

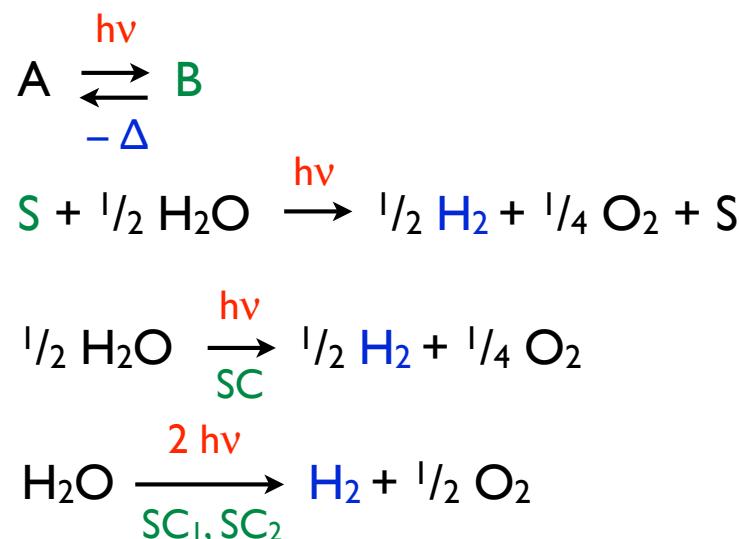
## 9.3 Artificial photosynthesis

### Photochemical conversion and storage of solar energy

Generation of electricity by photovoltaic systems suffer from the temporal mismatch of supply and demand. Storage of energy is often necessary for these systems to become a competing technology for conventional energy generation. One way to overcome the problem of storage is the development of photochemical systems that use sunlight directly to drive reversible chemical reactions leading to products that can be stored and later used to generate energy in another form. Because of their analogy with natural photosynthesis, such systems are often referred to *artificial photosynthesis*.

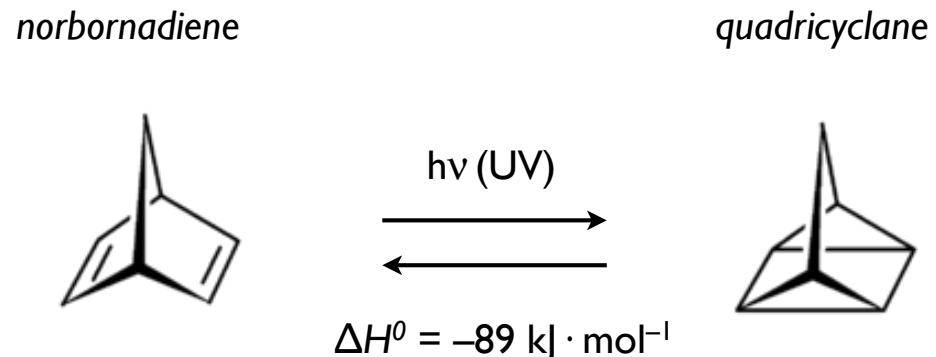
#### Various strategies for artificial photosynthesis

- reversible photo-reaction
- molecular water splitting
- photocatalytic water splitting
- photo-electrochemical hydrogen generation



## **Photochemical conversion and storage in a reversible molecular system**

Isomerization of 2,5 norbornadiene to quadricyclane has been early viewed as a potential mean for the conversion and storage of solar energy in a reversible molecular system, whose properties appear ideal:



- Norbornadiene is rather unexpensive (50 CHF / kg)
  - Reactant and product are liquids with low volatility
  - Photo-isomerization by visible light can be sensitized
  - Energy storage capacity is high ( $963 \text{ kJ} \cdot \text{l}^{-1}$ )
  - Quadricyclane is kinetically stable. Back isomerization in the presence of a catalyst is fast.

Thermal decomposition of quadricyclane accounts typically for a yield  $< 10^{-5}$ . This apparently insignificant lack of reversibility suffices, however, to prevent sustainable use of this system for photochemical conversion and storage of solar energy, which would require typically  $> 10^6$  turnover.

Generally, it is extremely difficult to ensure perfect reversibility for high energy-content molecules (parasitic reactions are always taking place in some extent). Another strategy must then be applied, which consists in the photosynthesis of a fuel.

## Photoredox water-splitting

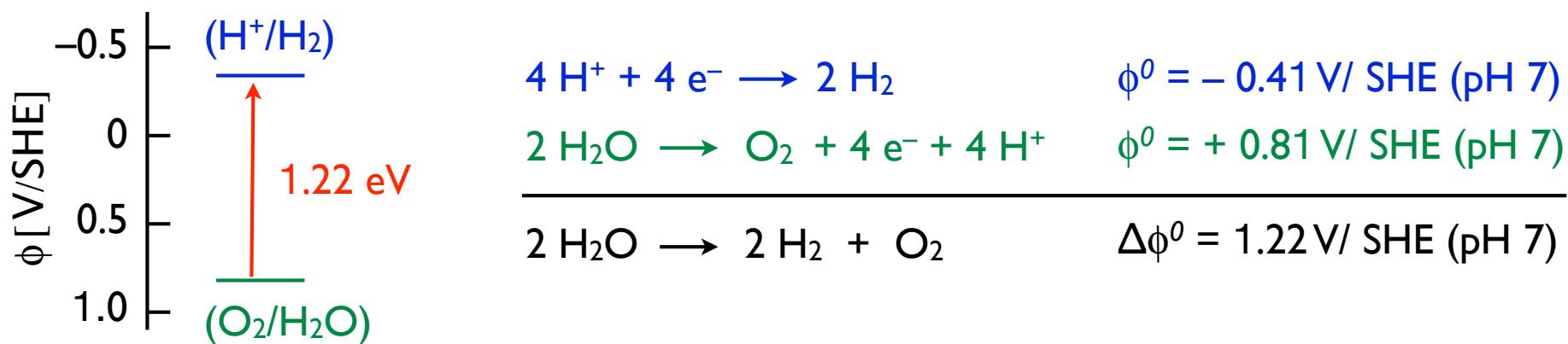
### Natural photosynthesis



### Artificial reactions analogs

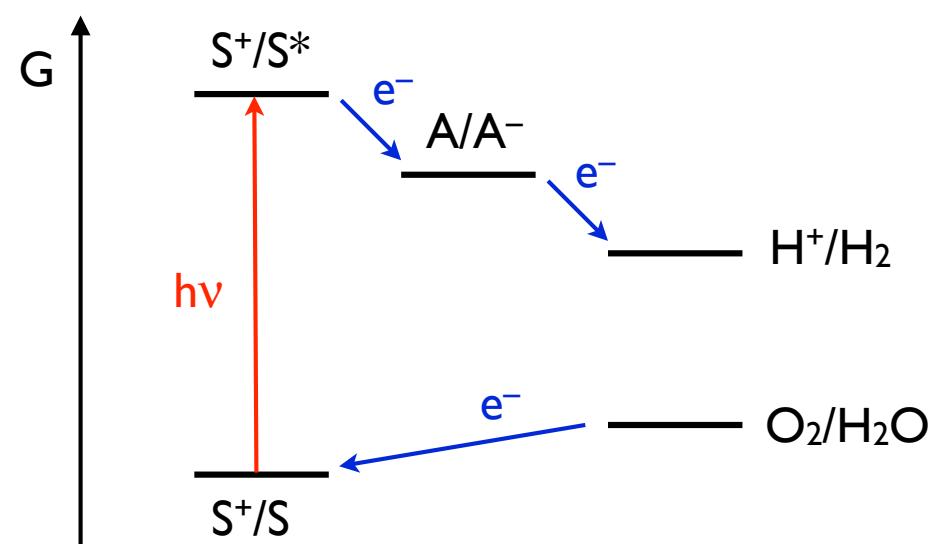
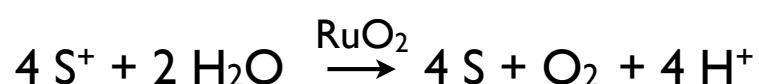
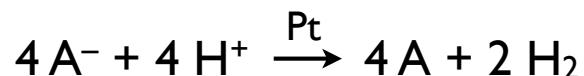
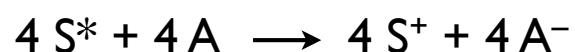
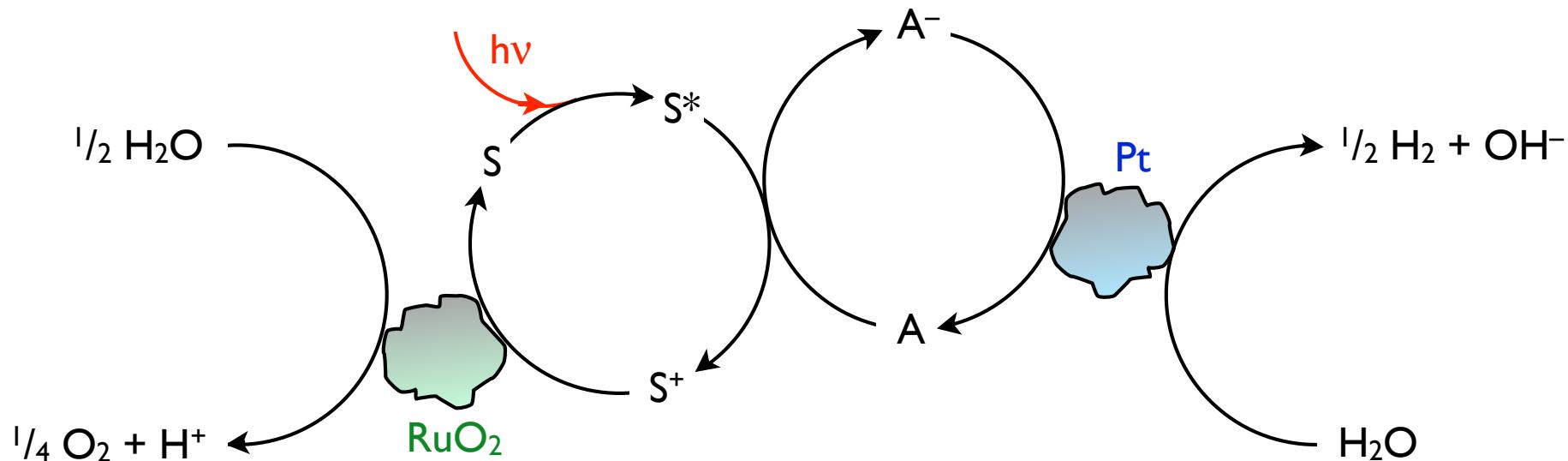


Homolytic water photolysis  $\text{H}_2\text{O} \rightarrow \cdot\text{H} + \cdot\text{OH}$  is only feasible for deep UV radiation with  $\lambda \leq 240 \text{ nm}$ . However, one can imagine a 4-electrons redox mechanism requiring for each step only  $472 / 4 = 118 \text{ kJ} \cdot \text{mol}^{-1}$ , corresponding to the absorption of photons of energy  $\text{h}\nu = 1.22 \text{ eV}$  ( $\lambda = \sim 1000 \text{ nm}$ ).



## Molecular water photolysis for hydrogen production

In practice, it is very difficult to carry out both water reduction and oxydation reactions simultaneously. In addition, multi-electron redox processes require the use of a catalyst able to store several redox equivalents.

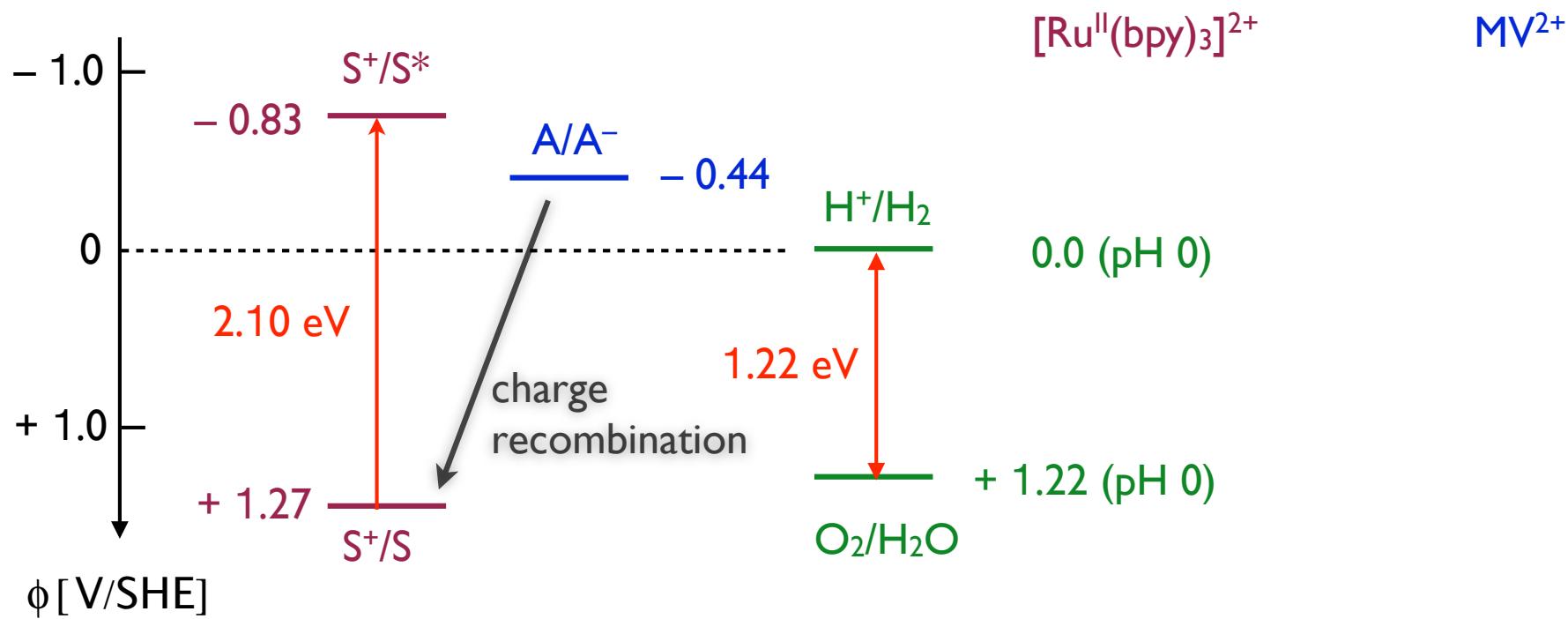
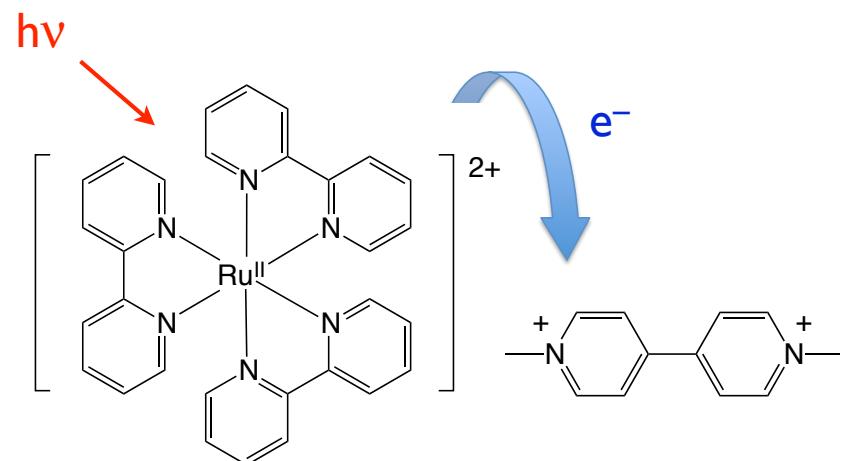


## Molecular water photolysis for hydrogen production

### Exemple

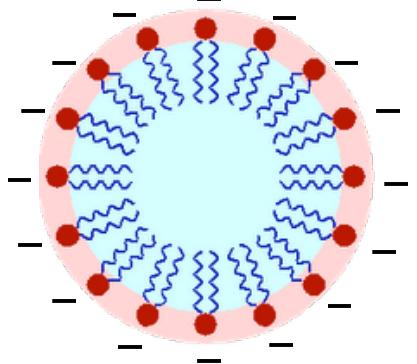
$$S = [\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+} \quad \phi^0(\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}) = +1.27 \text{ V/ SHE}$$

$$A = \text{MV}^{2+} \quad \phi^0(\text{MV}^{2+}/\text{MV}^+) = +1.27 \text{ V/ SHE}$$

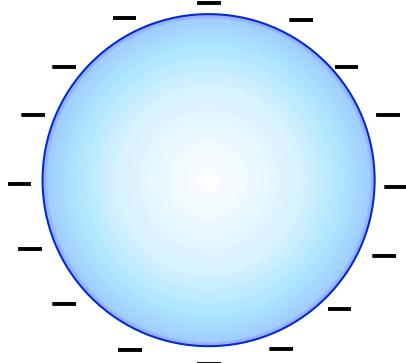


## **Hampering of charge recombination by electrostatic interaction**

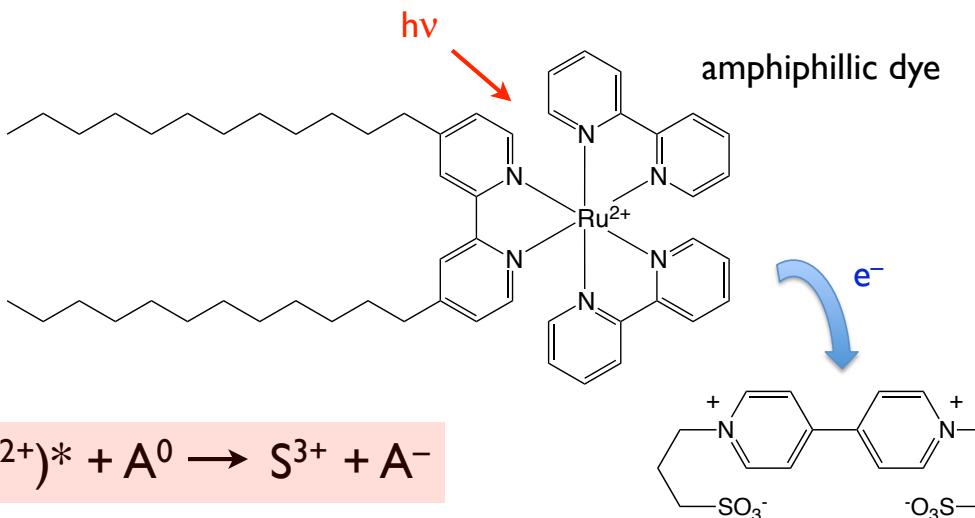
In both examples here below, electron transfer to zwitterionic (neutral) acceptor molecules yield reduced anions. These get repelled by the negatively charged micelles or colloidal particles, while dye cations are still strongly associated with the surface.



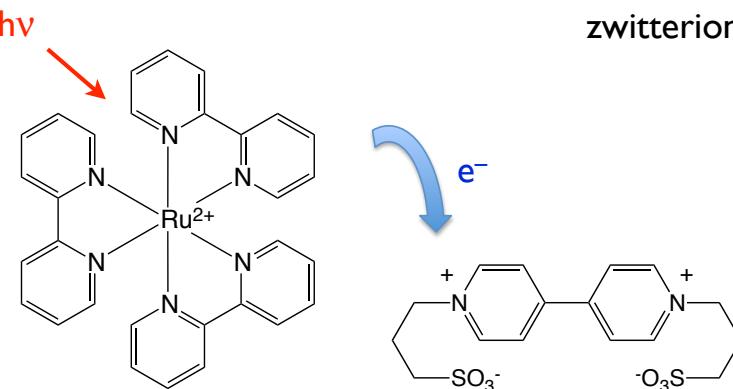
anionic surfactant micelle



colloidal metal oxide nanoparticle

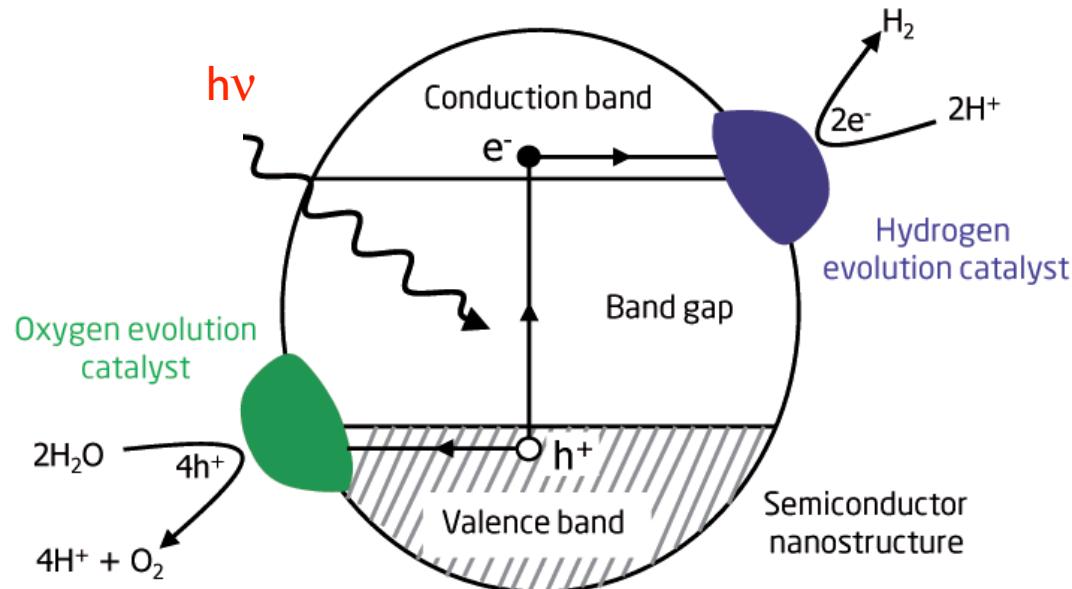


zwitterionic (neutral) acceptor



zwitterionic (neutral) acceptor

## Water-splitting using semiconductor photocatalysts

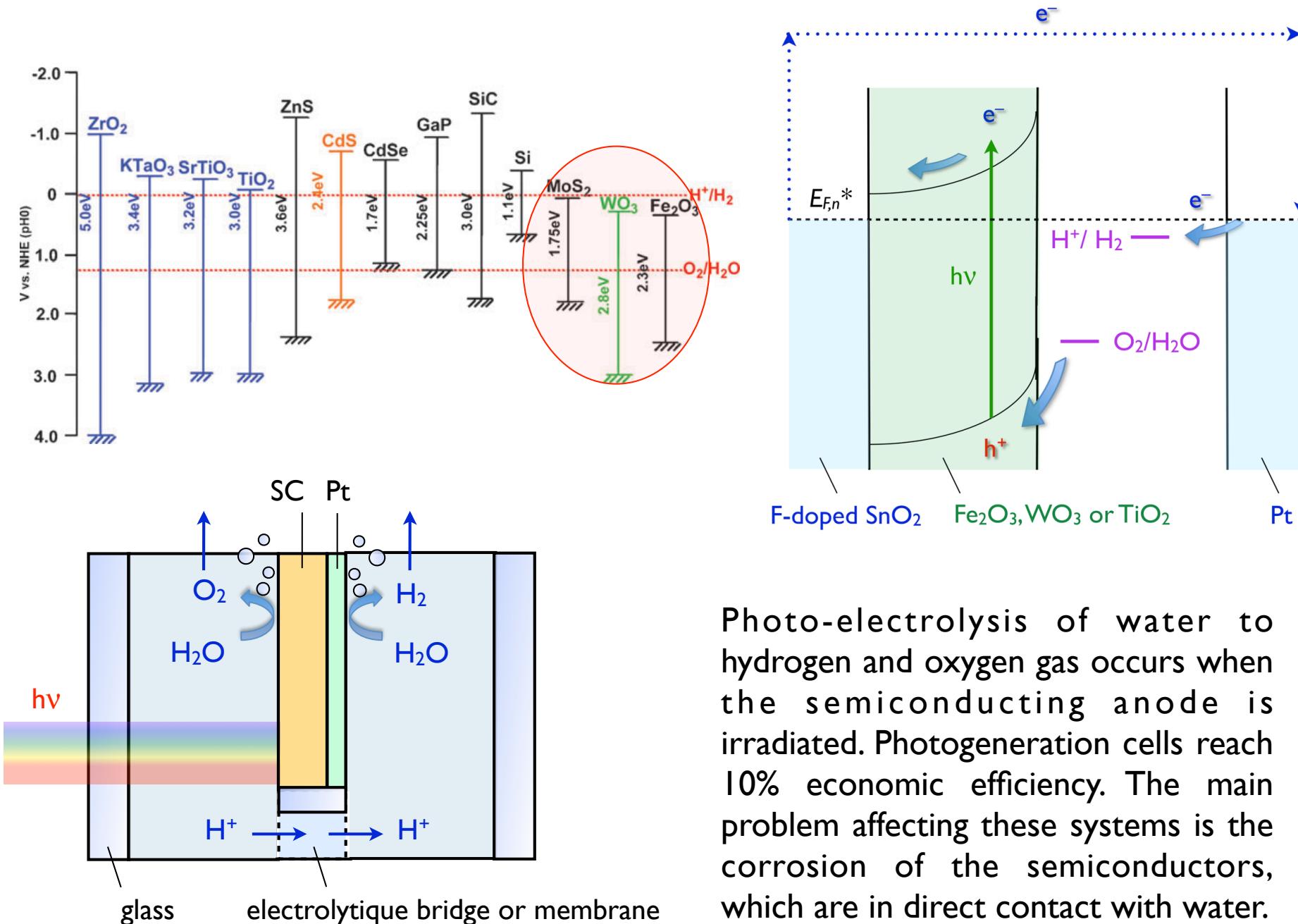


A. Fujishima, K. Honda  
*Nature* **1972**, *238*, 37-38

Pt clusters deposited on semiconducting nanoparticles are usually quite efficient in catalyzing hydrogen evolution. RuO<sub>2</sub> is a catalyst of choice for water oxydation. Because Ru<sup>IV</sup> can be successively oxidized to Ru<sup>V</sup>, Ru<sup>VI</sup>, Ru<sup>VII</sup> and Ru<sup>VIII</sup>, each ruthenium center in this metallic oxide can in principle store up to 4 oxydizing redox equivalents.

Simultaneous evolution of H<sub>2</sub> and O<sub>2</sub> from the same bulk and further separation of the two gases constitute a technical challenge. Systems allowing for separate evolution of hydrogen and oxygen in different compartments is therefore clearly preferred.

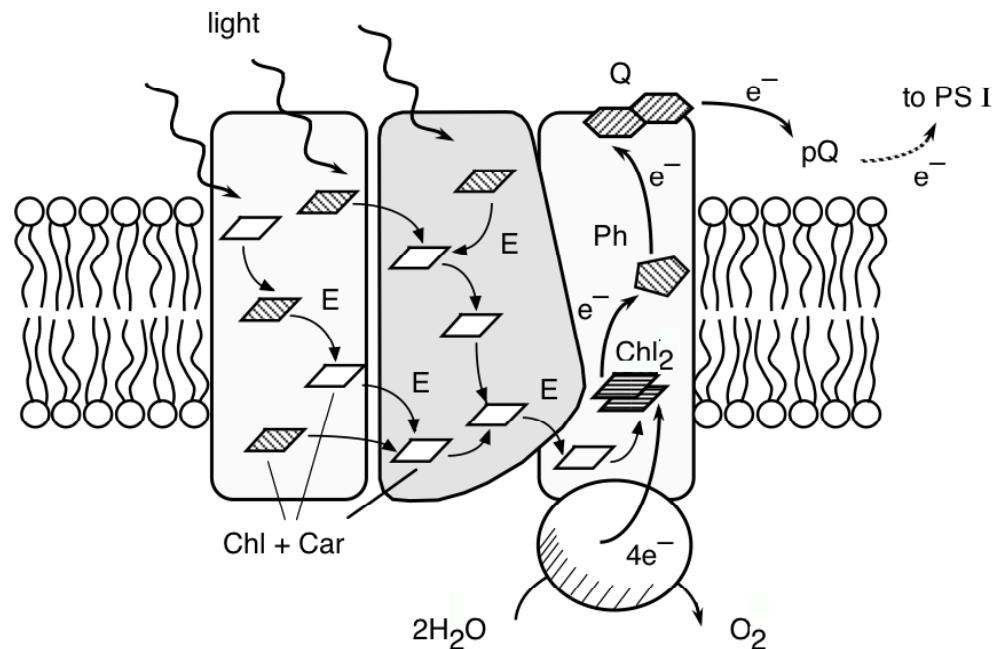
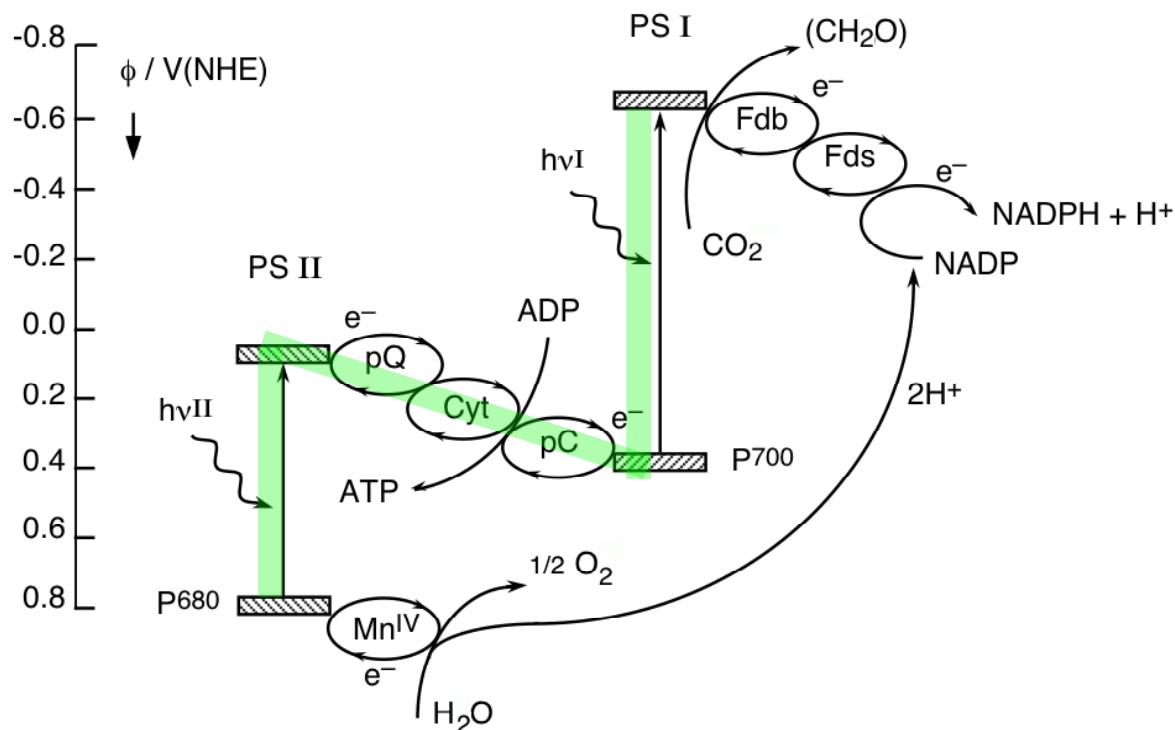
## Photo-electrochemical hydrogen generation



## Z-scheme tandem converter

### Natural photosynthesis

In natural photosynthesis, there are two light absorbing photosystems, PS I and PS II, each containing chlorophyll, that operate in series. Photoexcitation of PS II (right) initiates a series of redox steps resulting in the transfer of electrons from water to plastoquinone (pQ).

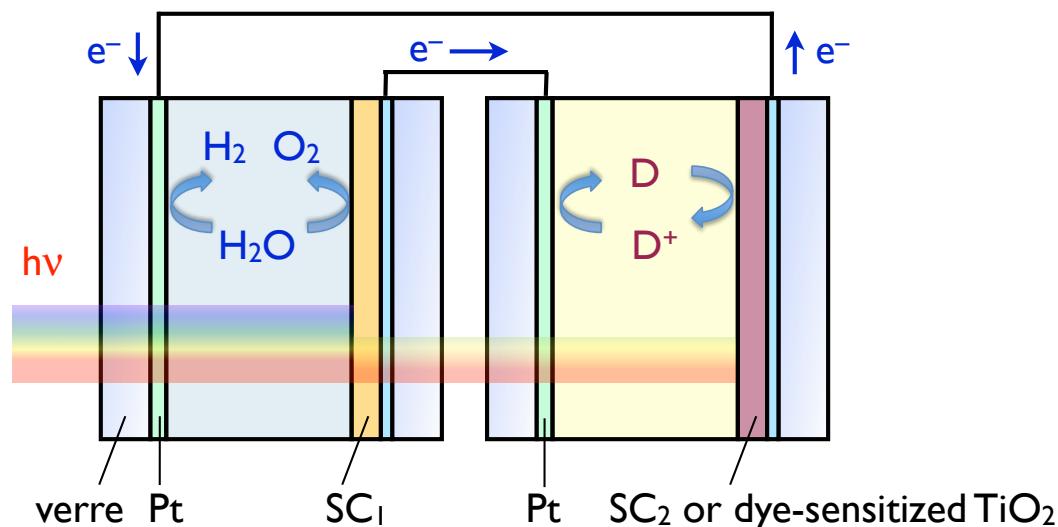
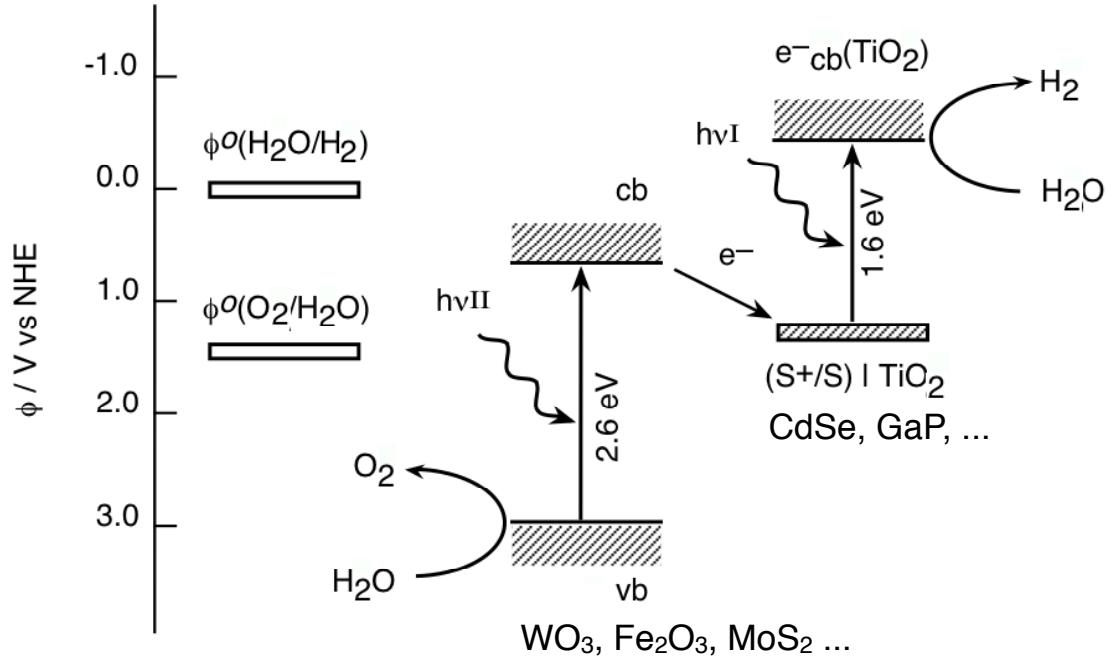


Plastoquinone (pQ), produced by PS II, is the electron donor for PS I, which under illumination performs the reduction of  $CO_2$  to carbon hydrate. Coupling of the two pigment systems PS II and PS I is often referred to a tandem- or Z-scheme (left).

## Z-scheme photo-electrochemical cells

### Tandem cell for hydrogen production

The most promising approach to reach the goal of water cleavage by visible light is by way of a tandem system employing two semiconductors having different bandgaps, coupled in a Z-scheme. Alternatively, one of the two photosystems can be constituted by a dye-sensitized wide bandgap semiconductor compartment.



A tandem system is particularly favorable, since complementary parts of the solar spectrum are exploited by the two photosystems that operate in series. The maximum thermodynamic efficiency of such a device can be > 42 %.

## 10. Semiconductor-assisted photocatalysis

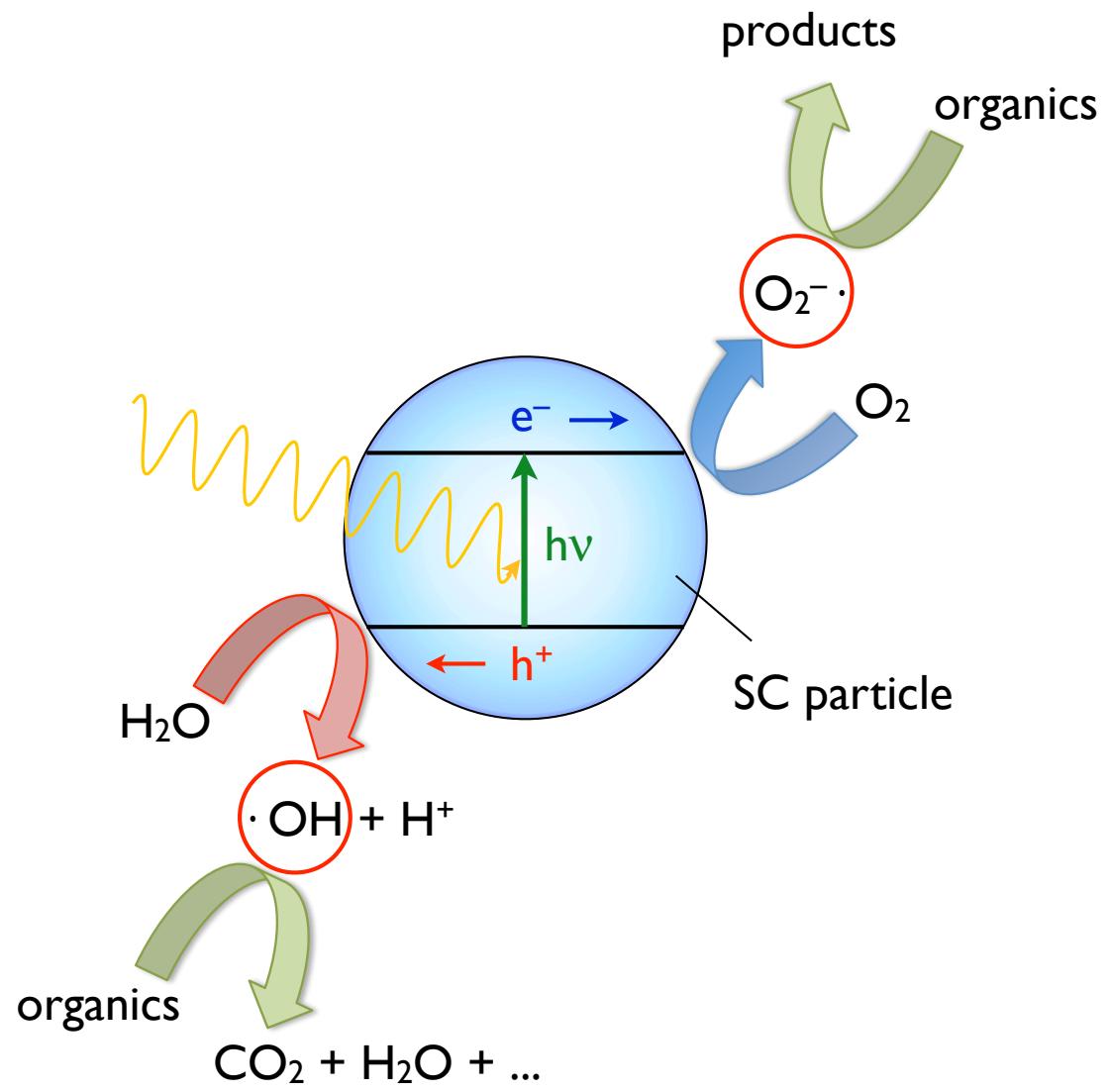
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## Advanced oxidation processes

**Photocatalysis** is the acceleration of a photoreaction in the presence of a catalyst. In catalysed photolysis, light is absorbed by an adsorbed substrate. In photogenerated catalysis, the photocatalytic activity (PCA) depends on the ability of the catalyst to create electron–hole pairs, which generate free radicals (hydroxyl and superoxy radicals:  $\cdot\text{OH}$ ,  $\cdot\text{O}_2^-$ ) able to undergo secondary reactions.

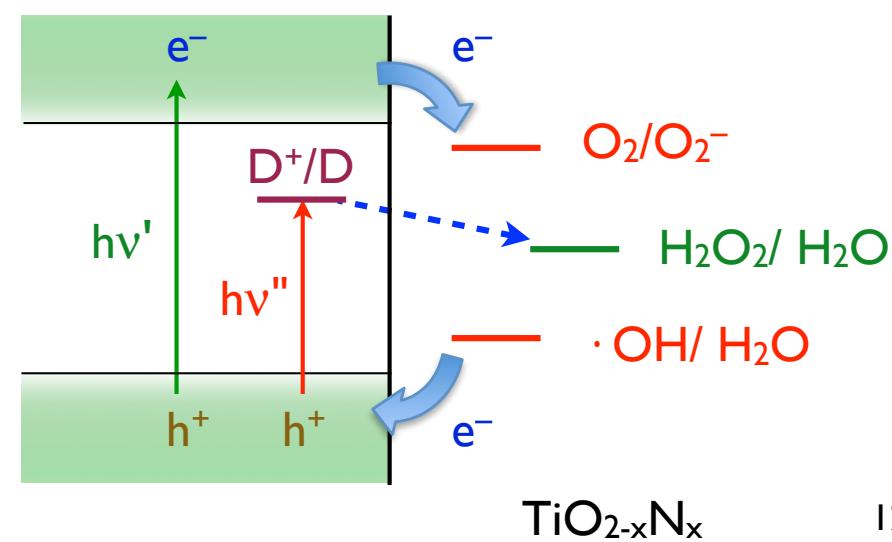
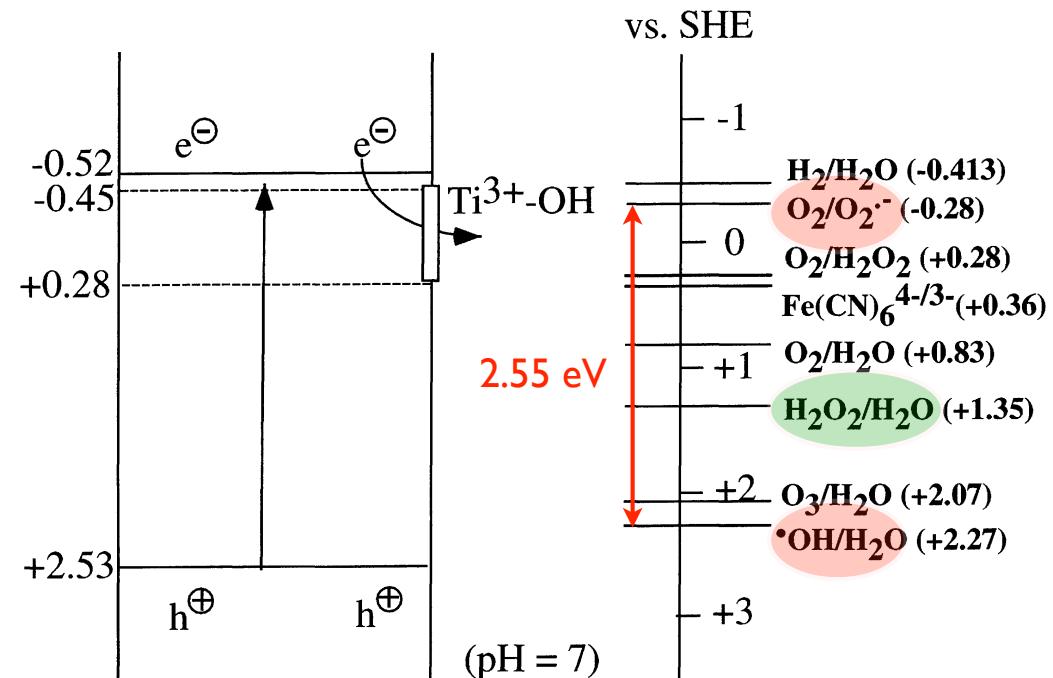
Commercial application of the process is called **Advanced Oxidation Process (AOP)**. There are several methods of achieving AOP's, that can but do not necessarily involve  $\text{TiO}_2$  or even the use of UV light. Generally the defining factor is the production and use of the hydroxyl radicals.



## Photocatalytic pollution remediation

Applications of photocatalysis has been particularly focused on the use of semiconductor materials for the removal of organic and inorganic species from aqueous or gas phase. This method has been suggested in environmental protection due to its ability to oxidise and mineralize organic pollutants.

Although requiring UV and blue light irradiation,  $\text{TiO}_2$  and  $\text{WO}_3$  are presently the most successful photo-catalysts. This is mainly due to the high potential of the valence band top edge of these oxides, allowing for oxidation of  $\text{H}_2\text{O}$  to  $\cdot\text{OH}$  radicals, and their intrinsic stability. Yellowish nitrogen-doped titania ( $\text{TiO}_{2-x}\text{N}_x$ ) can use visible light.  $\text{O}_2$  reduction is generally not thermodynamically feasible with this material, which requires another electron scavenger, such as  $\text{H}_2\text{O}_2$  or  $\text{Fe}^{3+}$ .



$\text{TiO}_{2-x}\text{N}_x$

124

## Fenton reaction



### Fenton reagent

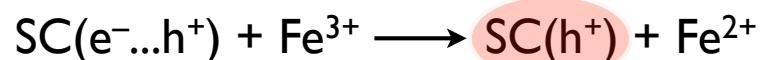
hydroxyl radical

superoxide radical ( $\text{O}_2^- + \text{H}^+ \rightleftharpoons \cdot\text{OOH}$ )

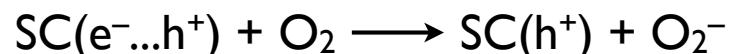
### Reactions of $\cdot\text{OH}$ with organic pollutants :



### Photo-Fenton reaction scheme :



} active oxidizing species



## **Photocatalytic water decontamination**

Conventional treatment systems like physico-chemical treatment followed by biological treatment are installed to treat a majority of industrial water effluents. Use of tertiary or advanced treatment methods may be required to remove particular contaminant or to prepare the treated effluent for reuse. Some common tertiary operations are removal of residual organic compounds by adsorption/ flocculation and removal of dissolved solids by membrane filtration. Waste water is also treated with ozone or other oxidizing agent to destroy harmful contaminants. Photocatalytic water decontamination is an interesting alternative for tertiary water treatment.  $\text{TiO}_2$  or  $\text{WO}_3$  semiconductors, derivatized with Pt catalyst, are often immobilized on the inner surface of glass tubes or coated on large-area falling-film solar reactors.

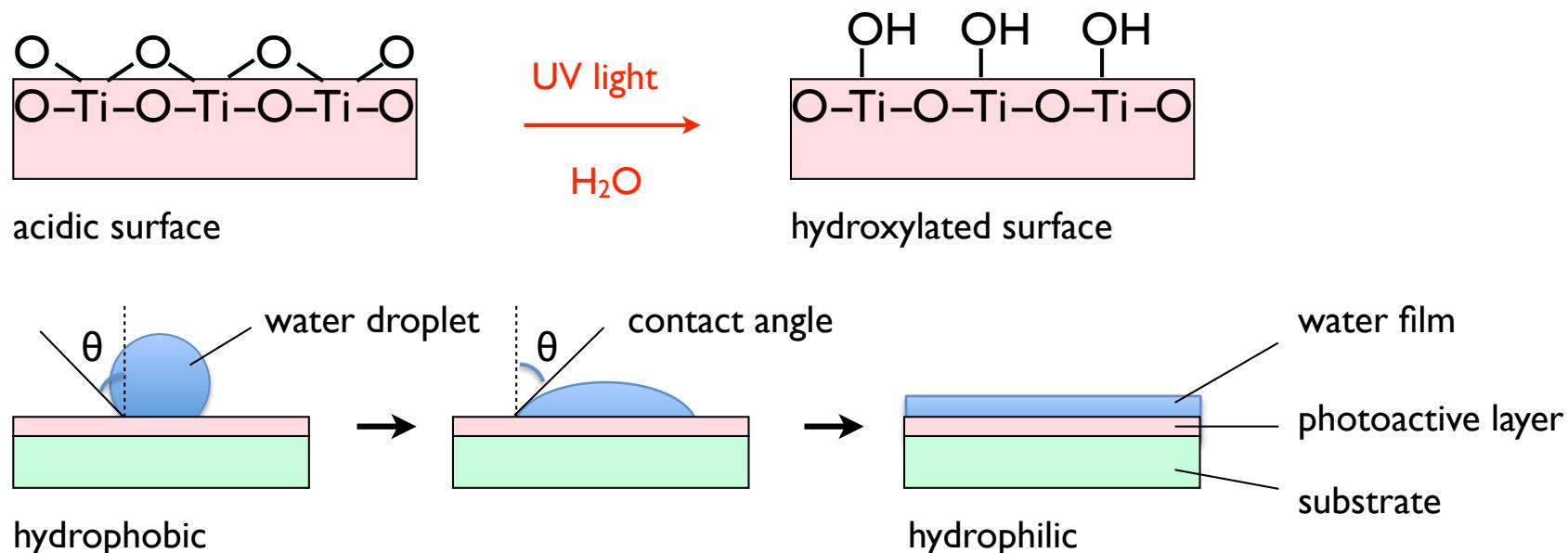


Photocatalytic solar water treatment unit for the decontamination of effluents of a textile industry (Borj Cedria, Tunisia)

## **Superhydrophilicity and self-cleaning surfaces**

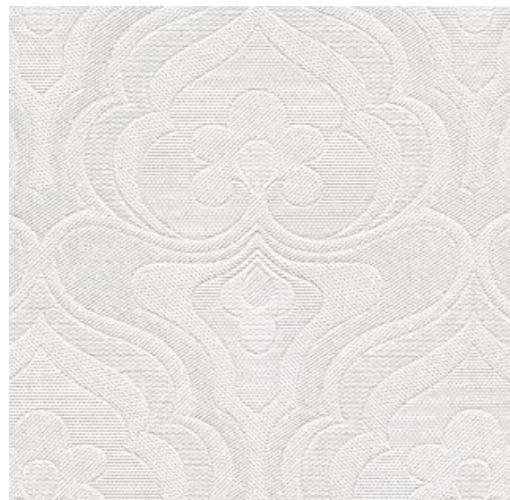
Under light irradiation, water dropped onto  $\text{TiO}_2$  forms almost 0 degrees contact angle. This effect is called **superhydrophilicity**. Superhydrophilic material has various advantages. For example, it can defog glass, and it can also enable oil spots to be swept away easily with water. Such materials are already commercialized as door mirrors for cars, coatings for buildings, self-cleaning tiles and glass windows, etc.

Titania ( $\text{TiO}_2$  anatase) has become the material of choice for self-cleaning windows, and hydrophilic self-cleaning surfaces in general, because of its favorable physical and chemical properties. Not only is titania highly efficient at photocatalysing the destruction of organic dirt in sunlight and reaching the superhydrophilic state, it is also relatively easy to handle and deposit into thin transparent films on glass and other substrate surfaces.



## ***Indoor air purification***

Volatile organic compounds (VOC) include pollutants such as formaldehyde, ammonia, solvents and many other common contaminants generally found in the home, which are released for instance by building materials, household cleaners, cooking and cigarette smoke.



Light bulbs, wallpaper, tiles and artificial plants coated with TiO<sub>2</sub> are now quite popular in Japan and Korea and are supposed to purify indoor air by removing bad smells, VOCs, airborne bacteria and fungi, and other noxious pollutants.

## **Photocatalytic biocidal activity**

Being strong oxidants, the reactive oxygen species generated by photocatalytic reactions also cause various damages to microorganisms ensuring their rapid inactivation. Destruction of potential organic nutrients by AOPs lead as well to bacteriostatic effects. TiO<sub>2</sub>-assisted photocatalytic biocidal activity has been demonstrated for a wide spectrum of pathogenic microorganisms, including bacteria (*Escherichia coli*, *Staphylococcus aureus*, ...), viruses, fungi and algae.

Photocatalysts can be applied to the disinfection of drinking water and to produce antimicrobial coatings on fabrics, carpets and tiles. In recent years, semiconductors, such as TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> and CdS, were applied in the field of phototherapy of malignant cells, and have been regarded as potential photosensitizing agents for photodynamic therapy (PDT) of cancer due to their unique phototoxic effect upon irradiation.

