



UNIVERSITY OF ICELAND

Summer School on  
'Materials for the hydrogen economy'  
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*PHOTOINDUCED PROCESSES AT  
SURFACES AND NANOSTRUCTURES*



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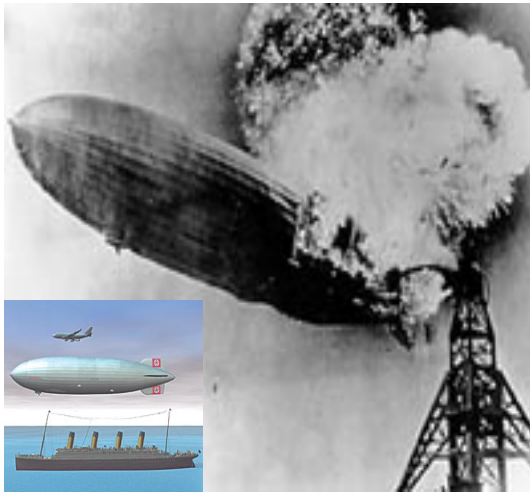
## Outline: *PART I - Hydrogen generation with solar light*

- **Hydrogen – fuel of the future;**
- **Hydrogen generation using solar energy – why?**
- **Principles and reaction mechanism of photocatalytic water decomposition;**
- **Energy and efficiency aspects of photo-electrochemical cells;**
- **Key functional properties of photo-electrodes;**
- **Progress in R&D;**
- **Summary**

## The Hydrogen - fuel of the future



Two tragic examples: of the unleashed energy of the combustion reaction of hydrogen, the **Hindenburg**, and the spaceshuttle **Challenger**.



## Hydrogen – fuel of the future

### Brief history of hydrogen as energy supplier

**1820** – H<sub>2</sub> combustion in a engine like device to do mechanical work – better than a steam engine as no warm-up time was needed

**1874** – science fiction prediction that hydrogen would be the chief fuel after coal by decomposing water using electricity

**1900** – first lab experiments with electrolysis

**1920** – Large scale plants in Canada using hydro-electricity from Niagara Falls to make hydrogen.

Company was Stuart Electrolyzer that is still in the business today (same family)

**1923** – hydrogen from wind generated electricity in England to avoid pollution from coal fired power plants. Hydrogen stored as a cryogenic liquid.

**1919** – hydrogen used as a fuel for vehicles in Germany

**1930** – hydrogen distributed in pipelines in Germany

**1930s** – hydrogen used for buoyancy in dirigibles and later burned as a fuel in flight.

**1937** – **Hindenburg** accident killing 36 people

**1930s** – hydrogen used in mixtures (usually injected into the cylinders) with liquid fuels to markedly increase engine power. Work done in Germany

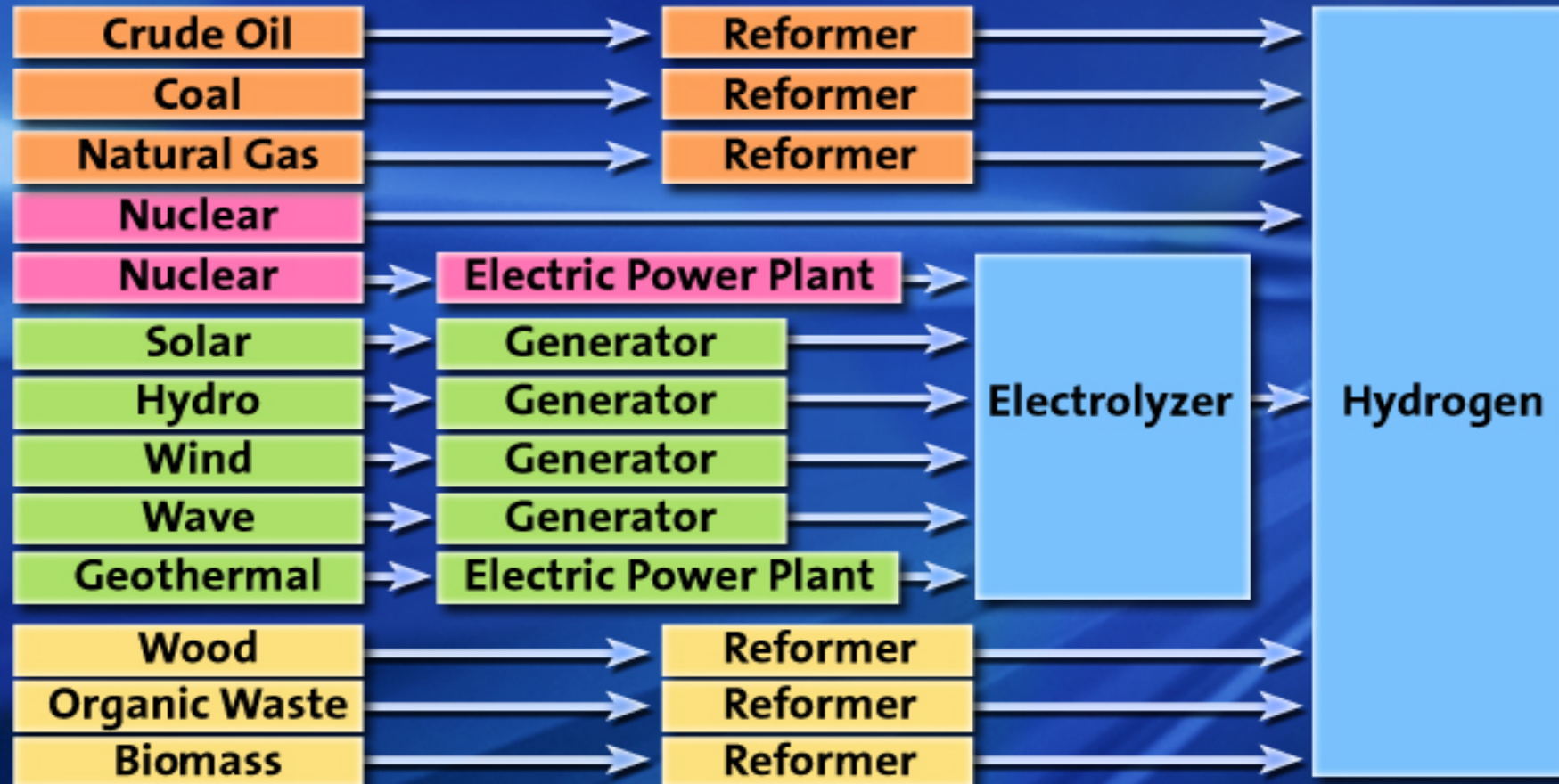
**1950** – first hydrogen/air fuel cell in lab in England

**1962** – fuel cell work in Germany in connection with splitting water with solar energy

**1962** – proposal to use solar energy to make hydrogen for fuel cells in urban areas to generate electricity

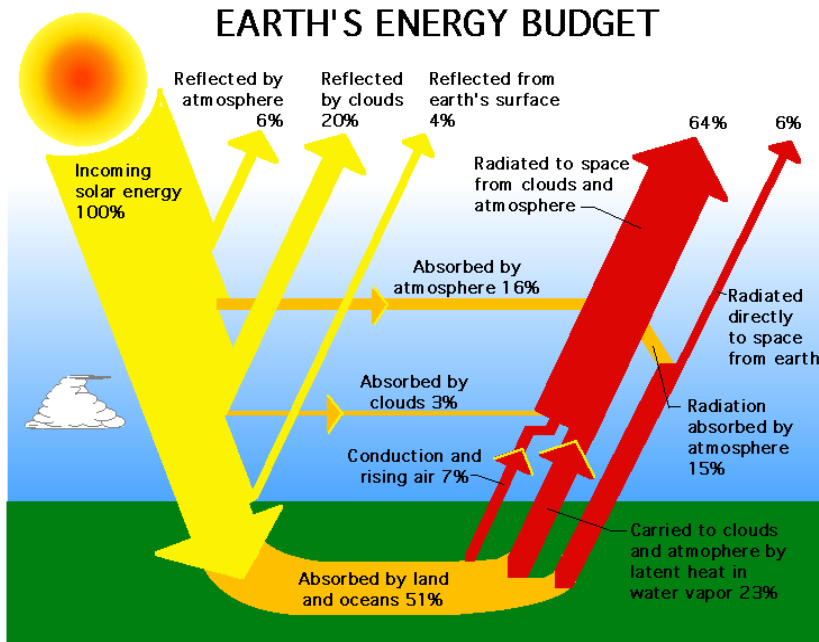
**1970** - General Motors proposed using the fuel cell in passenger cars to replace the gasoline engine

# Hydrogen Pathways



- **Hydrogen generation using solar energy – why?**

# SOLAR ENERGY



Yearly Solar fluxes & Human Energy Consumption	
Solar	3,850,000 EJ
Wind	2,250 EJ
Biomass	3,000 EJ
Primary energy use (2005)	487 EJ
Electricity (2005)	56.7 EJ

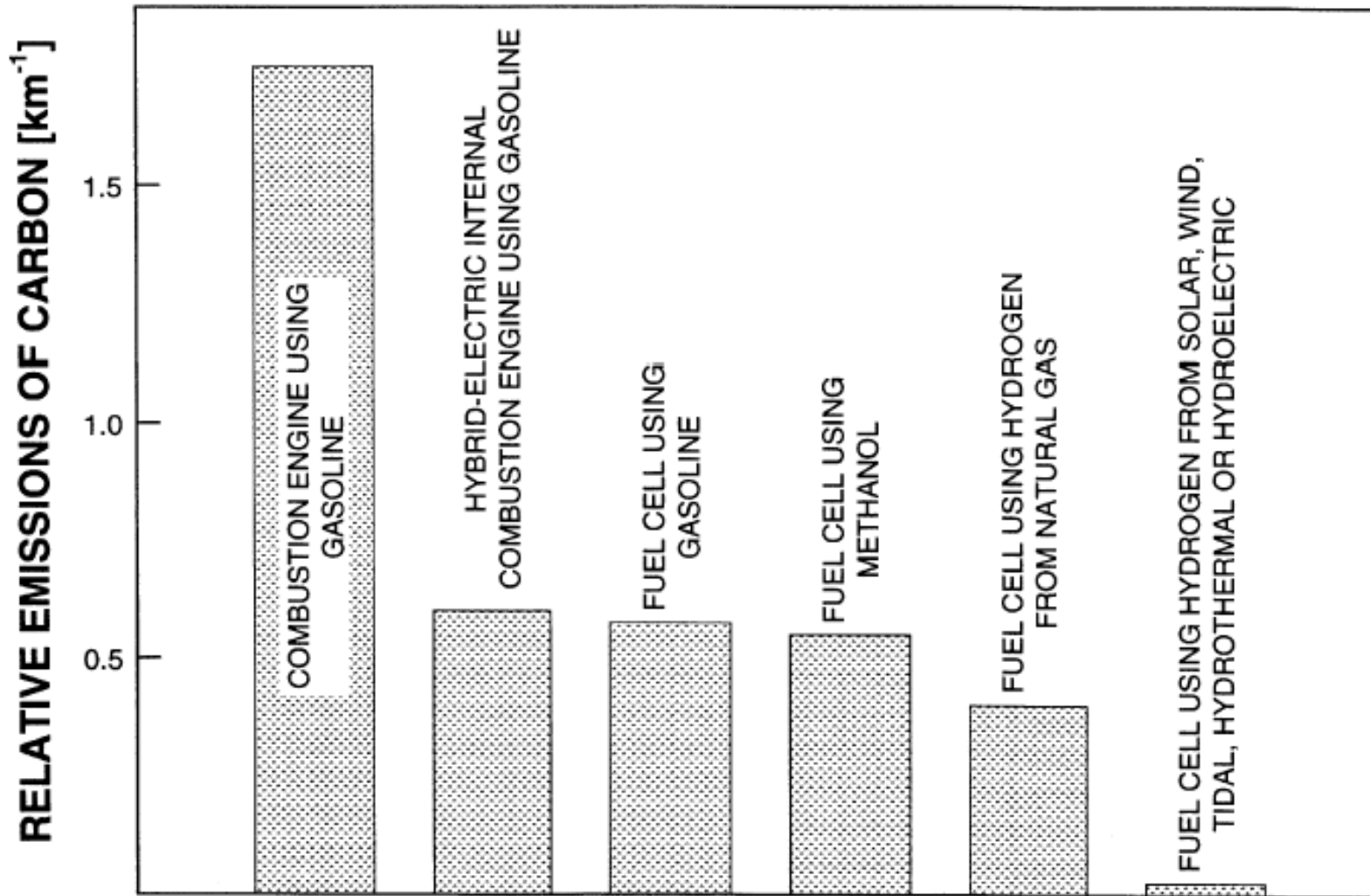
1 exajoule =  $10^{20}$  J



**THERMAL  
CONVERSION**

**QUANTUM  
CONVERSION**

- Low density!
- Intermittency!
- Defined wavelength distribution!



Relative emission of greenhouse gases (expressed in carbon units per km) for vehicles powered by today's internal combustion engine using gasoline compared to vehicles powered by fuel cells [The Economist Technology, Quarterly, March 25, 2001. p.29].





Starring:  
 Al Gore,  
 Director: Davis  
 Guggenheim

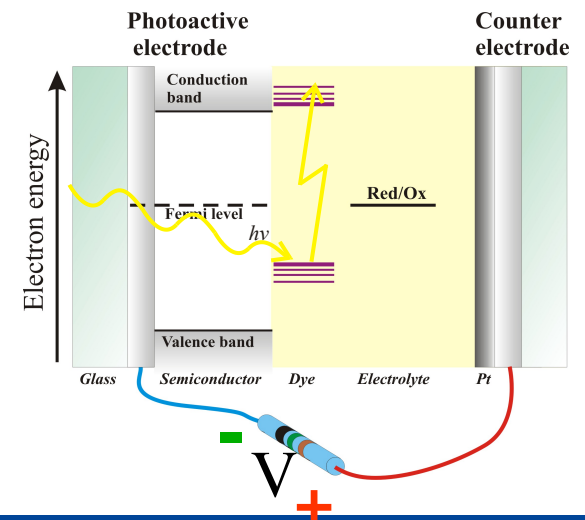
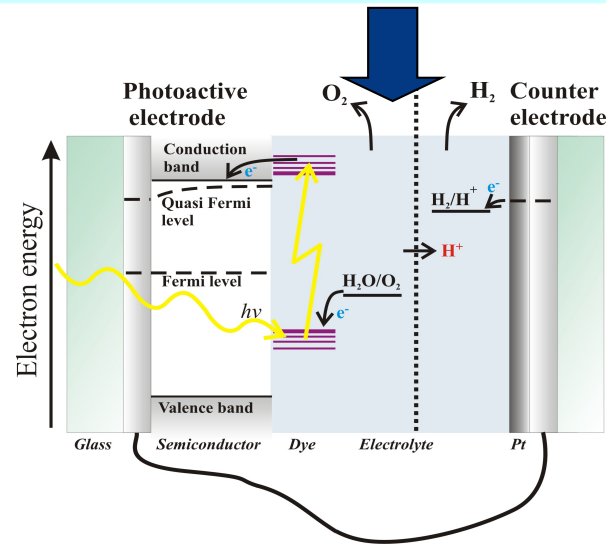
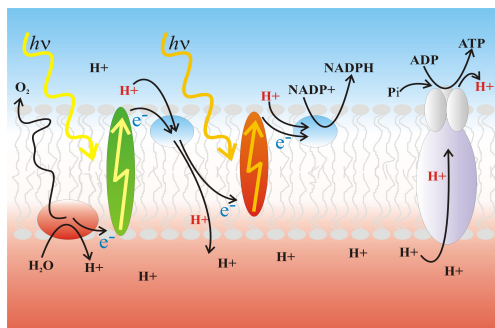
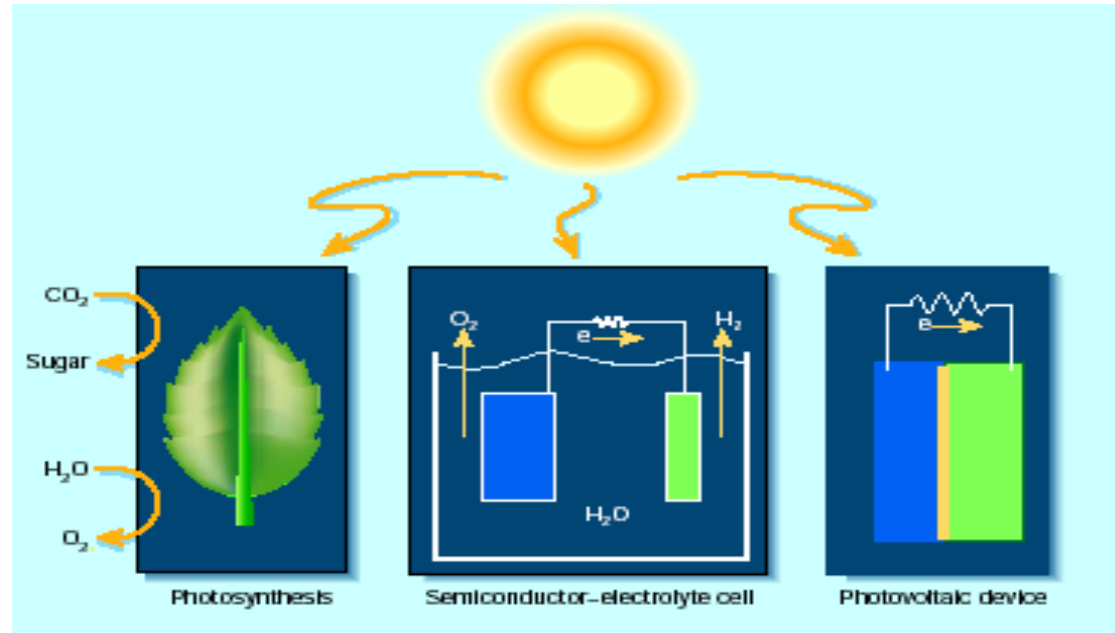
\$49 000 000



Starring:  
 Ian Holm, Deniris  
 Quaid, ...  
 Director: Roland  
 Emmerich

\$544 000 000

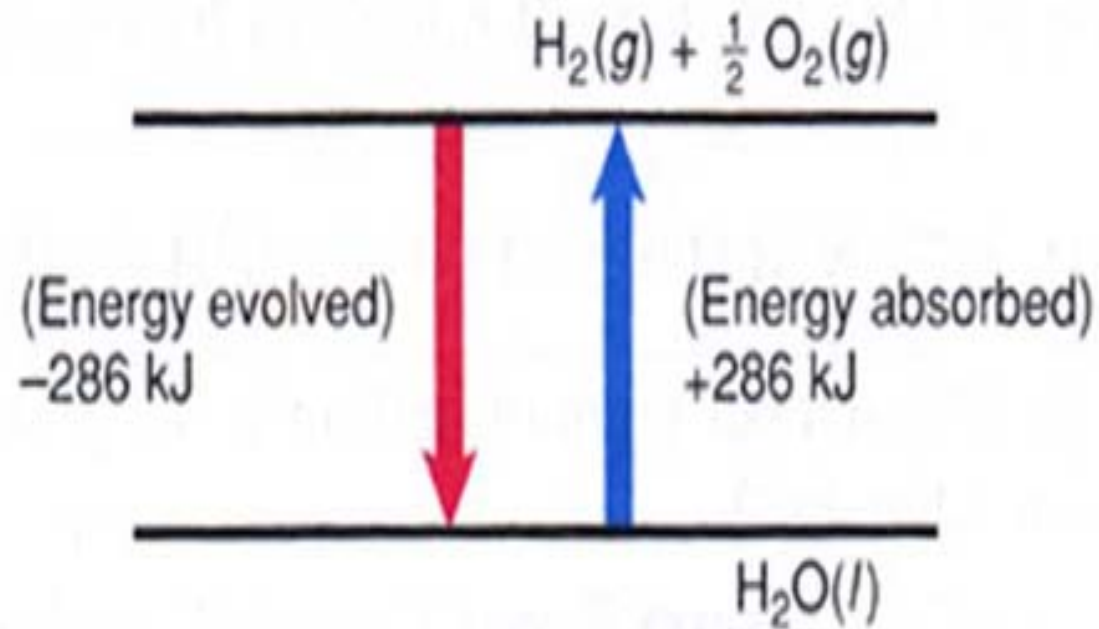
# SOLAR ENERGY CONVERSION SCHEMES



©N. S. Lewis, Nature 414 (2001) 589

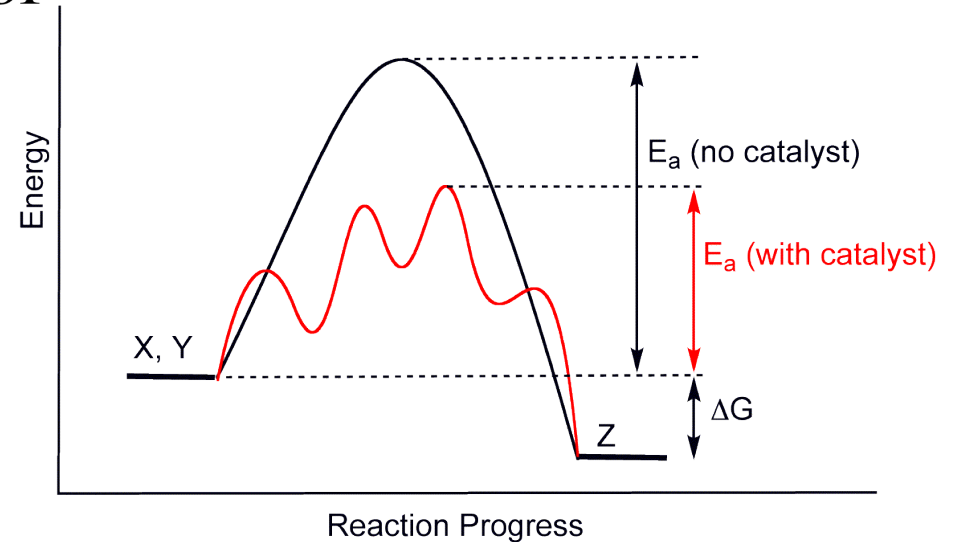
- **Principles and reaction mechanism of photocatalytic water decomposition;**

# Hydrogen Fuel



Comparison of the properties of

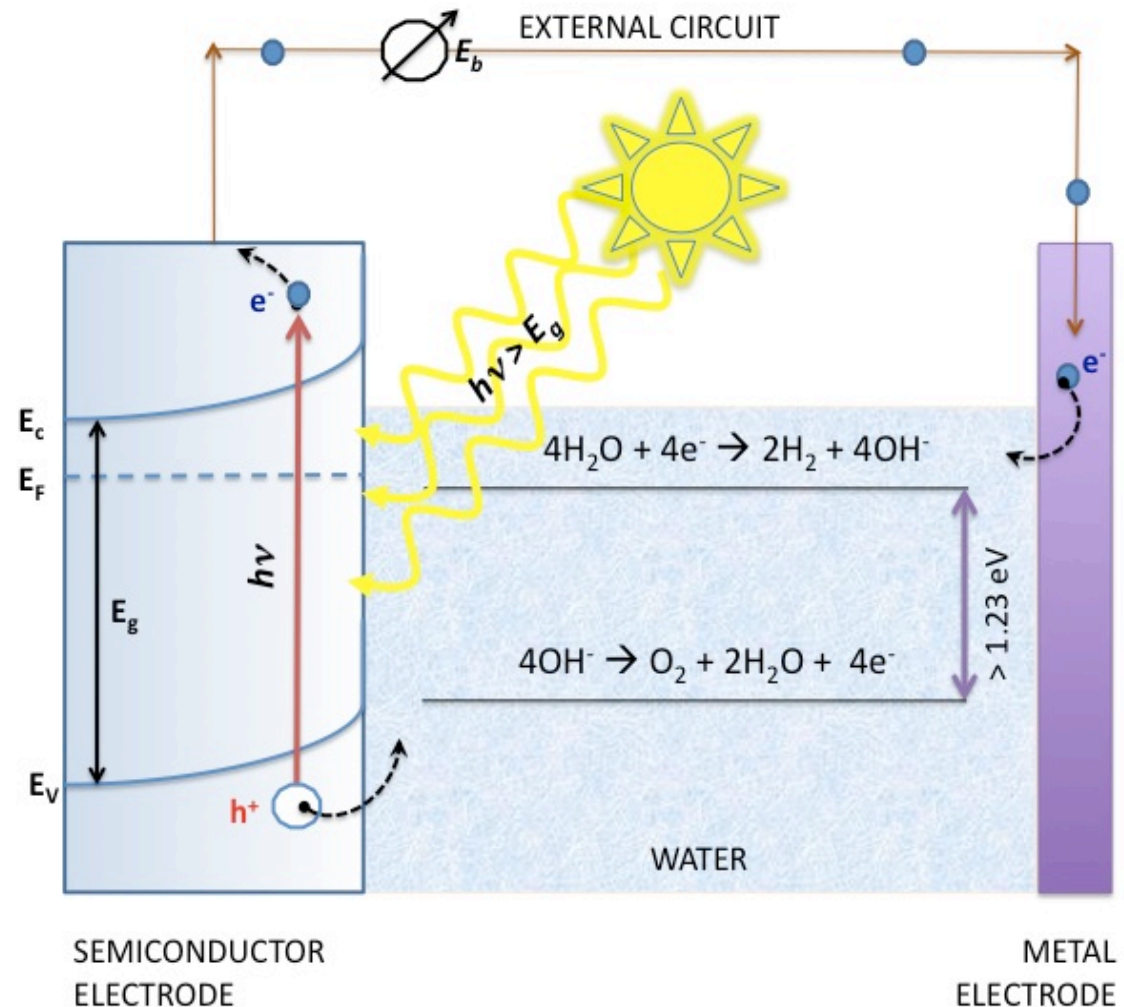
*Photocatalysts*  
with those of  
*Thermal Catalysts*



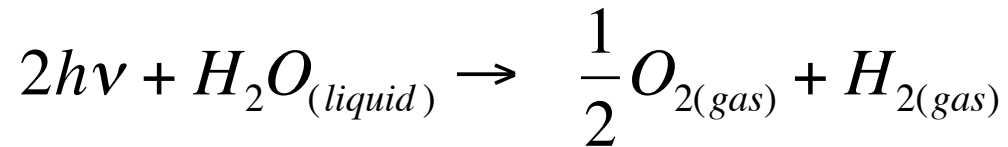
Catalyst Type	Input Energy	Free-Energy Change of the Reaction	Main Factors for the Function
<b>Thermal catalyst</b>	$kT$ (0.03 - 0.1 eV)	$\Delta G < 0$	Enhancement of reaction rate or the change of reaction path through interaction with catalyst surface.
<b>Photo-catalyst</b>	$h\nu$ (1 - 4 eV)	Even $\Delta G > 0$ is possible	Generation of electrons and holes by excitation of photocatalyst and their electron transfer reactions.

## Reaction mechanism

- light-induced intrinsic ionization of the semiconducting material (the photo-anode), resulting in the formation of electronic charge carriers (quasi-free electrons and electron holes);
- oxidation of water at the photo-anode by electron holes;
- transport of  $H^+$  ions from the photo-anode to the cathode through the electrolyte and transport of electrons from photo-anode to the cathode through the external circuit;
- reduction of hydrogen ions at the cathode by electrons.



The overall reaction of the PEC may be expressed in the form:



The reaction takes place when the energy of the photons absorbed by the photoanode are equal to or larger than  $E_i$ , the threshold energy:

$$E_i = \frac{\Delta G_{H_2O}^0}{2N_A}$$

$$E_i = h\nu = 1.23\text{eV}$$

Where  $\Delta G_{H_2O}^0 = 237.141\text{ kJ/mol}$

is the standard free enthalpy per mole of the reaction

$N_A$  = Avogadro's number =  $6.022 \times 10^{23}\text{ mol}^{-1}$

We seek as a “Holy Grail” a renewable energy scheme driven by solar light that produces a clean and storable fuel.

**More specifically:**

- \* We want an efficient and long-lived system for splitting water to  $\text{H}_2$  and  $\text{O}_2$  with light in the terrestrial solar spectrum.
- \* We want an energy efficiency of at least 10%. This means that the  $\text{H}_2$  and  $\text{O}_2$  produced in the system have a fuel value of at least 10% of the solar energy incident on the system.

(a) the system should produce  $\text{H}_2$  at a rate of about 0.7 g/s or 7.8 L(STP)/s per  $\text{m}^2$  of collector at maximum solar intensity.

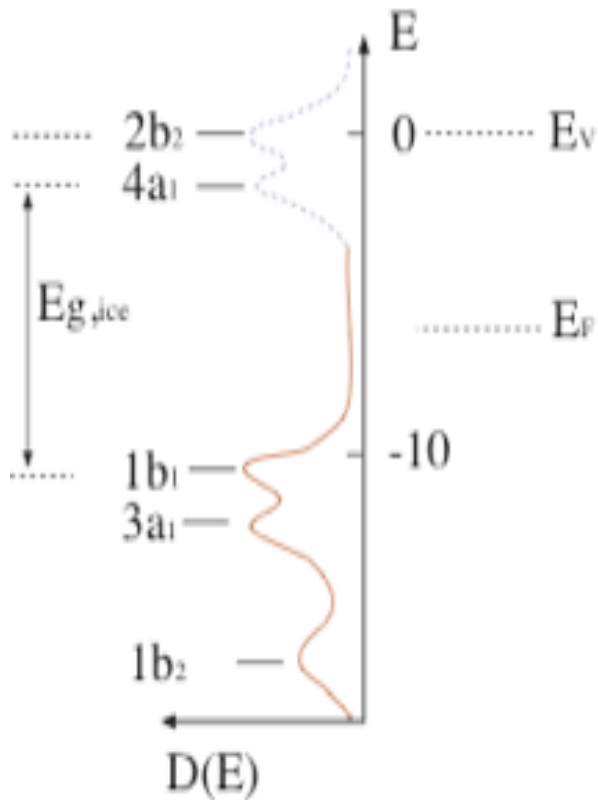
(b) Long-lived implies at least 10 years under irradiation.



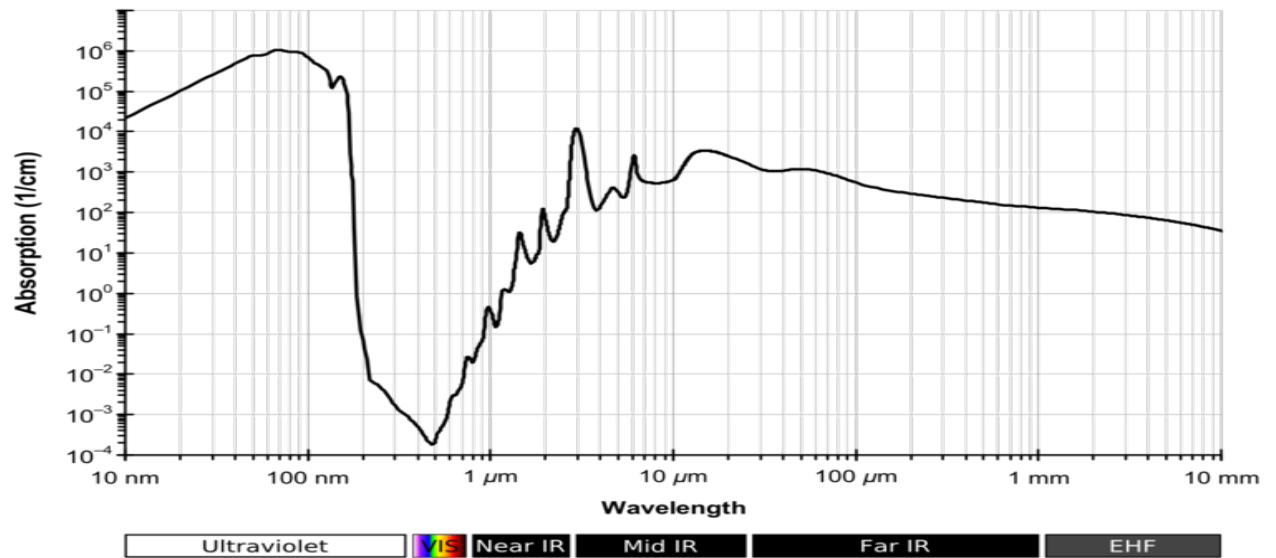
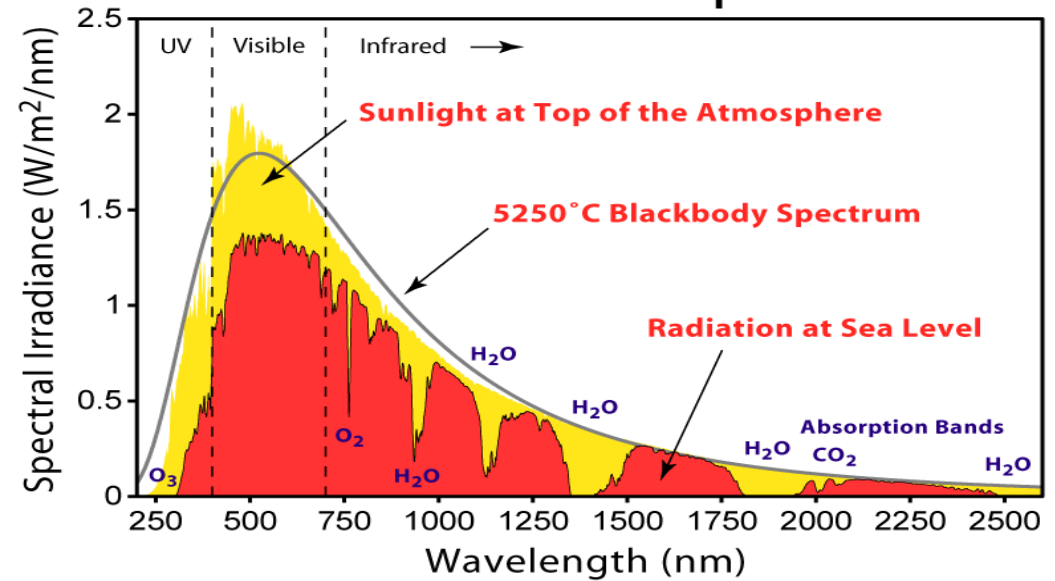
- **Energetic and efficiency aspects of photo-electrochemical cells;**

# H<sub>2</sub>O photodissociation

*“The absorption spectrum of the system must overlap the emission spectrum of the sun”.*



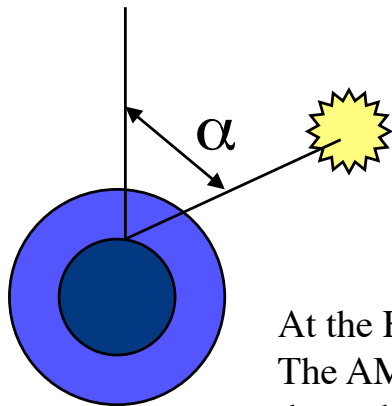
## Solar Radiation Spectrum



## Radiation standard

The effect of the earth's atmosphere on solar radiation is considered in terms of the so-called air mass (AM):

$$AM = \frac{1}{\cos \alpha},$$



where  $\alpha$  is the angle between the overhead and actual position of the sun.

At the Earth's surface, the AM assumes values between unity ( $\alpha = 0$ ) and infinity ( $\alpha = 90$ ). The AM characterizes the effect of the Earth atmosphere on solar radiation and, therefore, depends on geographical position, local time, and date.

Outside the Earth's atmosphere  $AM = 0$ .

**The radiation standard assumes an AM of 1.5, which corresponds to  $\alpha = 0.841$  radians or  $48^\circ$ .**

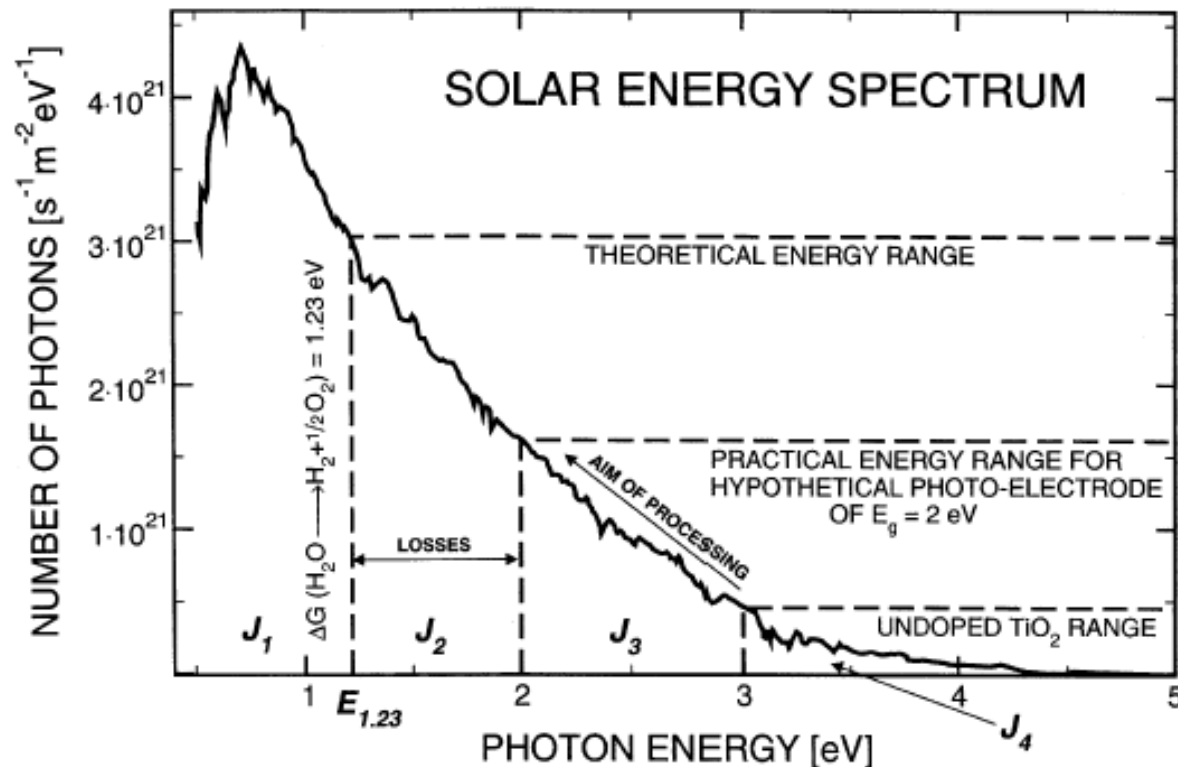
The solar energy available for conversion depends also on local atmospheric conditions, such as cloudiness, air pollution, airborne dust particles, and relative humidity.

## Efficiency

The free energy change for watersplitting reaction is 237.2 kJ/mol or **2.46 eV/molecule**.

For a single photoconverter system, wavelengths below 770 nm (or energies above 1.6 eV) are required to yield a maximum efficiency of about 30%.

### Impact of band structure of photo-electrode material on solar energy conversion efficiency



It is possible to cause water splitting thermally with light via concentrators and a solar furnace by heating water to 1500- 2500 K. However, the efficiency of this process is typically below 2%, and the cost of the capital equipment and material stability problems suggest that this approach to solar water splitting is not a promising one.

Solar energy spectrum (AM of 1.5) in terms of number of photons vs. photon energy, showing different flux photon regimes corresponding to specific properties of photo-electrodes. [Oriol-Instruments. Book of Photon Tools, 1999].

**Table 1 Performance of photovoltaic and photoelectrochemical solar cells**

Type of cell	Efficiency (%)*		Research and technology needs
	Cell	Module	
Crystalline silicon	24	10–15	Higher production yields, lowering of cost and energy content
Multicrystalline silicon	18	9–12	Lower manufacturing cost and complexity
Amorphous silicon	13	7	Lower production costs, increase production volume and stability
CuInSe <sub>2</sub>	19	12	Replace indium (too expensive and limited supply), replace CdS window layer, scale up production
Dye-sensitized nanostructured materials	10–11	7	Improve efficiency and high-temperature stability, scale up production
Bipolar AlGaAs/Si photoelectrochemical cells	19–20	—	Reduce materials cost, scale up
Organic solar cells	2–3	—	Improve stability and efficiency

\*Efficiency defined as conversion efficiency from solar to electrical power.

Compare with 3–4% of the total sunlight energy falling onto a leaf is converted into stored free energy by

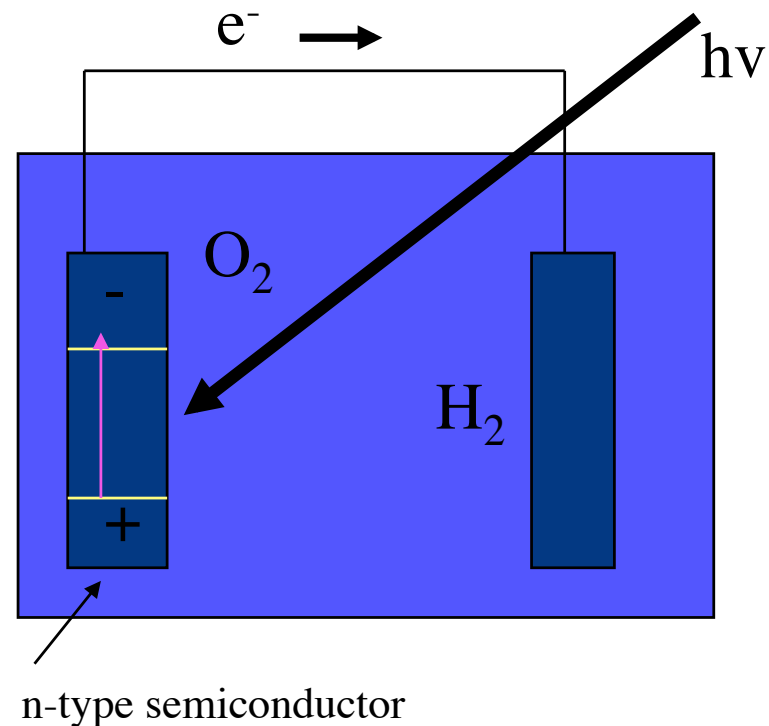
photosynthesis.

## Photo-electrochemistry of water decomposition

The principle of photoelectrochemical water decomposition is based on the conversion of light energy into electricity within a cell involving two electrodes, immersed in an aqueous electrolyte. At least one of the electrodes is made of a semiconductor and able to absorb the light. This electricity is then used for water electrolysis.

Three options for the arrangement of photo-electrodes in the assembly of PECs:

- photo-anode made of n-type semiconductor and cathode made of metal;
- photo-anode made of n-type semiconductor and photo-cathode made of p-type semiconductor;
- photo-cathode made of p-type semiconductor and anode made of metal.

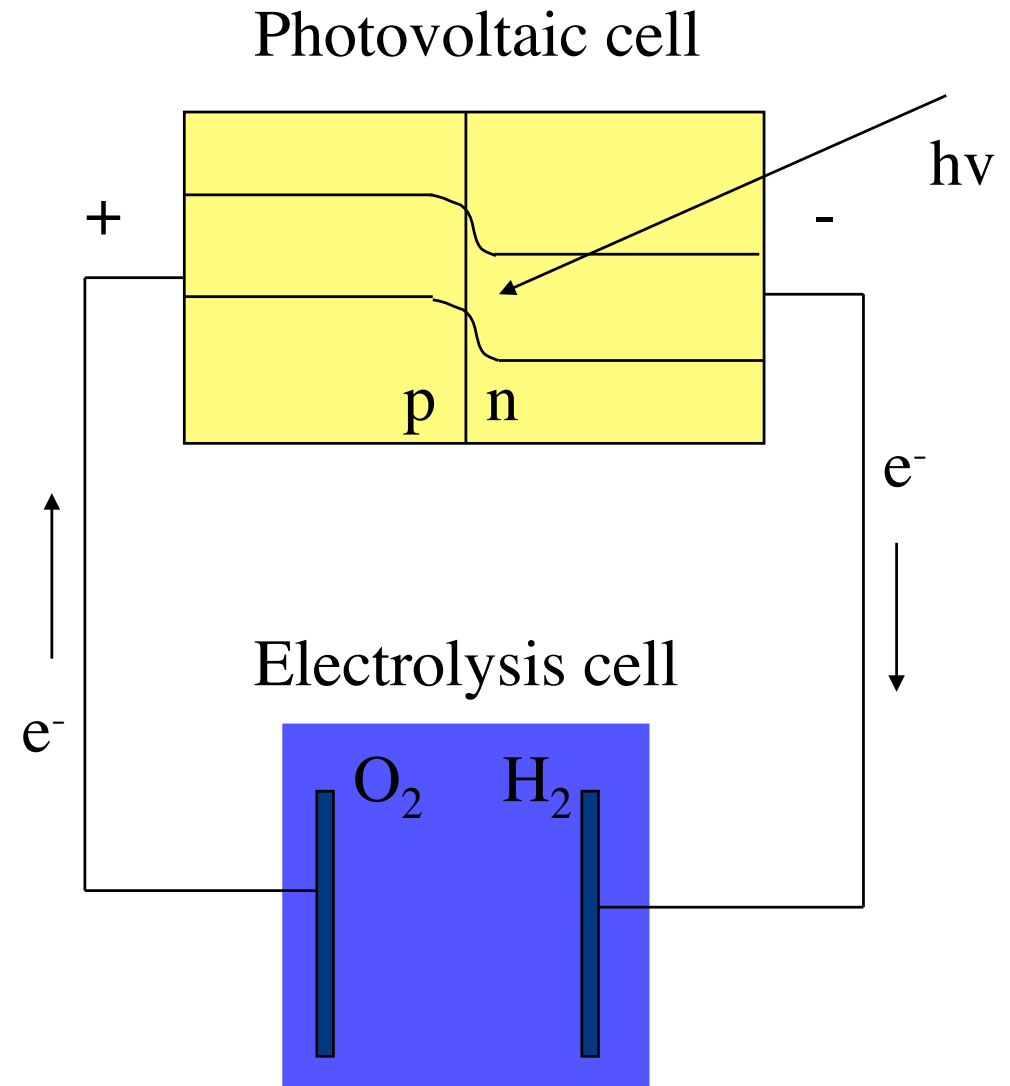


# Semiconductor Solid State Photovoltaic-Based Systems

“Brute force” approach: employs a solid state photovoltaic solar cell to generate electricity that is then passed into a commercial type water electrolyzer.

The maximum theoretical efficiency for a Si photovoltaic cell is **33%**, and the efficiencies of the best laboratory cells have been reported to be about 24%. Commercial single-crystal Si solar cells generally have efficiencies in the 12-16% range. The electrolysis of water at a reasonable rate in a practical cell requires applied voltages significantly larger than the theoretical value (1.23 V at 25 °C), and electrolysis energy efficiencies of about 60% are typical. Thus, the efficiency of the combined solar/electrolyzer system using commercially available components is close to the desired 10% defined for solar hydrogen generation. Moreover, the components are rugged and should be long-lived.

**The problem with such a system is its cost.**

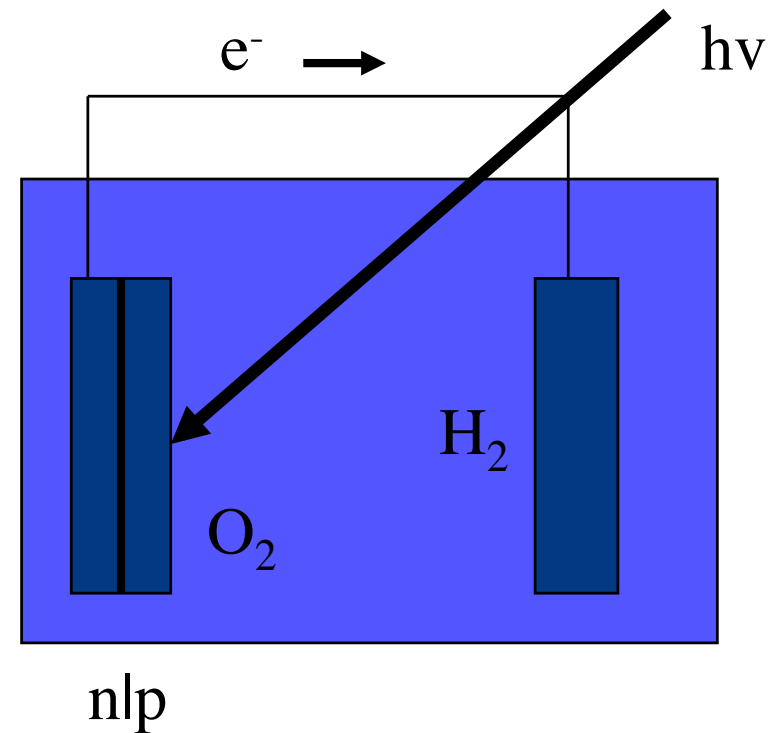


## Semiconductor photovoltaic cell

- immersed directly in the aqueous system. This eliminates the costs and mechanical difficulties associated with separate construction and interconnection of solar and electrochemical cells. In one such system, the electrodes are composed of single or multiple semiconductor p/n junctions that are irradiated while they are within the cell.

This simpler apparatus is attained at the cost of encapsulating and coating the semiconductors to protect them from the liquid environment and probably with a more limited choice of electro-catalyst for  $O_2$  or  $H_2$  evolution.

Moreover, the open-circuit photovoltage of a single Si p/n junction is only 0.55 V, so at least three of these in series would be needed to generate the necessary potential for water splitting.

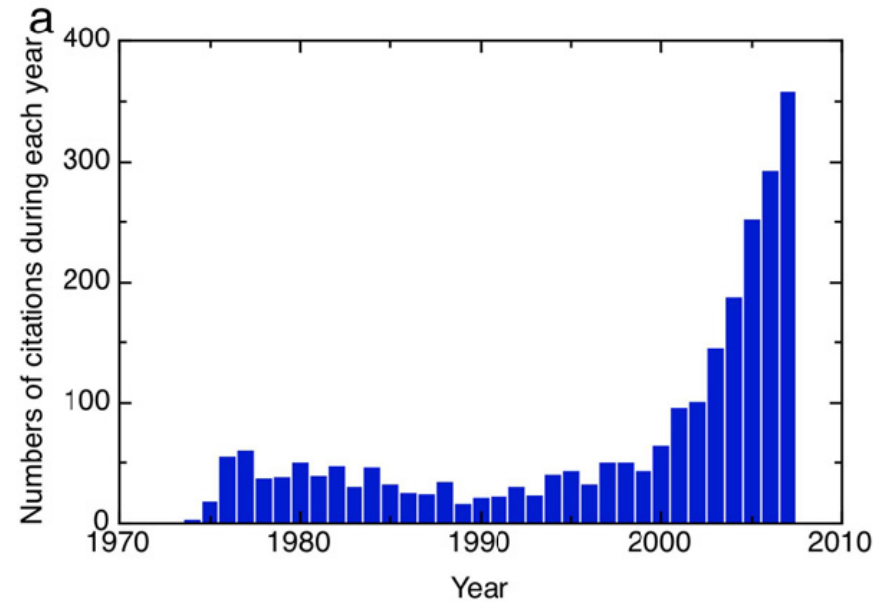
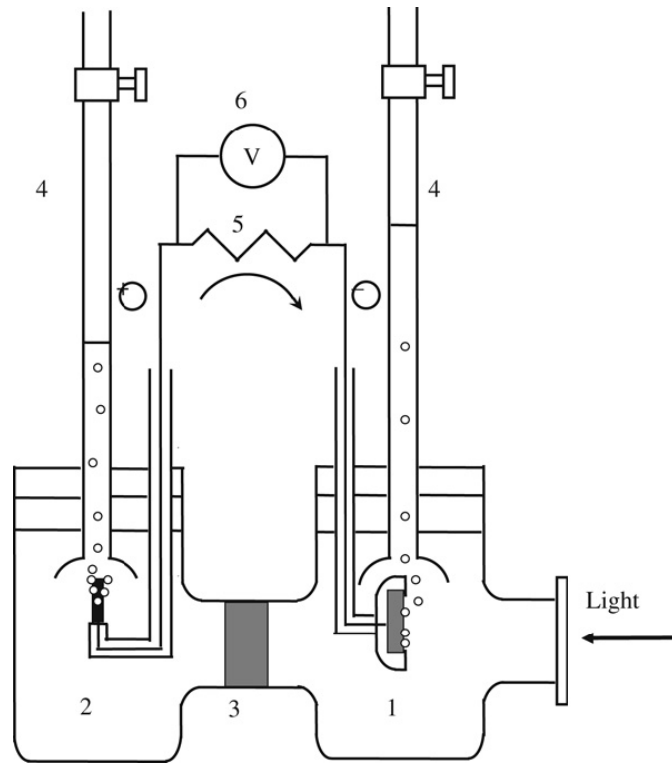




- **Key functional properties of photo-electrodes;**

**The modern era of semiconductor electrodes** and photoelectrochemical devices for energy conversion can be traced to the work of Honda and Fujishima on single-crystal TiO<sub>2</sub> electrode.

[AKIRA FUJISHIMA & KENICHI HONDA Nature 238, 37 - 38 (07 July 1972) Electrochemical Photolysis of Water at a Semiconductor Electrode]



A. Fujishima *et al.*, Surface Science Reports 63 (2008), 515-582

**main bottleneck: energy conversion efficiency at the anode**

## The problem is:

The materials that are stable in water and can split water into H<sub>2</sub> and O<sub>2</sub> do not absorb sunlight effectively,  
(optical function )  
and

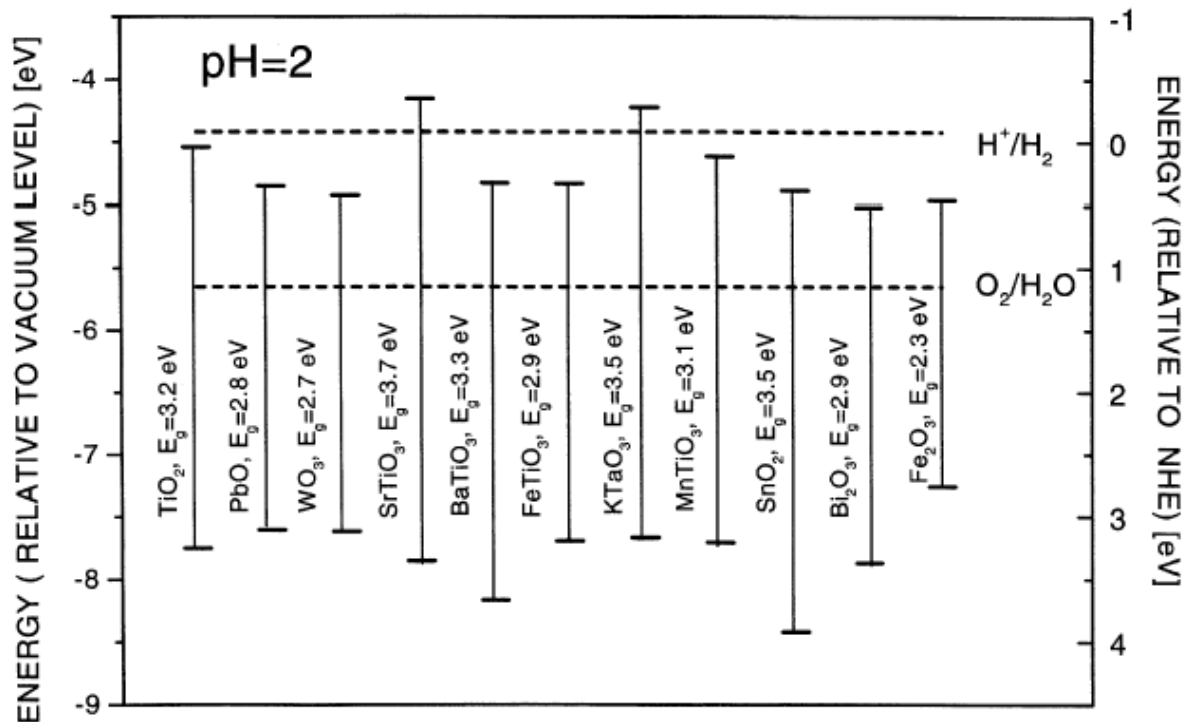
the materials that absorb sunlight effectively cannot sustain photochemically induced water-splitting.  
(catalytic function and durability)

## Key functional properties of photo-electrodes:

- Band gap
- Flat-band potential
- Schottky barrier
- Electrical resistance
  - Electrodes
  - Electrolyte
  - Electrical leads
  - Electrical connections
- Helmholtz potential barrier
- Corrosion and photo-corrosion resistance
- Microstructure
- .....

## Band gap

The band gap,  $E_g$ , is the smallest energy difference between the top of the valence band and the bottom of the conduction band. The width between the bands, through which the photon-induced ionization takes place, is an important quantity for materials that are candidates for photo-electrodes. The optimal band gap for high performance photo-electrodes is  $\sim 2$  eV.



Material, which satisfies this requirement and is corrosion resistant, is not available commercially.

**We need to process such a material!**

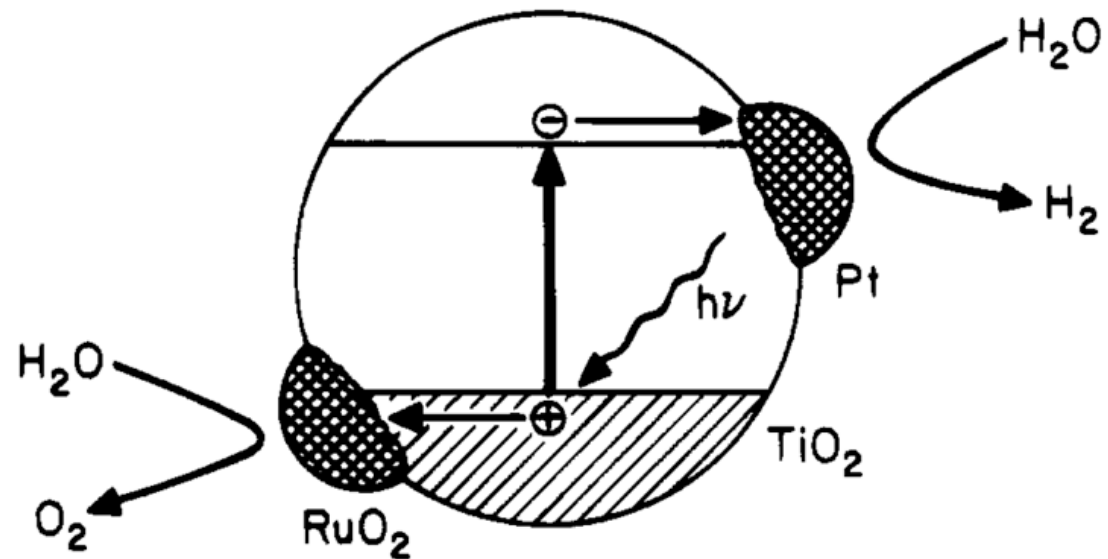
One possibility is through the imposition of a band located  $\sim 2$  eV below the conduction band. Experimentally, this impurity band can be achieved through the heavy doping of TiO<sub>2</sub> with aliovalent ions.

## TiO<sub>2</sub>

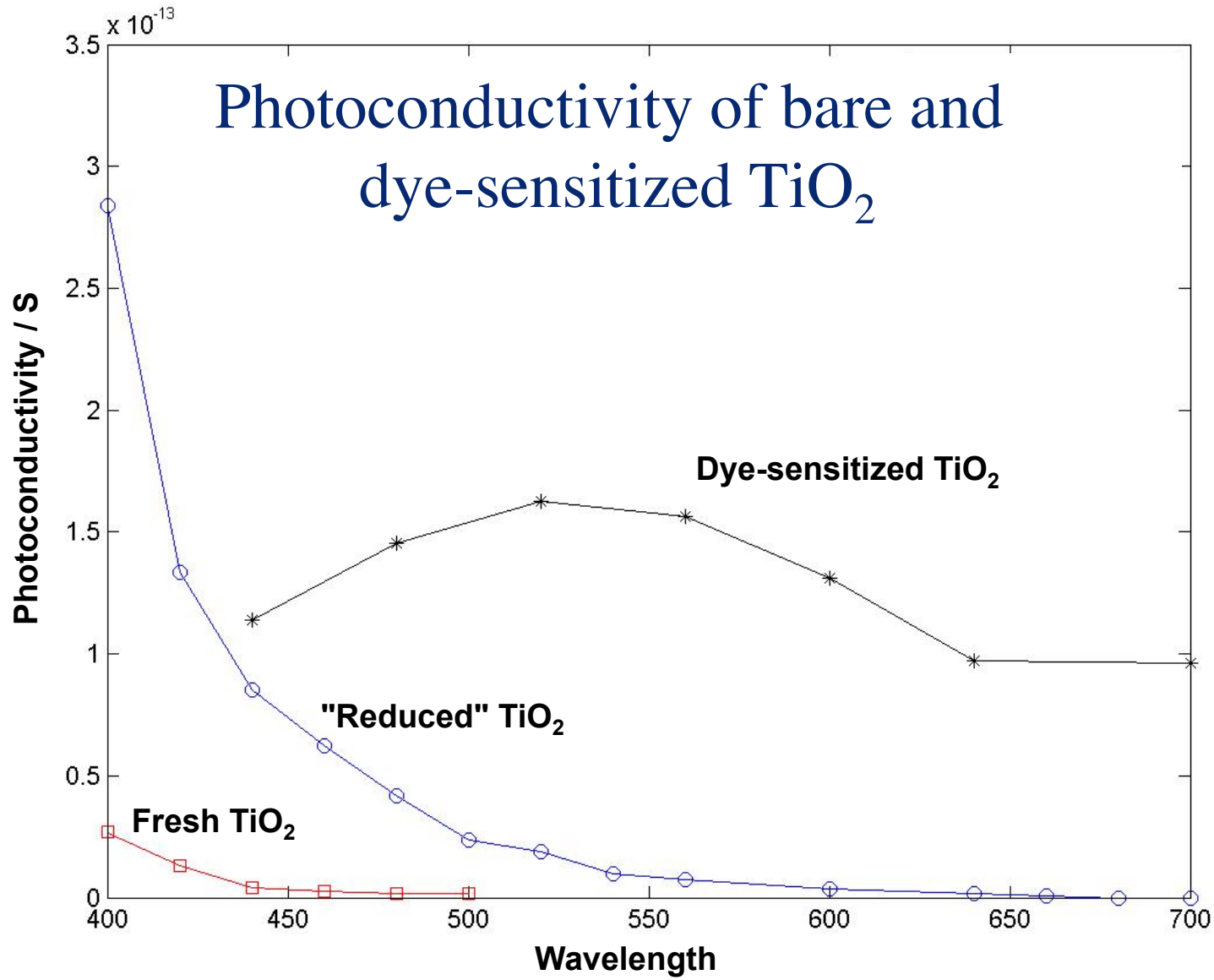
- TiO<sub>2</sub> is desirable for photocatalysis due to its:
  - inertness, stability, and low cost.
  - It is self regenerating and recyclable.
  - Its redox potential of the H<sub>2</sub>O/\*OH couple (-2.8 eV) lies within the band gap.
  - However, its large band gap (E<sub>g</sub>=3.2 eV) only allows absorption the UV of solar spectrum; --> an absorber in the visible range is desired.
  - Absorption in the visible range can be improved by dye sensitization, doping, particle size modification, and surface modification by noble metals.

# TiO<sub>2</sub>

The problem with TiO<sub>2</sub> is that the conduction band is too low (i.e., at an insufficiently negative potential) to generate hydrogen at a useful rate. Moreover, because the TiO<sub>2</sub> band gap is large (3.0 eV for rutile), only a small fraction of the solar light is absorbed and the efficiency of TiO<sub>2</sub>-based cells can never attain the specified 10% level. Cells with TiO<sub>2</sub> electrodes of various types (e.g., single crystal, polycrystalline, thin film) have nevertheless been heavily investigated, largely because TiO<sub>2</sub> is very stable and is a good model for understanding the semiconductor/liquid interface.



Schematic illustrating the elementary reaction steps of photocatalytic hydrogen production via water splitting on semiconductor nanoparticles and additional co-catalysts for oxygen and hydrogen evolution. Reprinted with permission from [Linsebigler AL, Lu G and Yates JT Jr. (1995) Photocatalysis on TiO<sub>2</sub> Surfaces: Principles, Mechanisms, and Selected Results. Chem. Rev. 95:735-758]

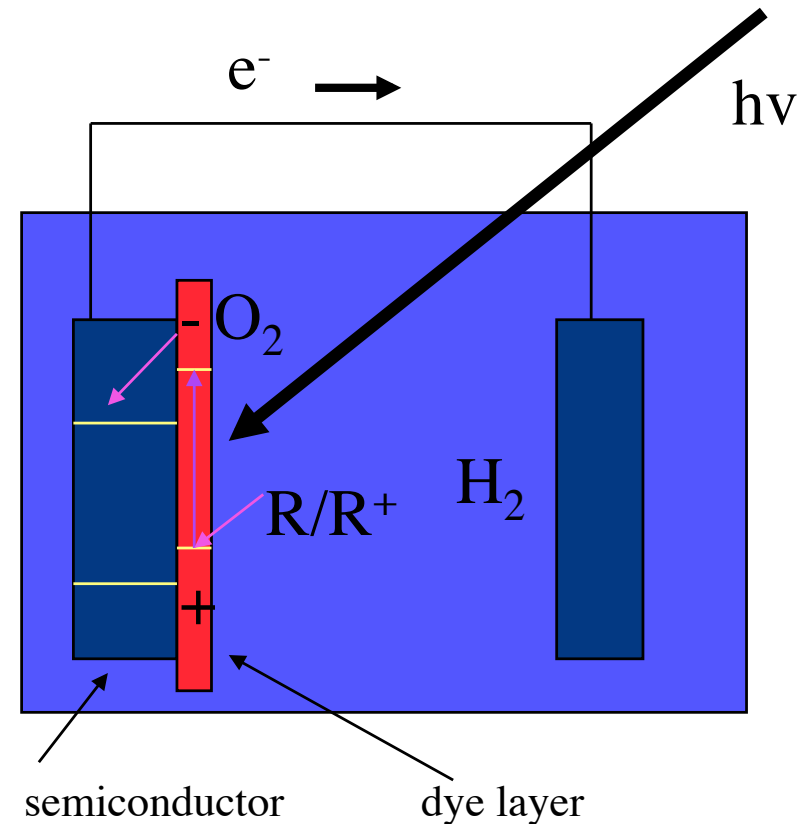


C. Hägglund



### Sensitized Semiconductor Systems:

To overcome the problems of a large band gap and inefficient utilization of the solar spectrum, e.g., with  $\text{TiO}_2$ , dye sensitizers can be adsorbed on the surface of the electrode or particle. The photon absorbed in the dye creates an electron which passes into the semiconductor, eventually causing a reduction reaction, and the hole is filled by an electron from an adsorbed or solution species in an oxidation reaction. With a thin film of dye, the quantum efficiency, i.e., the number of electrons injected into the semiconductor per photon *absorbed*, can be very high. However, with a thin dye layer, even in dyes with high extinction coefficients, only a small fraction of the incident photons are absorbed, so the overall solar efficiency tends to be small (usually  $\sim 1\%$  and more often  $<0.1\%$ ). The total absorbance by the dye layer can be increased by increasing its thickness, but in that case, since most of the photons are absorbed away from the interface between semiconductor and solution and must diffuse and migrate to that site before reaction, the quantum efficiency decreases sharply. A recent advance has been the use of highly porous  $\text{TiO}_2$  electrodes with very large surface areas (“fractal electrodes”) as substrates for the dye sensitizer. [MG]



## Progress in R&D

### Current research:

- \* Photoreactions at low temperatures
- \* Grätzel cell
- \* Water splitting for hydrogen and fuel production
- \* Sensors (!)

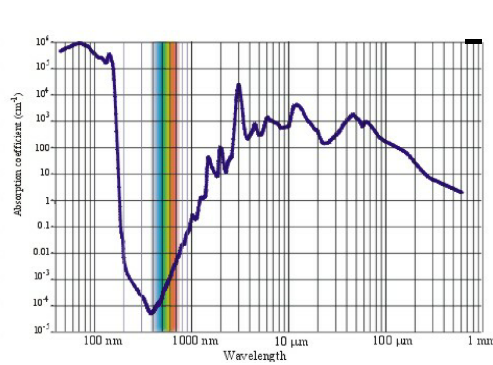


Garrett, Edmund H. (1853-1929), "Launcelot Beholds the Towers of Castle Carbonek"  
from: Francis Nimmo Greene. Legends of King Arthur and His Court. Boston: Ginn & Co., 1901.

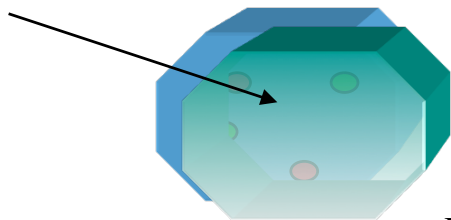
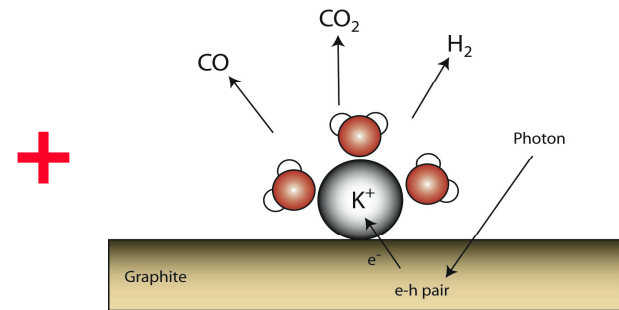
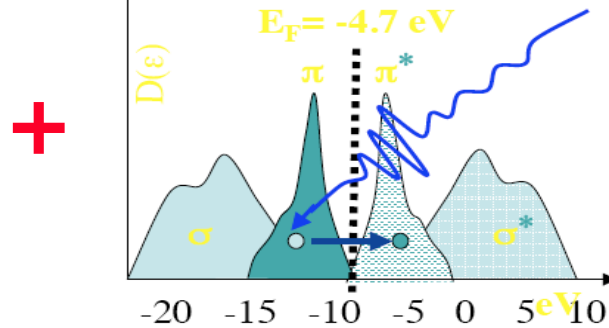
# How to split water with low energy photons?

**MODIFY!**

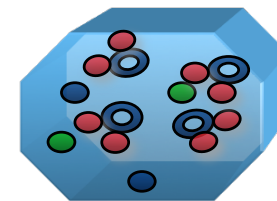
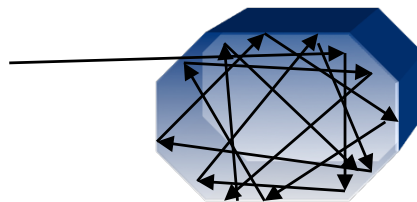
- WATER,
- SURFACE,



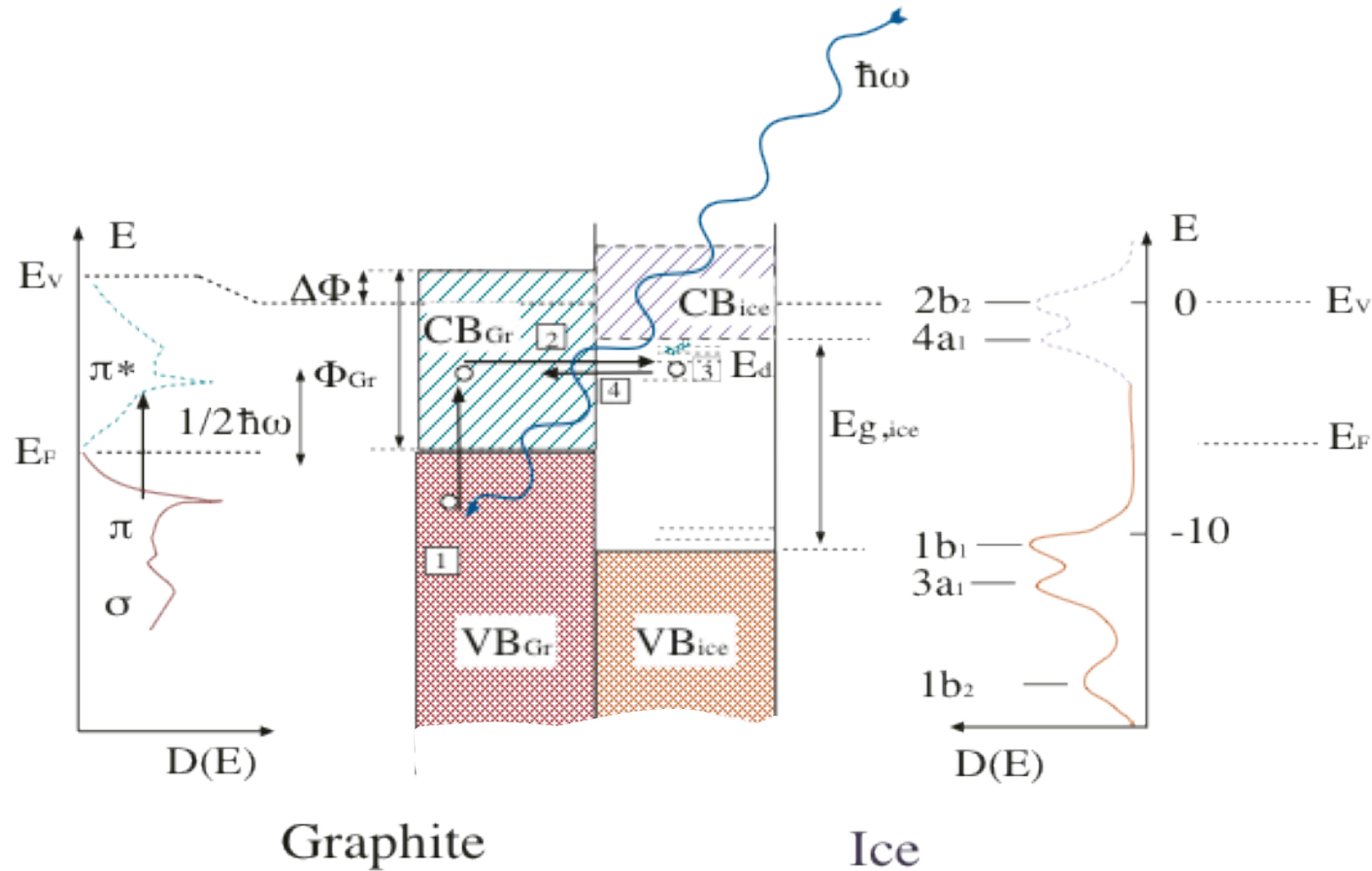
PRODUCTS



Light capture

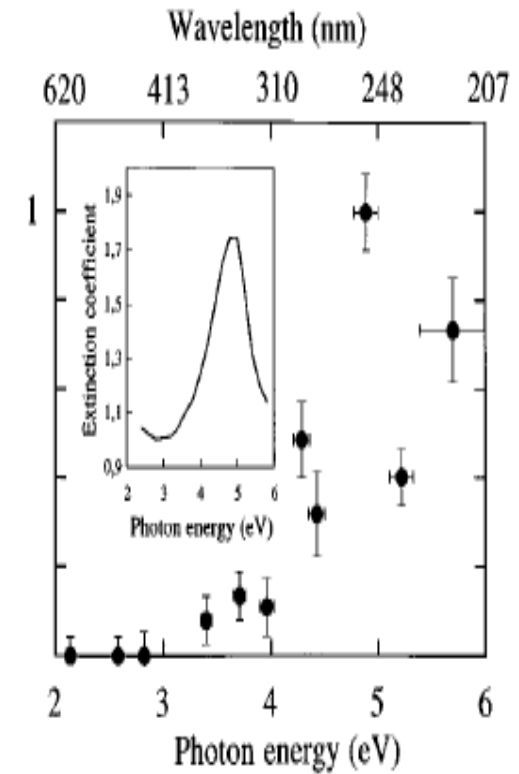
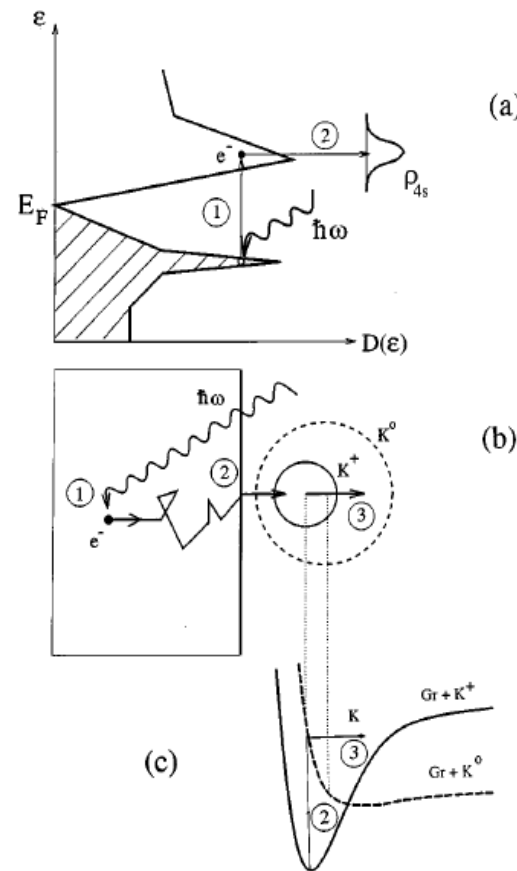
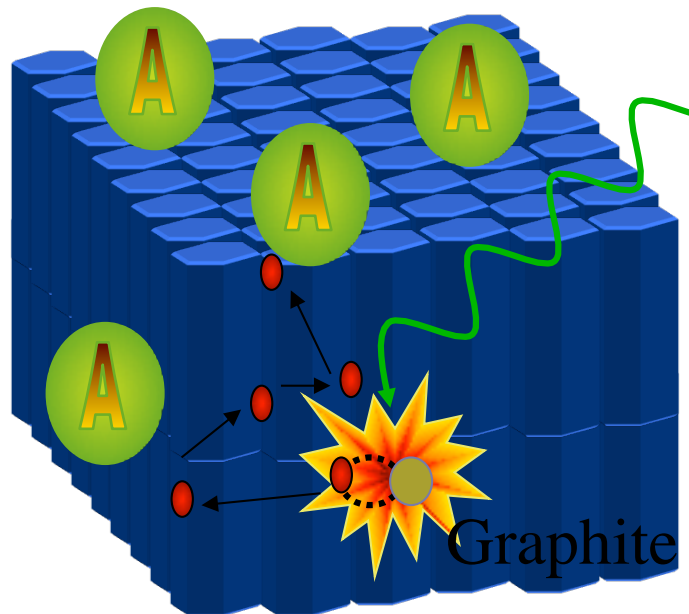


Products capture



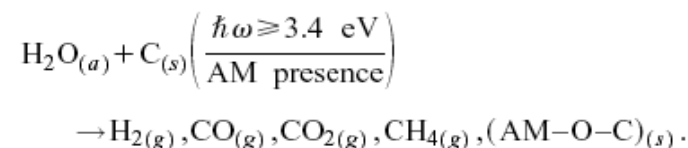
1. Photoexcitation of electron-hole pairs in graphite.
2. Tunneling of the electron into unoccupied defect states near but below the CB edge of ice.
3. Vibrational excitation.
4. Return of the electron after the local ice structure has relaxed into higher coordination.

PHOTO DESORPTION/ PHOTO MANIPULATION OF ALKALI ATOMS



Bo Hellsing et al., *J. Chem. Phys.* **106** (3), 982, 1997

# Photoreactions



J. Chem. Phys., Vol. 115, No. 20, 22 November 2001

Photoreactions of water and carbon at 90 K 9479

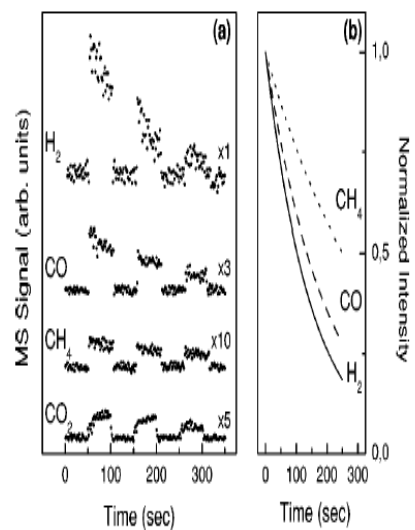


FIG. 1. (a) Photoinduced desorption spectra (PID) recorded for H<sub>2</sub> (m/e=2), CO (m/e=28), CH<sub>4</sub> (m/e=16), and CO<sub>2</sub> (m/e=44) during irradiation ( $\lambda=280 \text{ nm}$ ,  $1.6 \times 10^{16} \text{ photons} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ ) of a H<sub>2</sub>O and K co-adsorbed layer on graphite at 90 K. The coverages are 1.1 ML H<sub>2</sub>O co-adsorbed with 0.22 ML K. Opening and closing the shutter causes the rapid changes. This irradiation procedure with 50 s duty cycle is chosen to account for the background signal changes. (b) The result of single exponential fits to the initial decay of the H<sub>2</sub>, CO, and CH<sub>4</sub> signals upon irradiation.

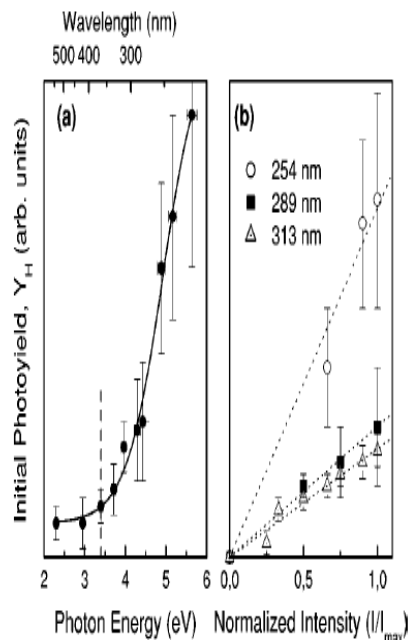
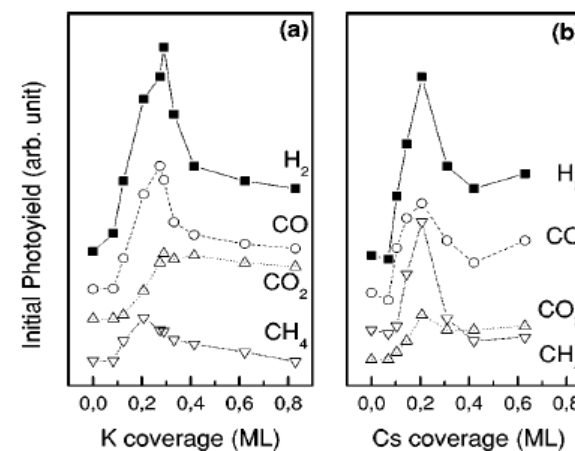
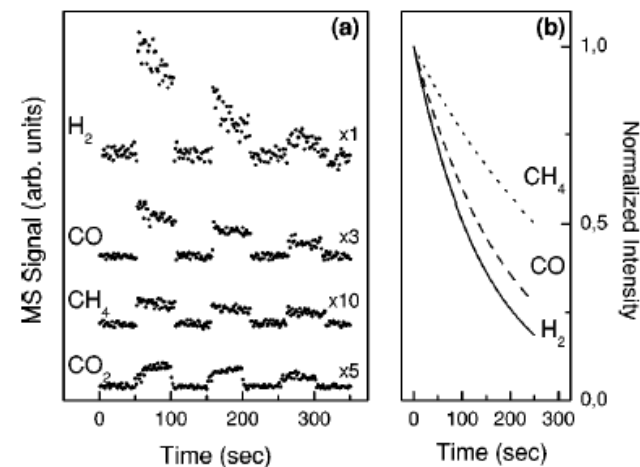
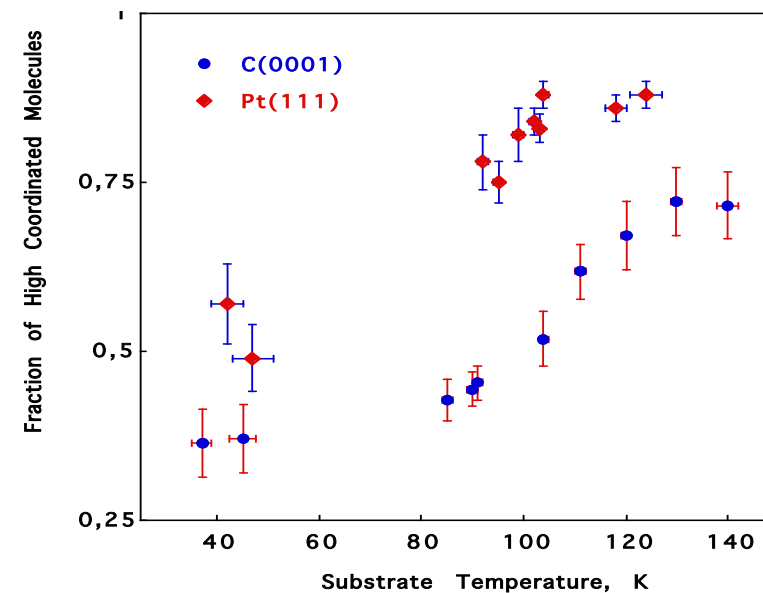
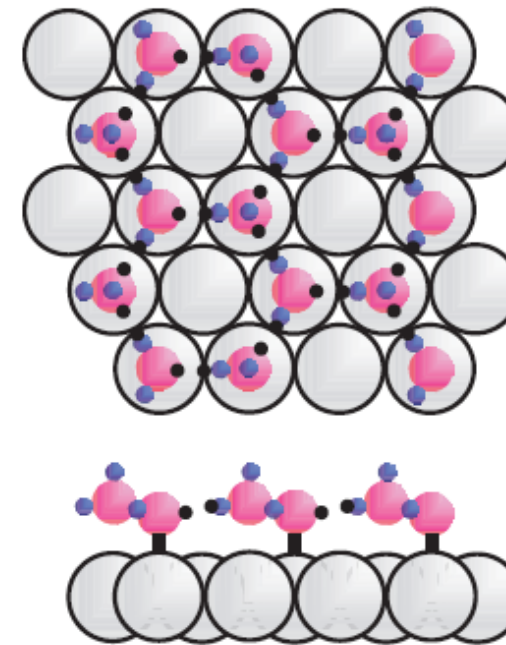
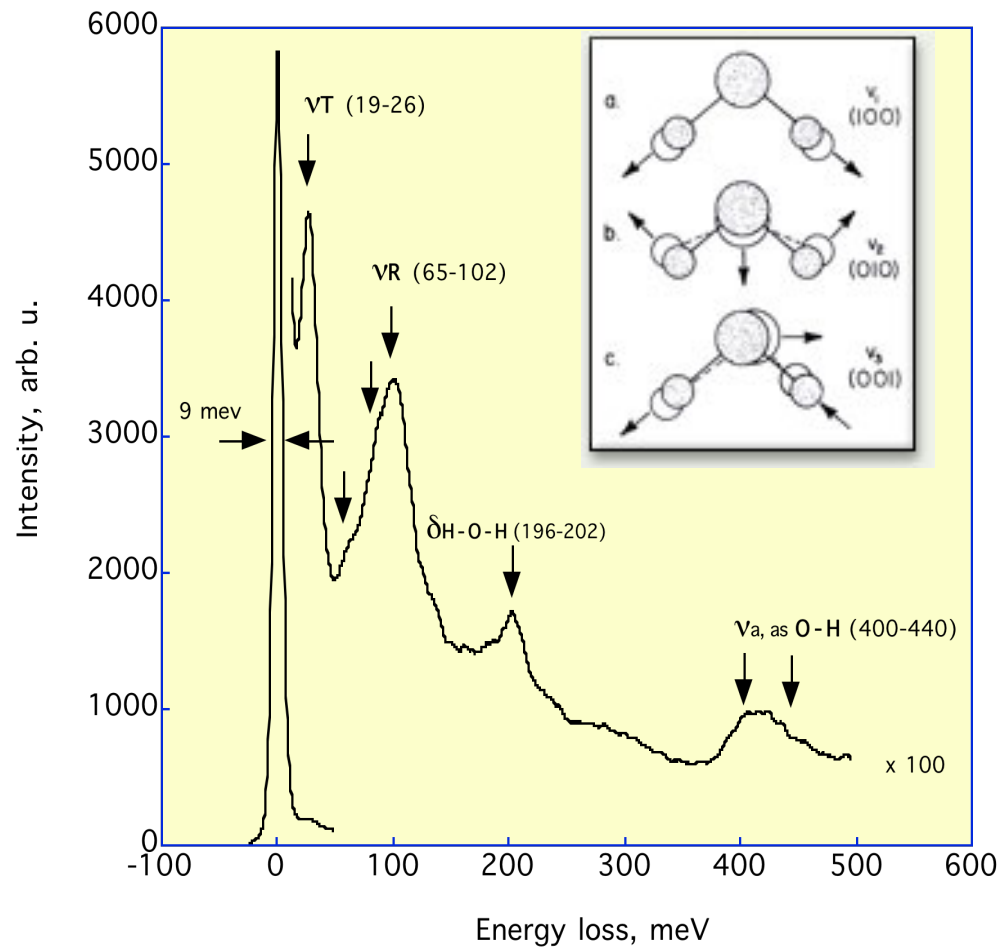


FIG. 2. Wavelength (a), and photon flux (b) dependence of the magnitude of the initial jump in the photodesorption signal for H<sub>2</sub>.  $\theta_{\text{H}_2\text{O}}=1.1 \text{ ML}$  and  $\theta_{\text{K}}=0.22 \text{ ML}$ .

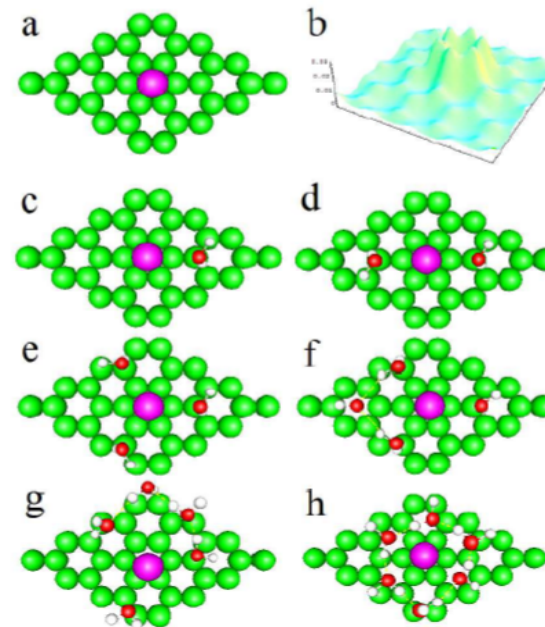
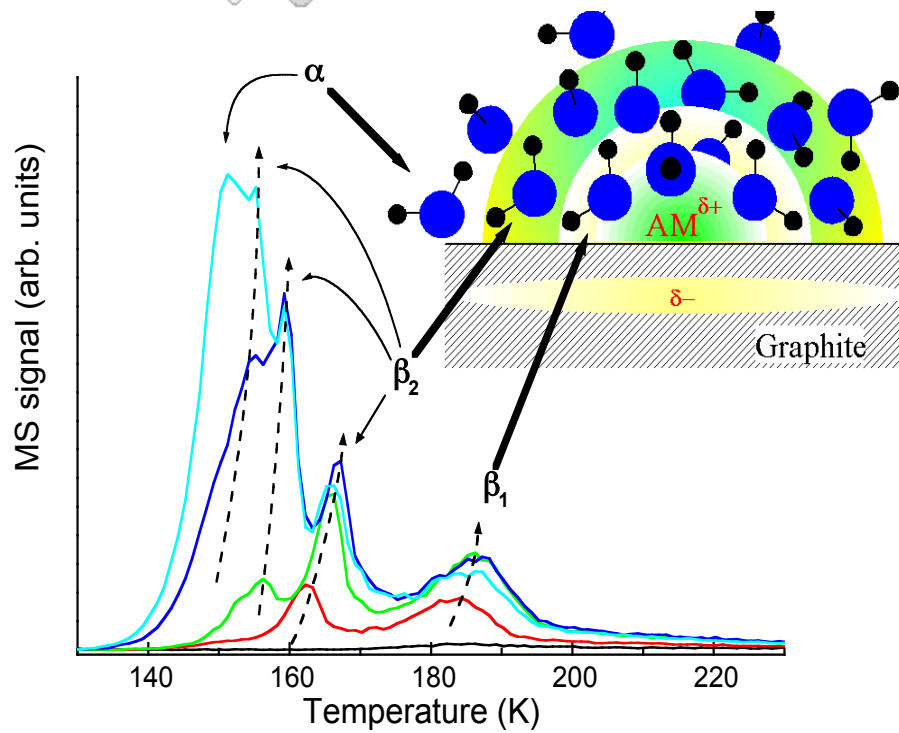
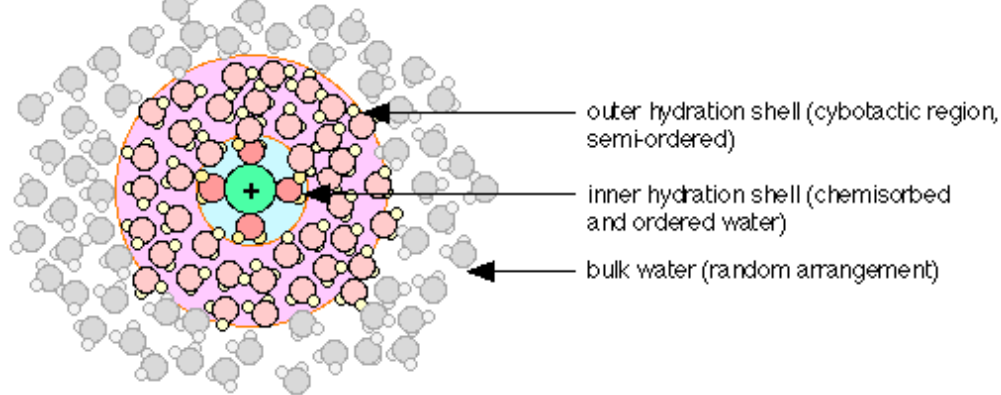


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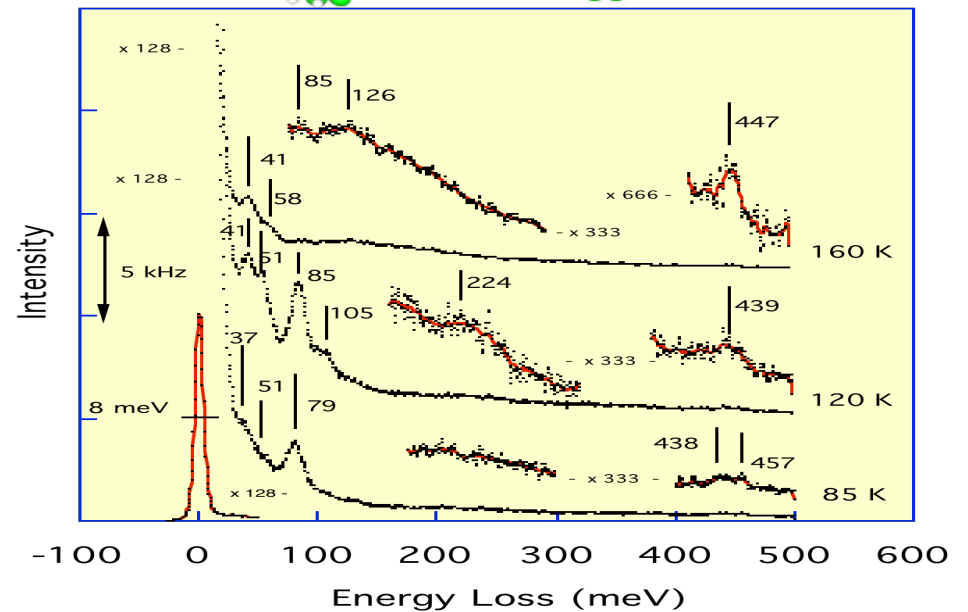
# Water absorption and photodissociation



# WATER + IONS

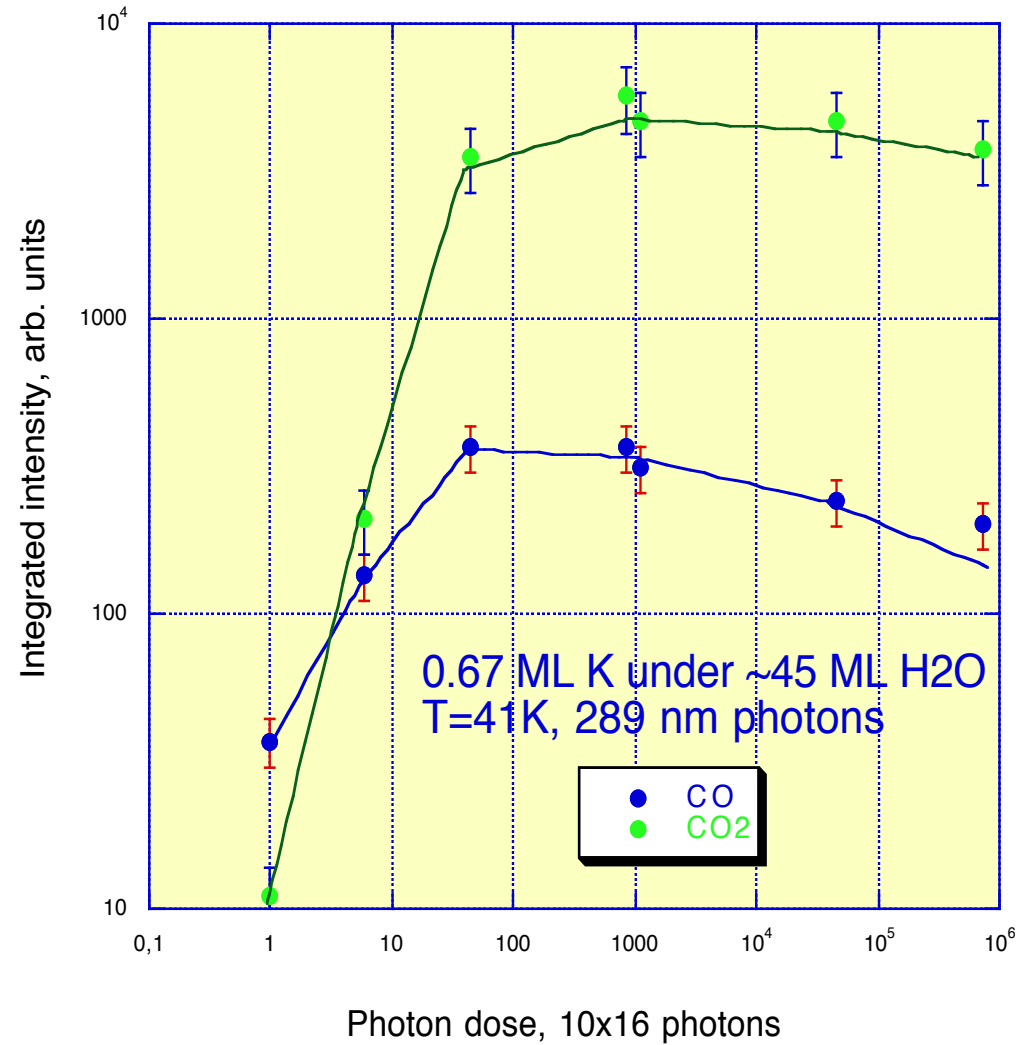
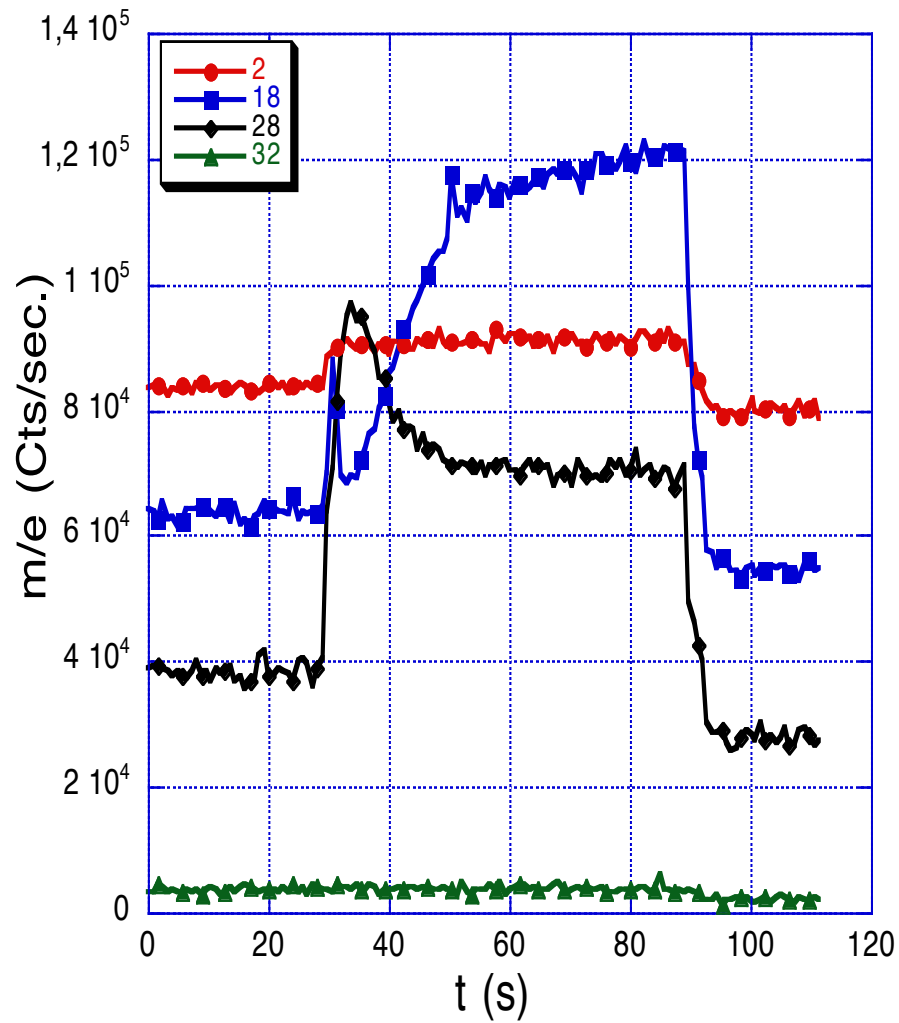


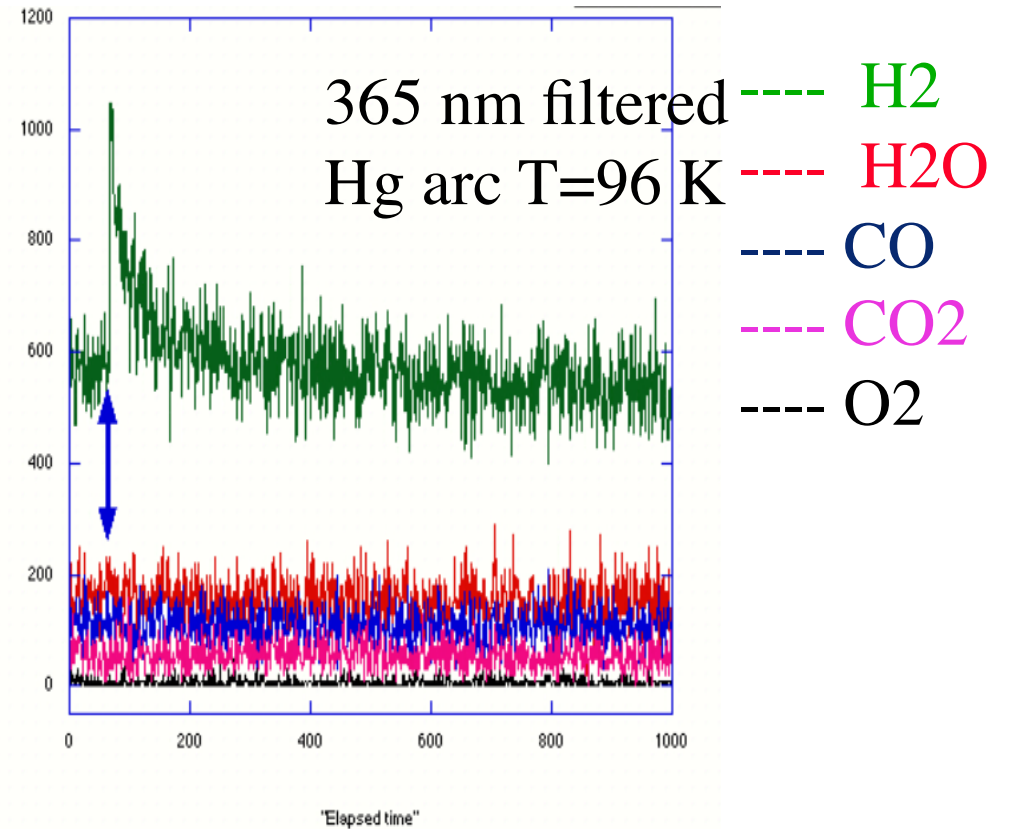
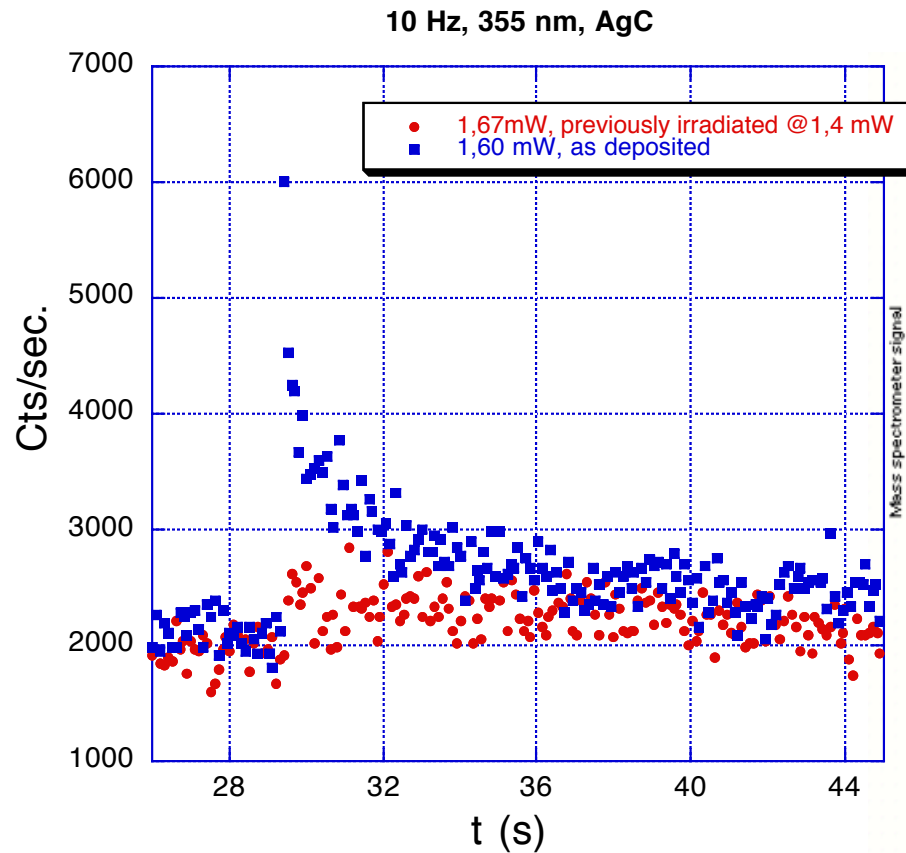
Sheng Meng, et al., JCP 121 12572 (2004).



*Appl. Surface Sci.*, **235** 91 (2004).







- Pulsed vs cw irradiation
- Laser pretreatment