cells
Organic cells (various types)
Organic tandem cells
Inorganic cells
Quantum dot cells
44.0%
37.8%
37.7%
32.6%
30.8%
29.1%
28.8%
27.6%
26.4%
25.0%
24.7%
20.4%
20.4%
20.1%
18.7%
13.4%
12.0%
11.4%
11.1%
11.1%
7.0%
(Rev. 03-2013)

Si solar cell

How solar cells turn light into electricity



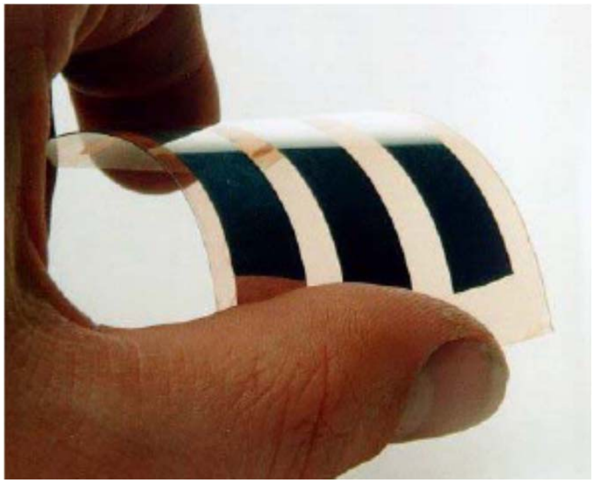


A solar cell is a sandwich of n-type silicon and p-type silicon

1. When sunlight shines on the cell, photons bombard the upper surface.
2. The photons carry their energy down through the cell.
3. The photons give up their energy to electrons in the lower, p-type layer.
4. The electrons use this energy to jump across the barrier into the upper, n-type layer and escape out into the circuit.
5. Flowing around the circuit, the electrons make the lamp light up.

Organic solar cells

- Efficiency is high (25-30%) for Si or GaAs but requires high quality, **costly**, crystalline materials
- Seek cheap materials with lower efficiency for net cost reductions
- Organic materials offer:
  – Flexibility
  – Large area deposition
  – Color, semi-transparency
  – Performance in low and diffuse light
  – Insensitivity to temperature

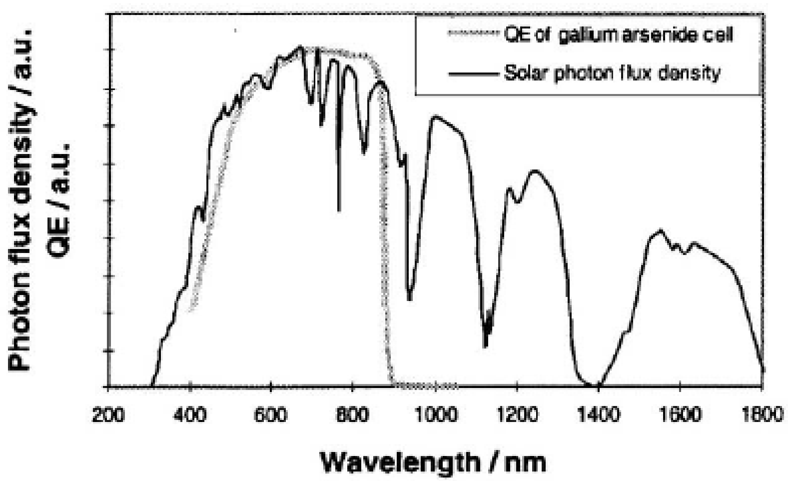


Processes necessary for photovoltaic activity:

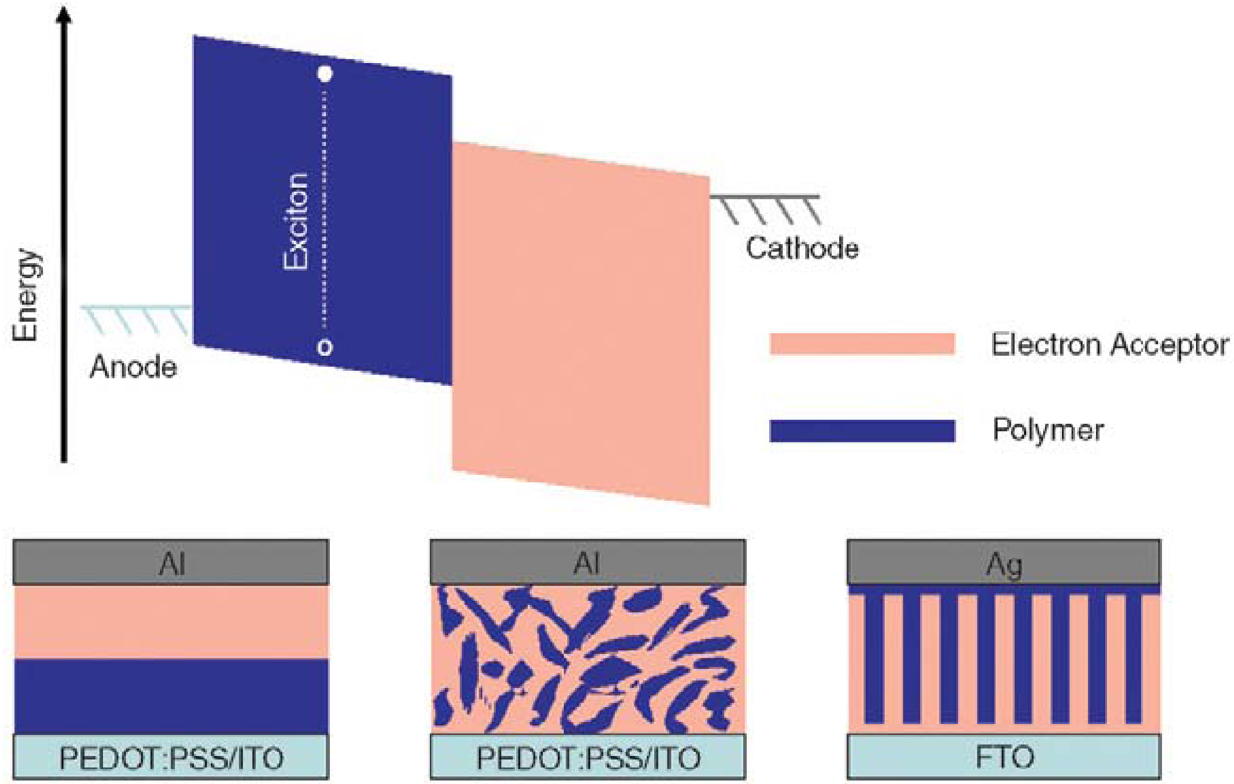
- Light Absorption: *matching the solar spectrum*

- Charge Generation: *efficient photoinduced charge transfer (long-lived CS)*

- Charge Transport and Collection at the Electrodes: *better charge carrier mobility (optimal cell morphology and interaction with electrodes)*

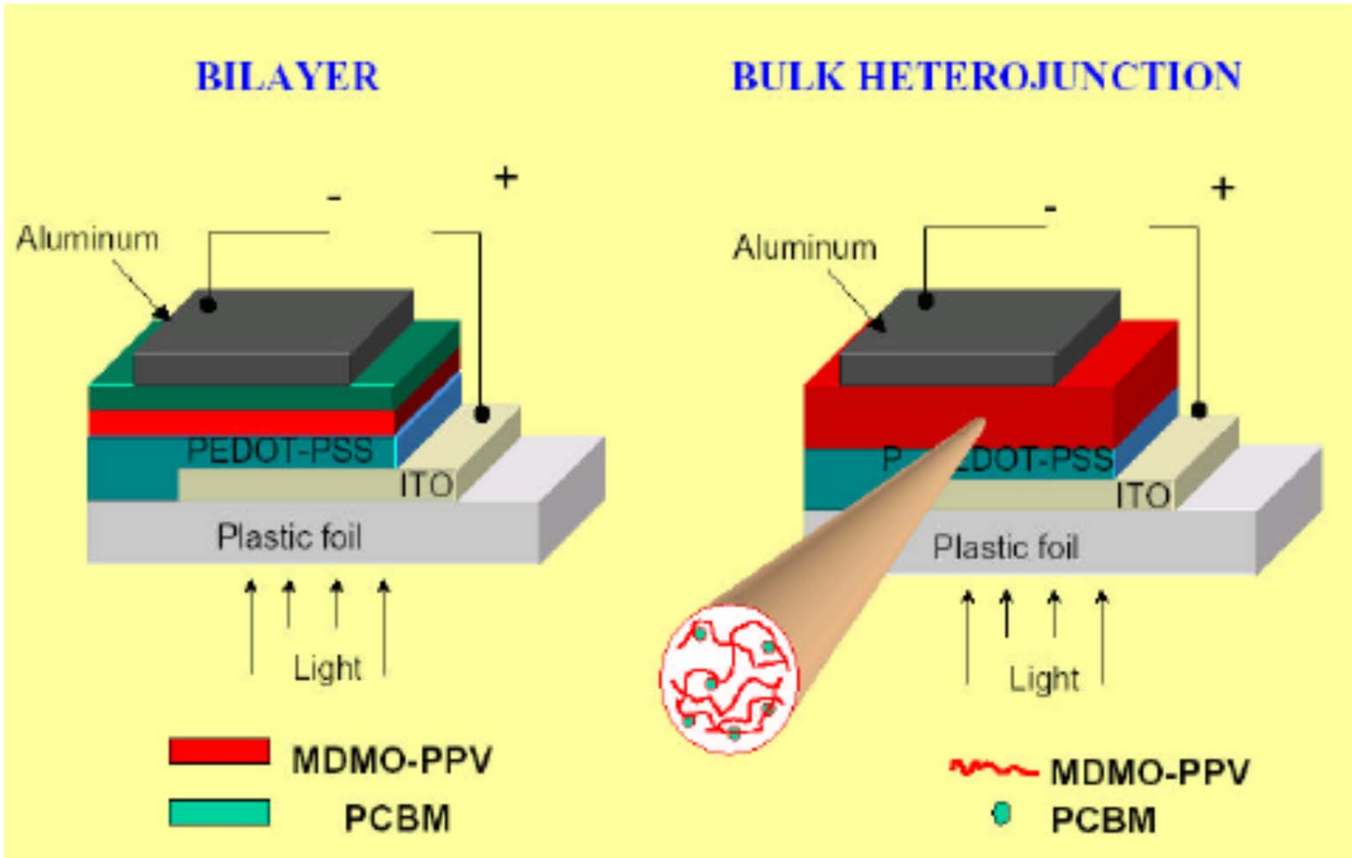


Organic Solar Cells

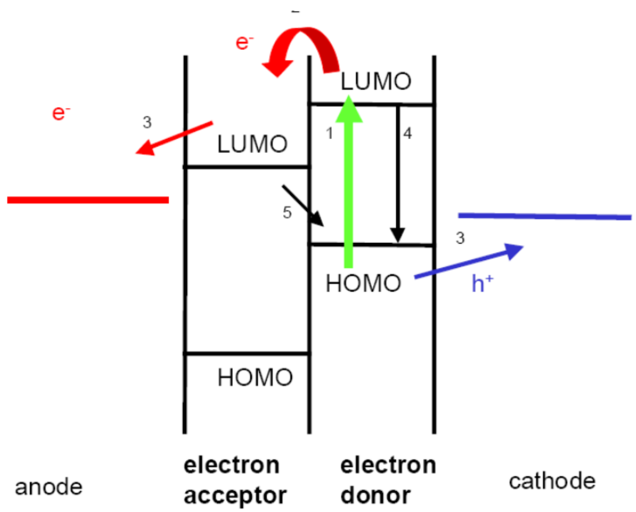


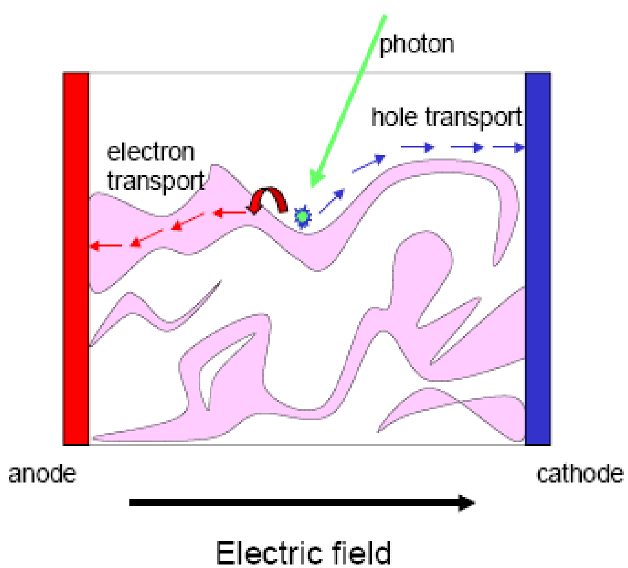
Bulk heterojunction **ordered heterojunction**

McGehee et al. *Materials Today* **2007**, *10*, 28

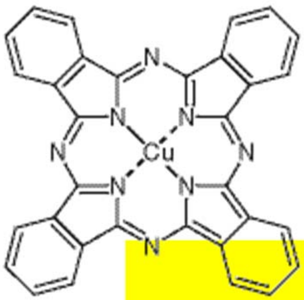

BILAYER
BULK HETEROJUNCTION
Aluminum
-
+
PEDOT-PSS
ITO
Plastic foil
Light
MDMO-PPV
PCBM
Aluminum
-
+
PEDOT-PSS
ITO
Plastic foil
Light
MDMO-PPV
PCBM

Bulk heterojunction solar cells

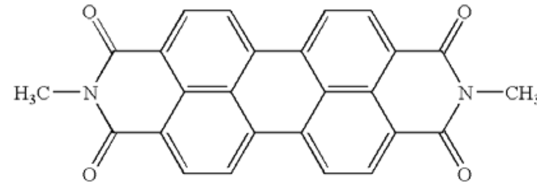




- Blend hole accepting with electron accepting material
- Length scale of blend ~ exciton diffusion length
- Charge separation at D-A interface
- Efficient injection into electrode



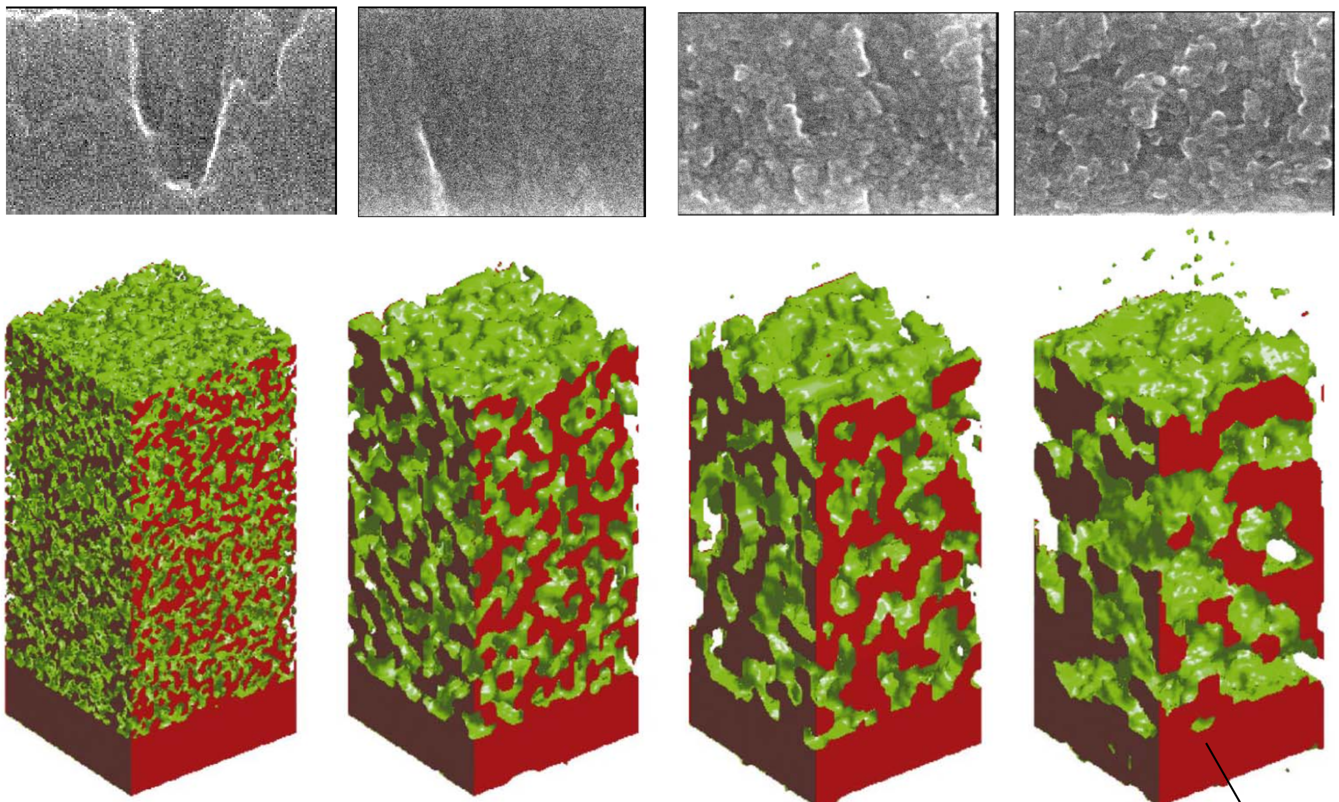
Magic of Annealing?



CuPc:PTCBI (3:4), 1.4% efficiency

Copper phthalocyanine/3,4,9,10-perylene tetracarboxylic bis-benzimidazole

SEM

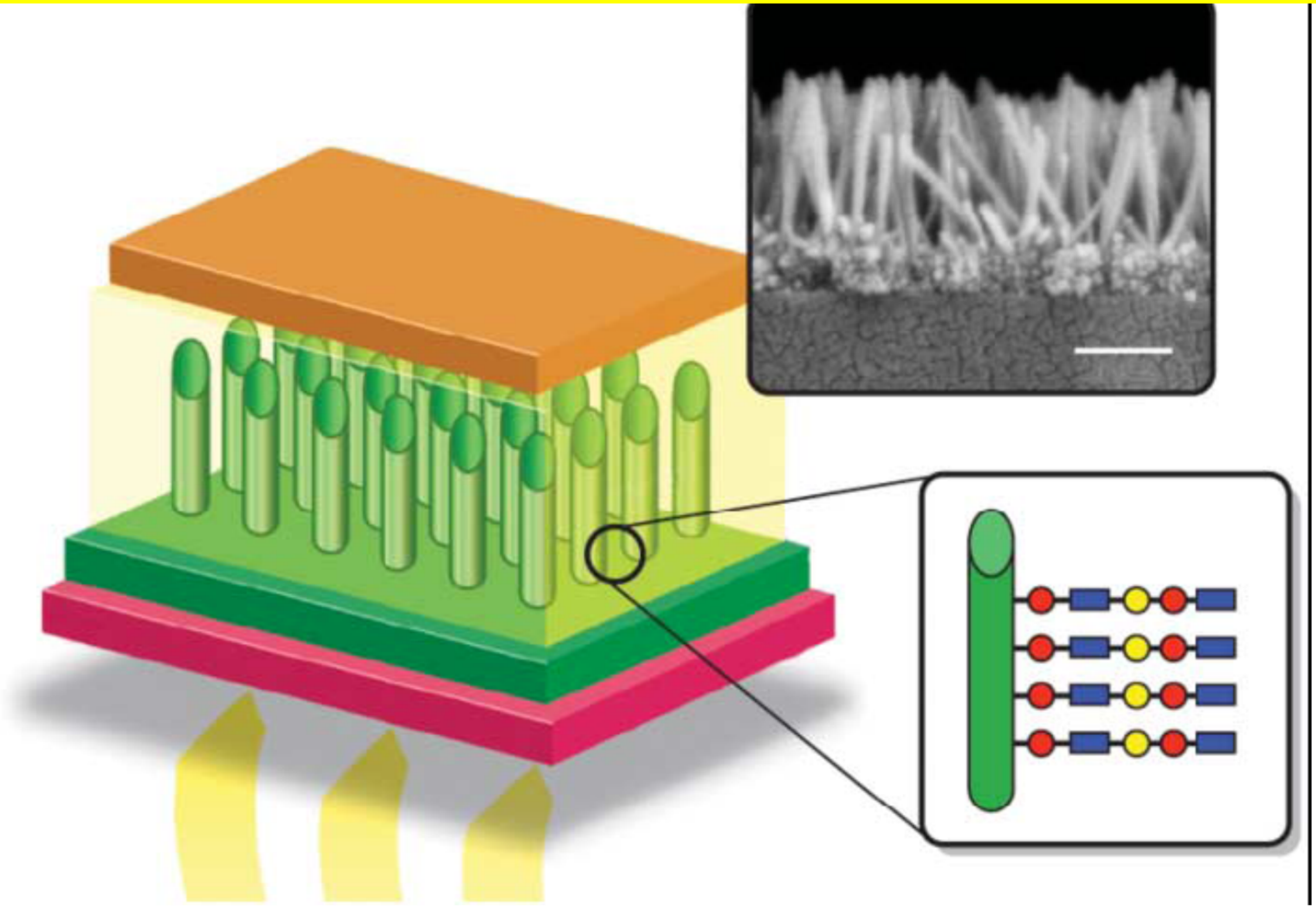


Most efficient

Forrest et al. *Nature* **2003**, *425*, 158

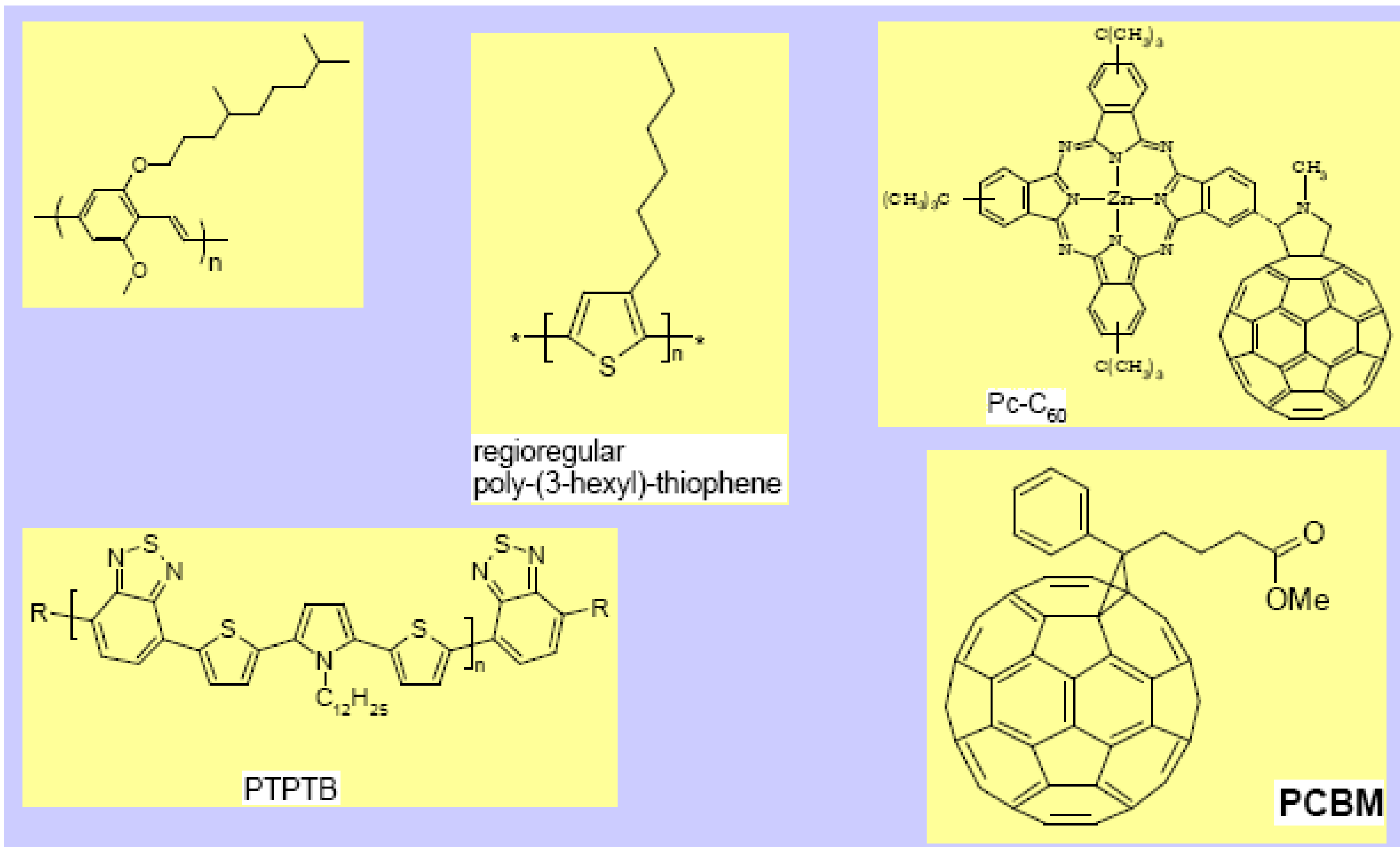
Ideal?

Arrays of nanorods - an approach to orthogonalization of the directions of light absorption (down the length of the rods) and charge carrier collection (radially outward to the surface of the rods)



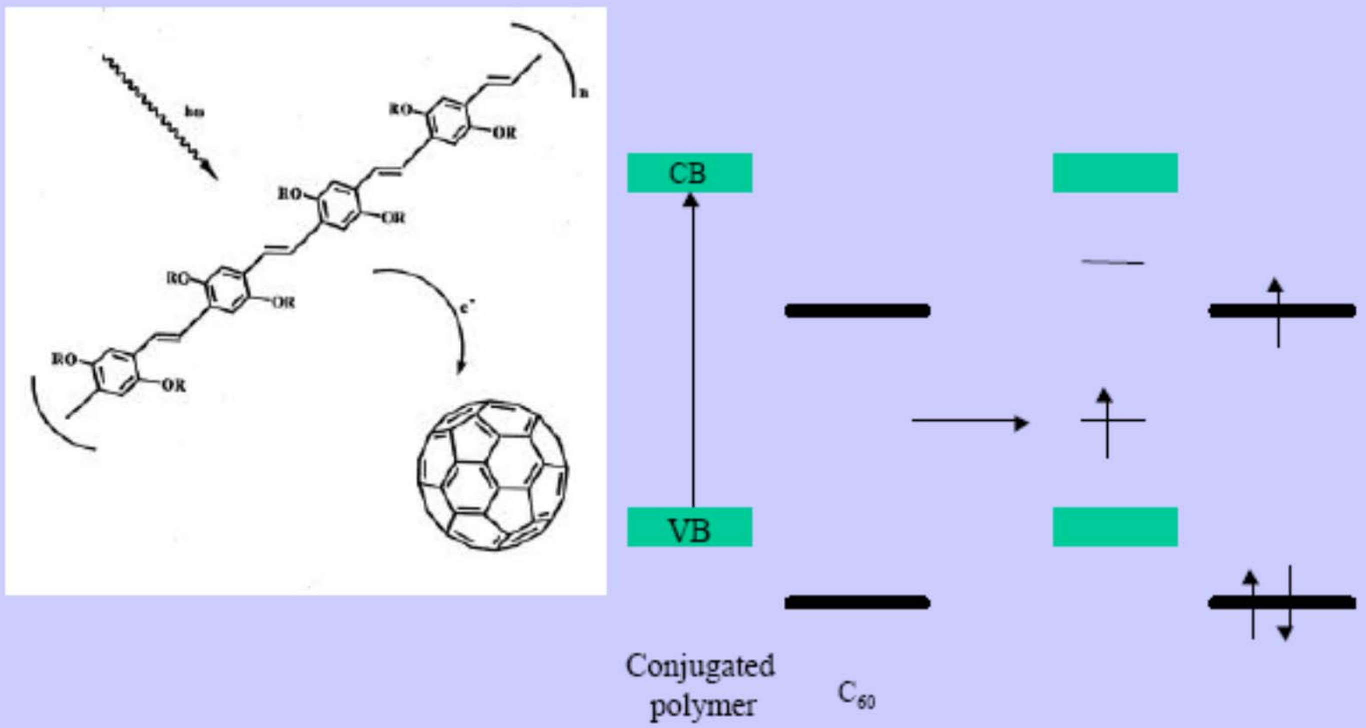
N. Lewis *Science*, **2007**, *315*, 798

Materials: most popular mixture – conducting polymer + fullerene.



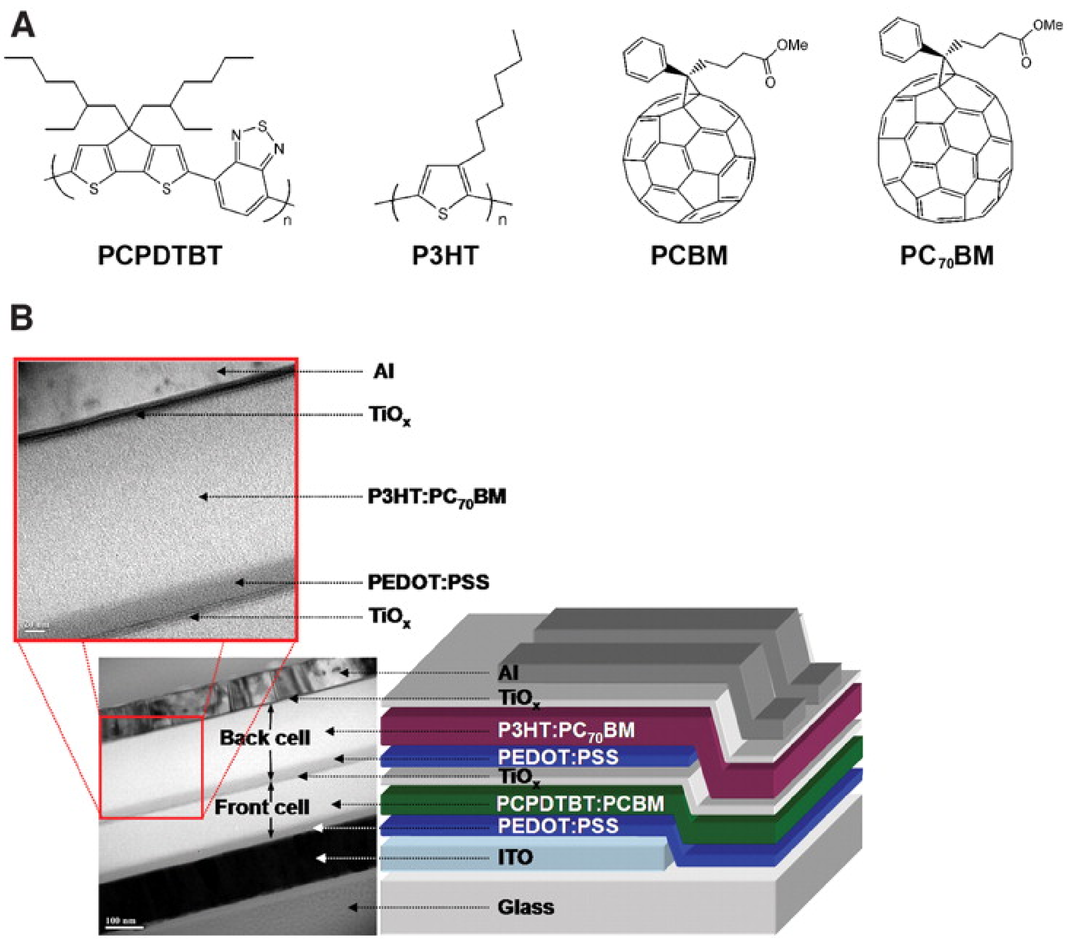
Conjugated polymers = organic semiconductors

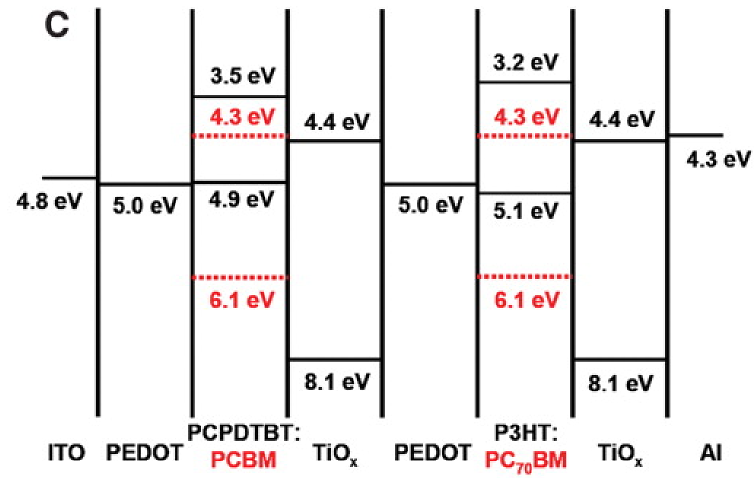
Charge generation



N.S. Sariciftci, L. Smilowitz, A.J. Heeger, F. Wudl, *Science* **258**, 1474 (1992).

Tandem Organic Solar Cell





6.5% efficiency (?)

Heeger et al. *Science* **2007**, 317, 222 - 225

Summary: organic solar cells

- Organics are cheap and show possibility for easy processing
- Photoinduced charge transfer and interpenetrating network are needed
- Long-term stability problem
- Possible Improvement:

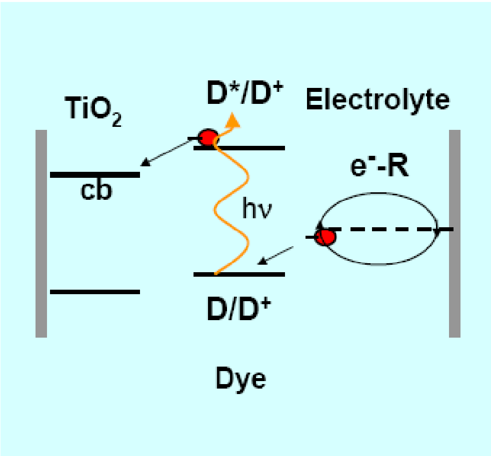
  -Materials parameter (absorption, band positions)

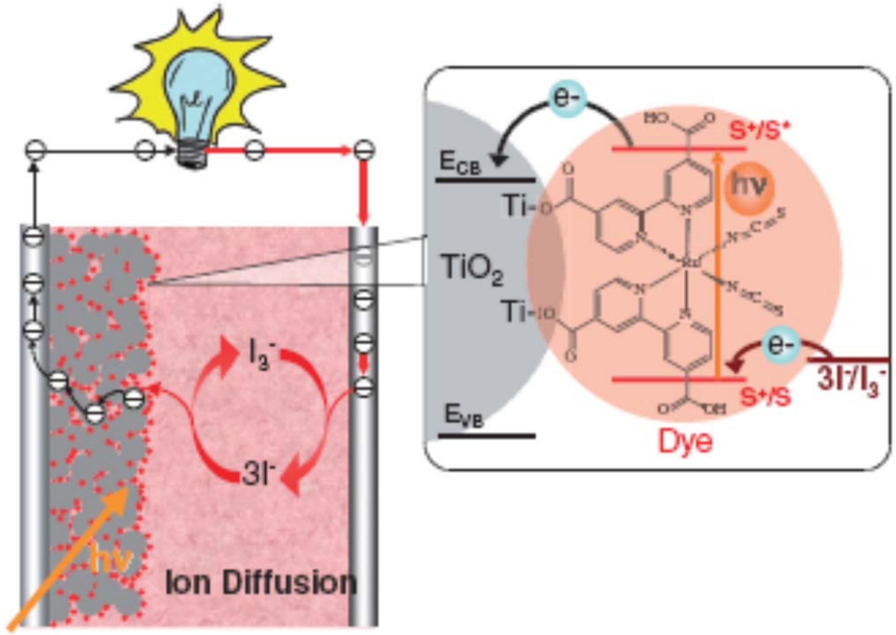
  -Morphology

  -Device structure

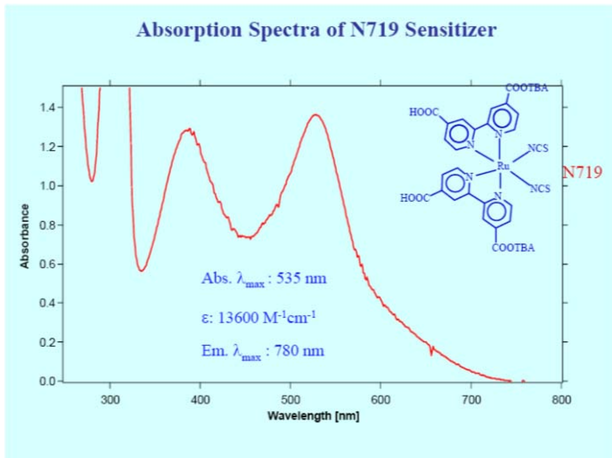
Grätzel cell

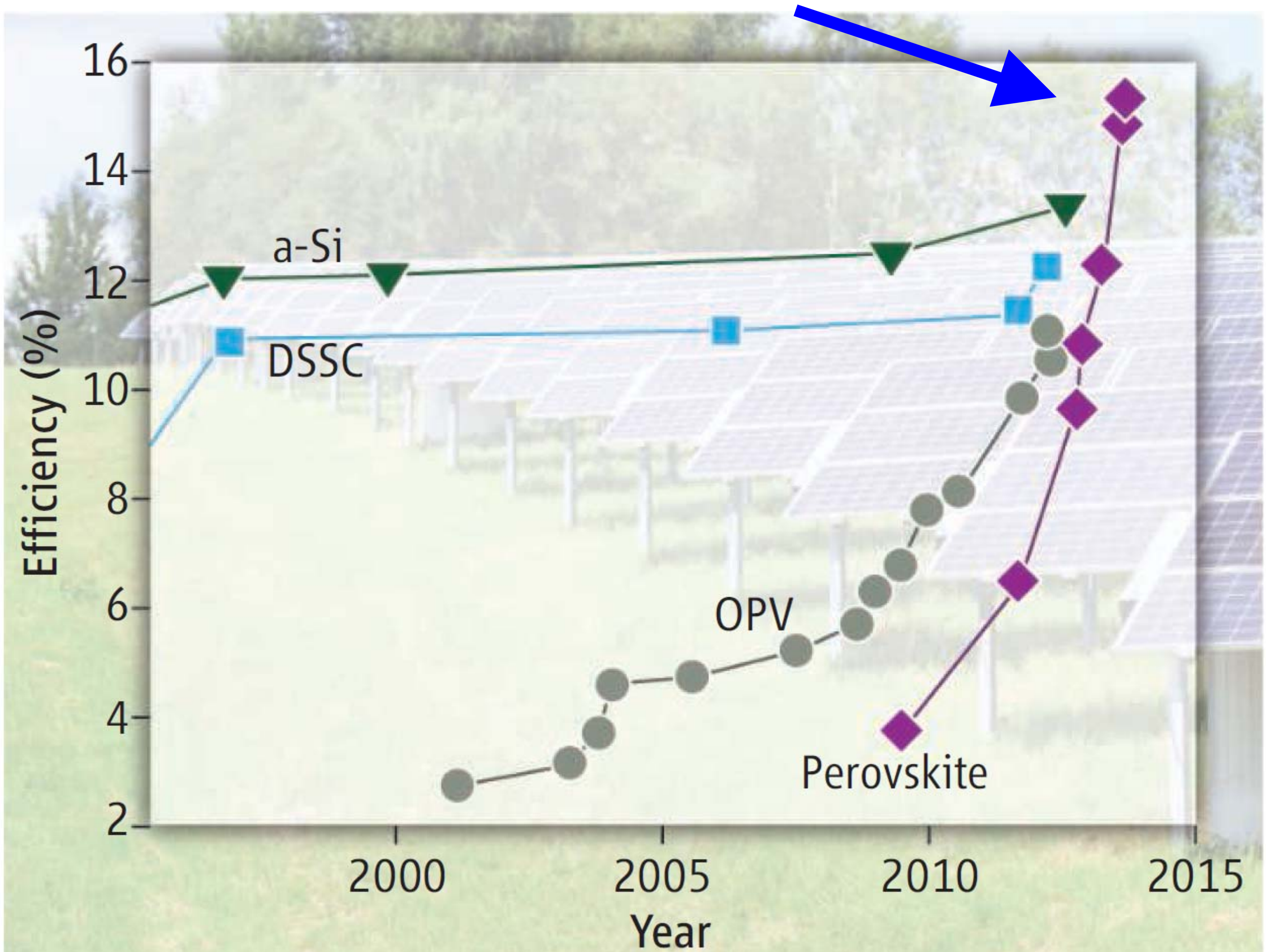
Principle





Relatively cheap and stable
Up to 16% efficiency
Not economical so far.

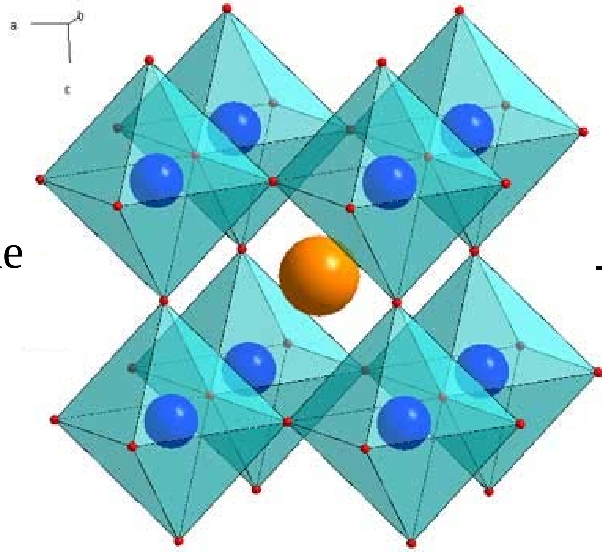




Emerging PV technologies.
Hodes, Science 2013
Nayak and Cahen, Advanced Materials, 2013

Organic/Inrganic solution-processed hybrid PV for integration into catalytic system

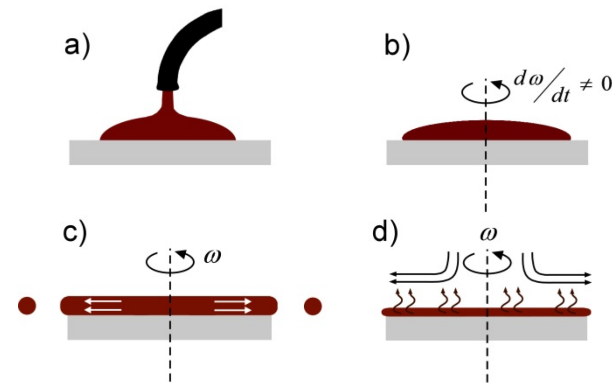
Lead Amine Halide perovskite

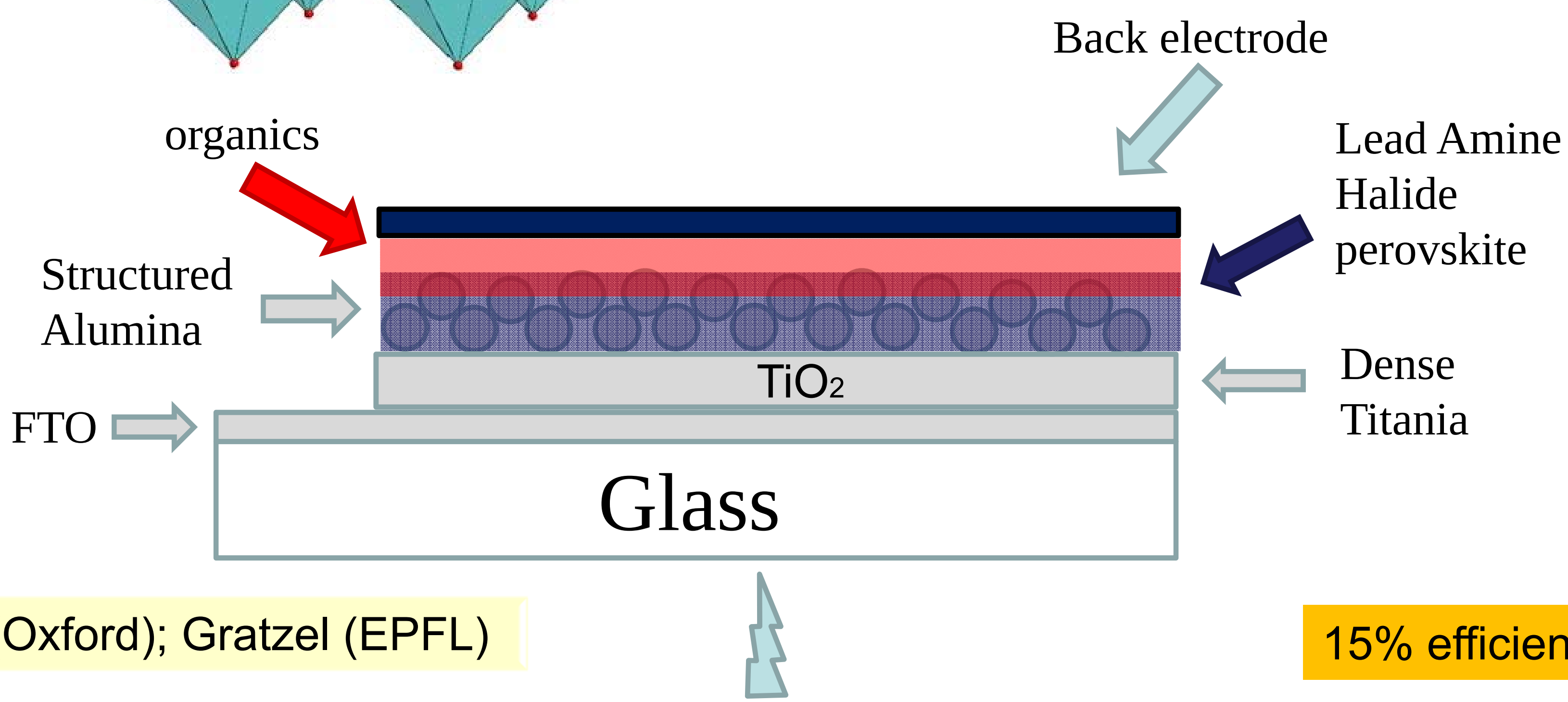


+

organic chromophore

Spin coat production

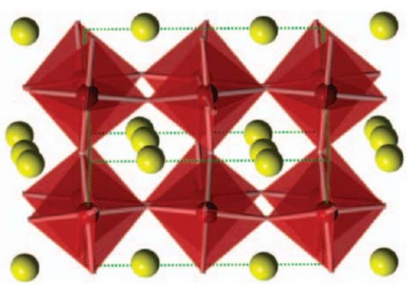


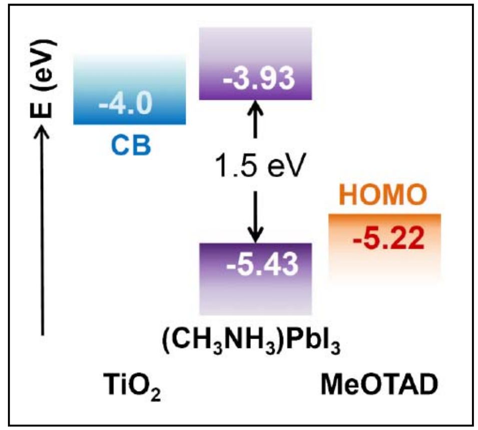


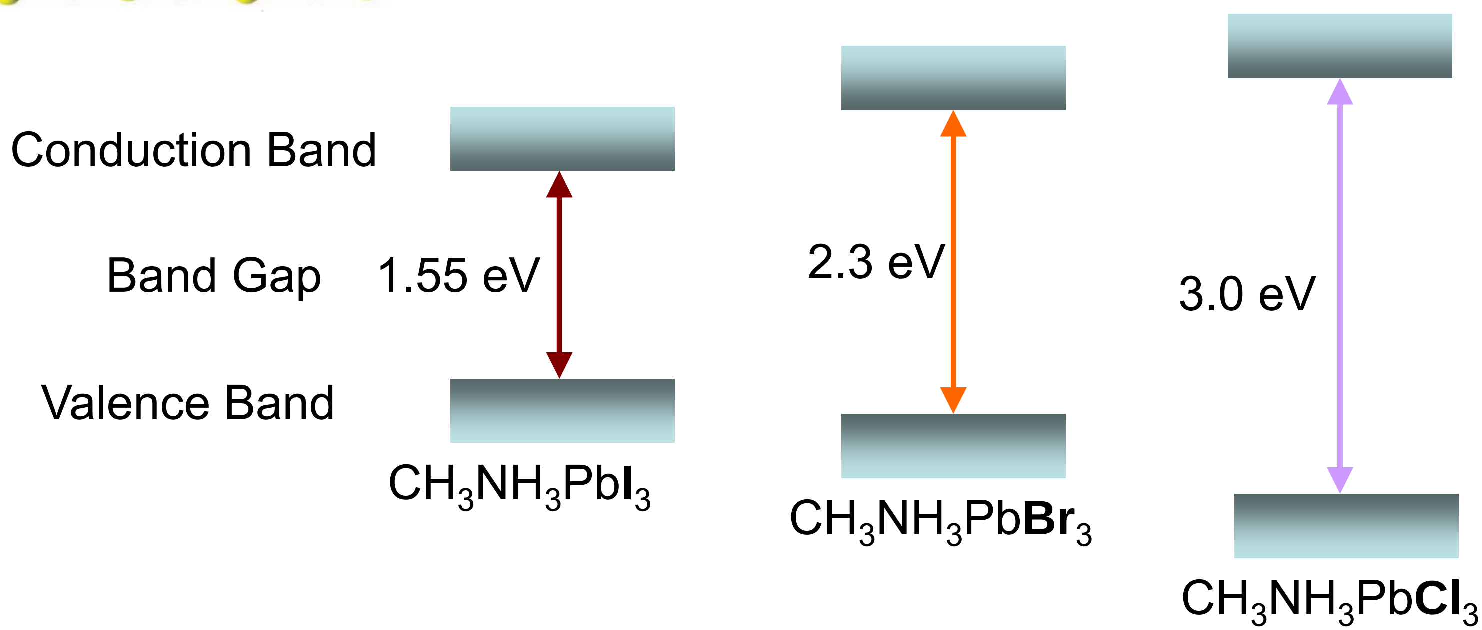
Snaith (Oxford); Gratzel (EPFL)

15% efficiency

Methyl ammonium lead Halides



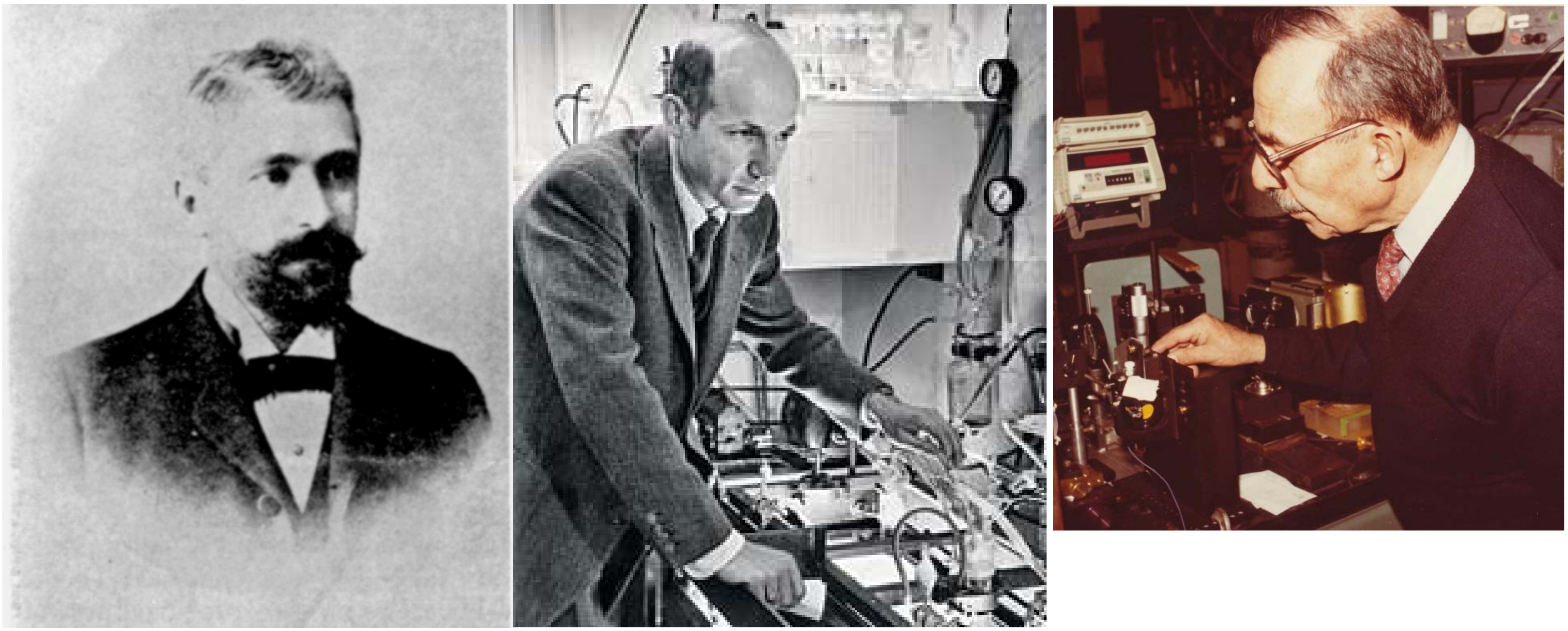




Chemical solar energy conversion

- Artificial PS - **artificial photosynthesis** is defined as a sunlight-driven process leading to the formation of energy-rich compounds that can be used as fuels
- High-energy reactions – fuel production
- Energy storage in chemical bonds

Artificial PS visionaries



Left: Giacomo Ciamician. Center: Melvin Calvin (from C&EN, **2008**, *86*, 60-61). Right: Joseph J. Katz (Argonne National Laboratory, 1982).

An energy input of 1.23 eV is needed to drive water splitting (eq 2), which can be supplied by the energy of sunlight that, for example, has an energy of 2.25 eV in the middle of the visible spectrum at 550 nm. The hydrogen fuel produced by this overall process can react with oxygen to release the energy again; thus, hydrogen is a “solar fuel”, analogous to conventional hydrocarbon fuels that release energy when oxidized (burned) with oxygen. Reactions with oxygen lead to oxidation of the fuels and recycling of the substrates (carbon dioxide and water), **creating a sustainable energy supply cycle that needs only sunlight as an energy source.**

$$2H_2O + CO_2 \xrightarrow{8h\nu} CH_4 + 2O_2 \qquad (1)$$

$$2H_2O \xrightarrow{4h\nu} 2H_2 + O_2 \qquad (2)$$

Reactions 1 and 2 each involve both oxidation and reduction, and thus, each can be split into two half-reactions (oxidation and reduction). For example, in the case of water splitting:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

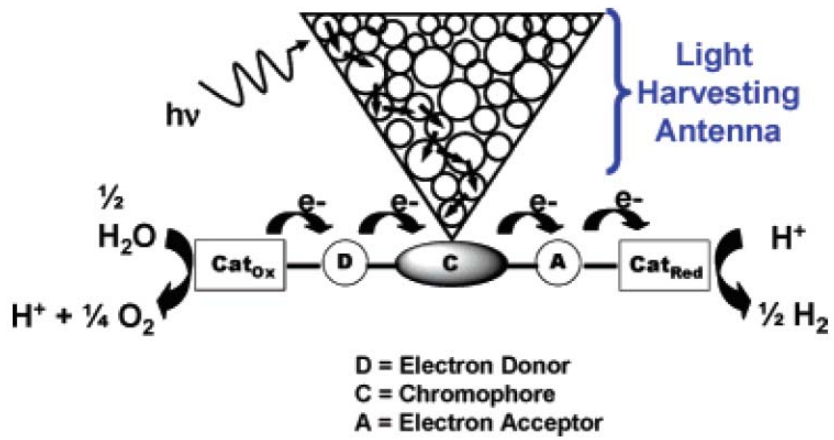
$$4H^+ + 4e^- \rightarrow 2H_2$$

Importantly, water splitting and carbon dioxide reduction are multiphoton, multielectron processes coupled to proton transfer.

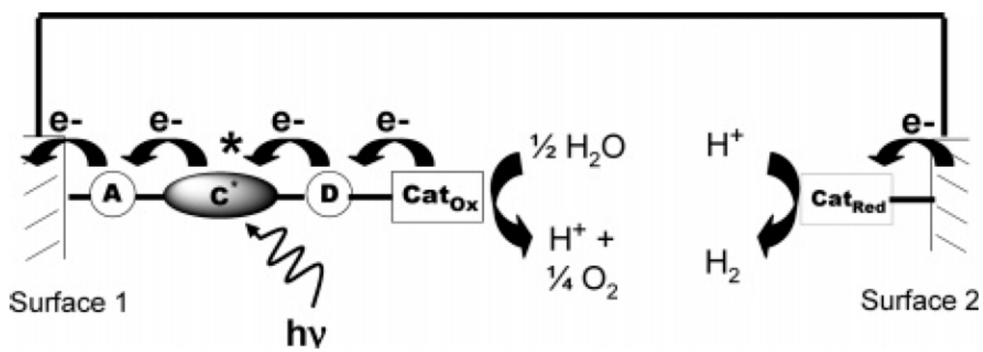
What modules do we need?

- Light harvesting (energy absorbing/transferring antenna)
- Charge separation (long-lived)
- Charge transfer cascade/wire
- Redox catalysts (stable, multielectron)

Designs



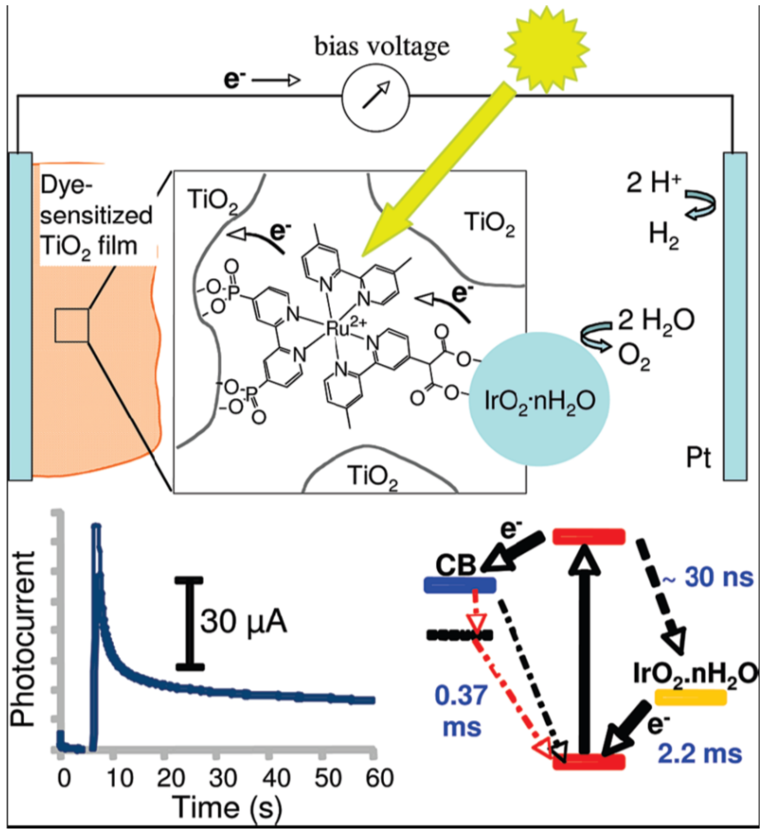
Spatially Integrated Molecular Assemblies.



Photoelectrochemical synthesis (PES) Cells.

Meyer et al. *Inorg. Chem.* **2005**, *44*, 6802-6827

DSSC coupled to a water-splitting catalyst



Mallouk et al. Visible Light Water Splitting using Dye-Sensitized Oxide Semiconductors, *Acc. Chem. Res.* **2009**, *42*, 1966-1973.

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Wireless Solar Water Splitting Using Silicon-Based Semiconductors and Earth-Abundant Catalysts

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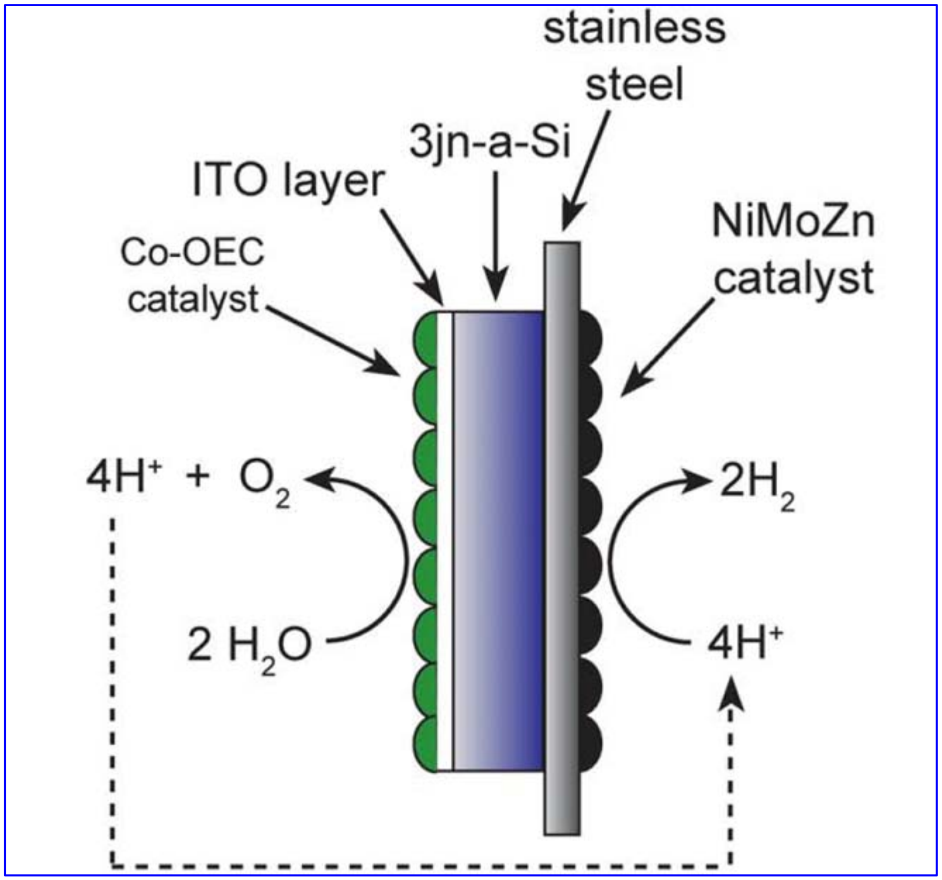
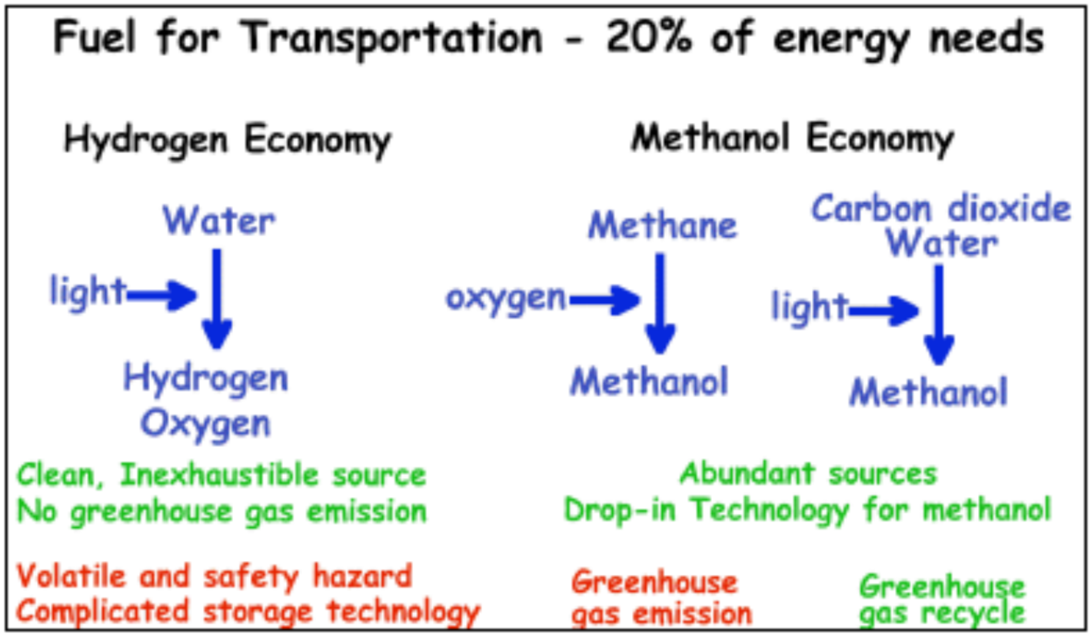


Solar powered electrolysis. Solar photons can be converted into fuels using a two-stage approach in which (1) a solar cell powers electrolysis (2) to split water into hydrogen and oxygen or perform other energy-storing reactions. The advantage of such a scheme lies in the fact that both solar cells and electrolysis technologies are readily available, and significant effort is currently being devoted to making more efficient solar cells and electrolytic systems. The latter are improved by developing new electrocatalysts that have redox potentials matched to those of the reaction of interest and significantly speed up the chemical reaction.

Energy storage and transportation fuel: Hydrogen or methanol?



Hydrogen is a dangerous gas, but it is cleanly burnt to give water, unlike methanol. If Methanol is made from CO_2, the latter is recycled, and environmental balance is OK.

Thomas Faunce
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The Sustainocene

Imagine a world where every road, vehicle and building ceases to "bludge off" nature and "pays its way" by doing photosynthesis more efficiently than plants including producing its own hydrogen fuel and making its own basic starches from absorbed carbon dioxide. This is a world ripe to allow the emergence of environmental sustainability as social virtue at the heart of legal systems, alongside the more traditional, human-centred justice and equity.
Such a multimillion-year era of stewardship has been termed the Sustainocene. It may need to last for millions of years if humanity is to morally repay its debt to nature. In the Sustainocene, instead of the cargo-cult ideology of perpetual economic growth through corporate pillage of nature, globalised artificial photosynthesis will facilitate a steady state economy and further technological revolutions such as domestic nano-factories and e-democratic input to local communal and global governance structures. In such a world, humans will no longer feel economically threatened, but rather proud, that their moral growth has allowed them to uphold rights of nature.

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