Wasserstoffproduktion durch lichtinduzierte Wasserspaltung

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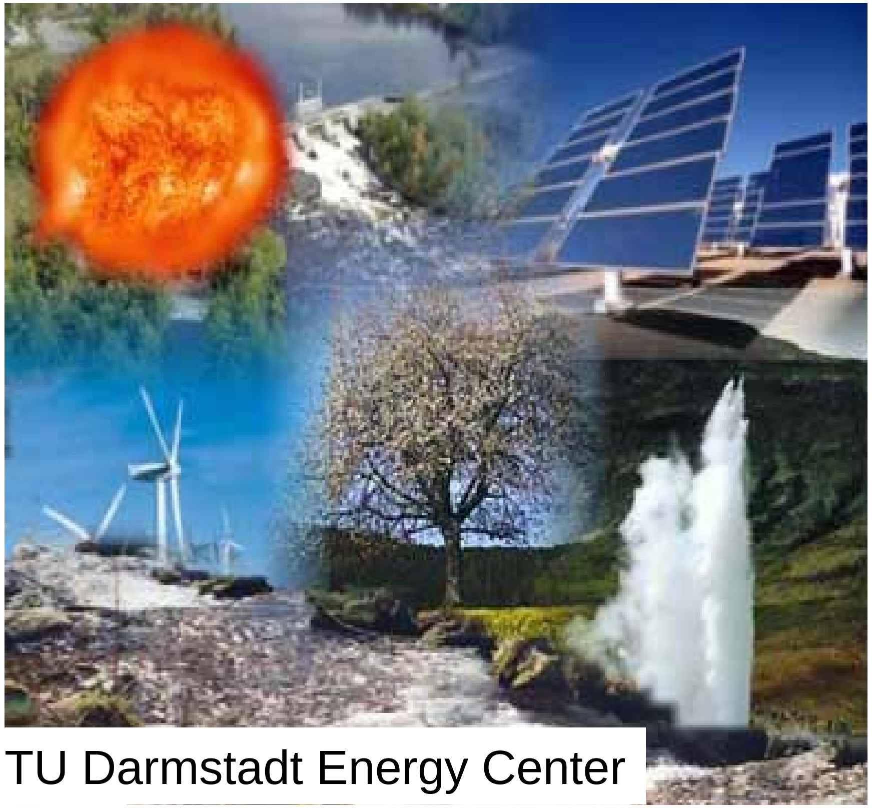
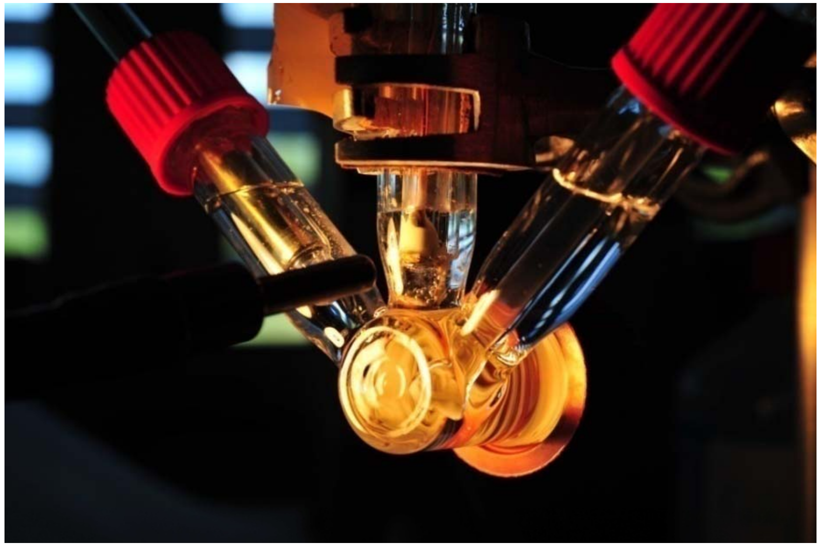


TU Darmstadt Energy Center

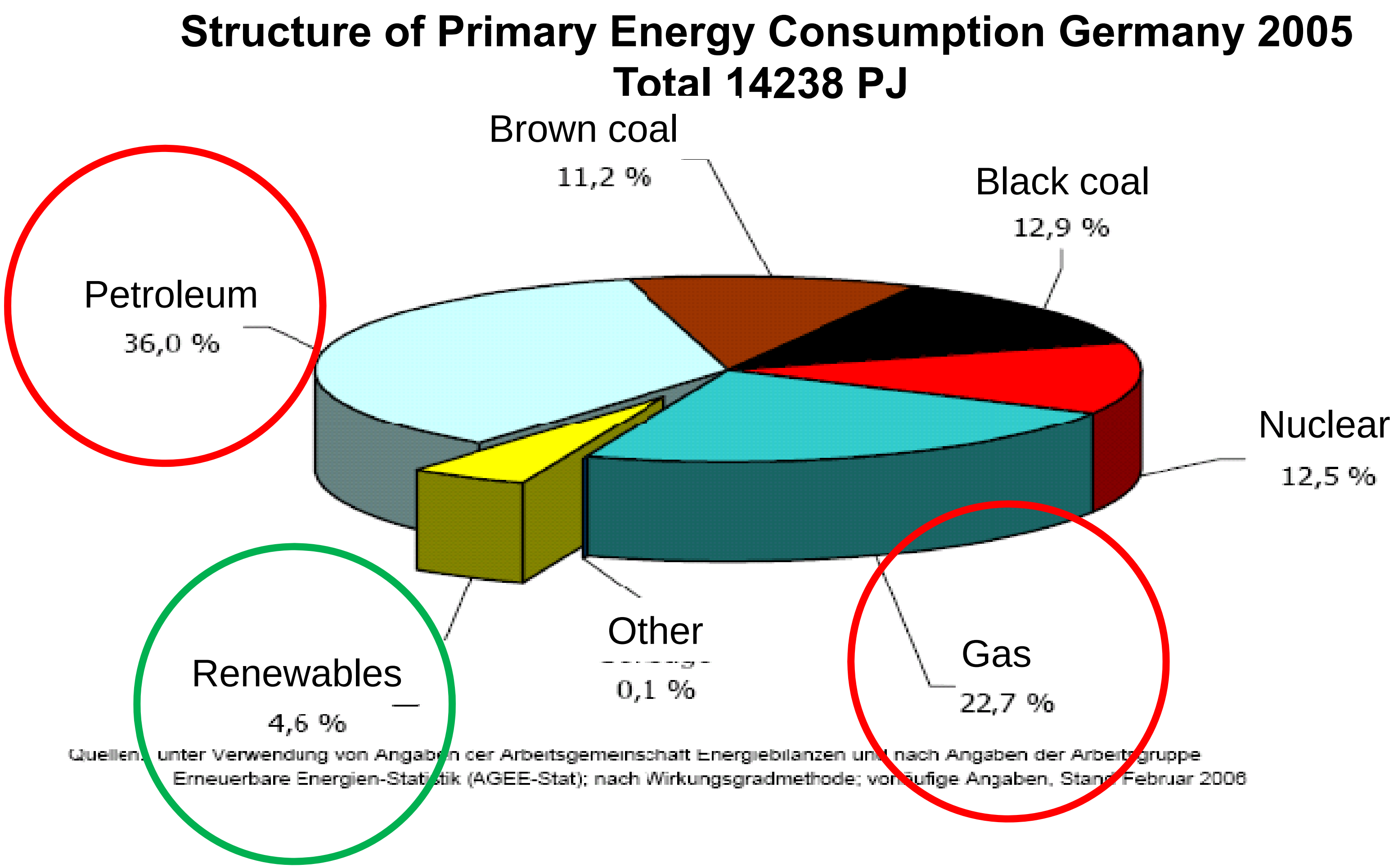
Inhalt: Solar erzeugter H_2

- **Grundsätzliche Überlegungen**
- **Thermodynamische Aspekte**
- **Kinetische Aspekte**
- **Realisierungsstrategien**
- **Schlussfolgerungen**

Experiment p-GaAs/H_2SO_4/Pt

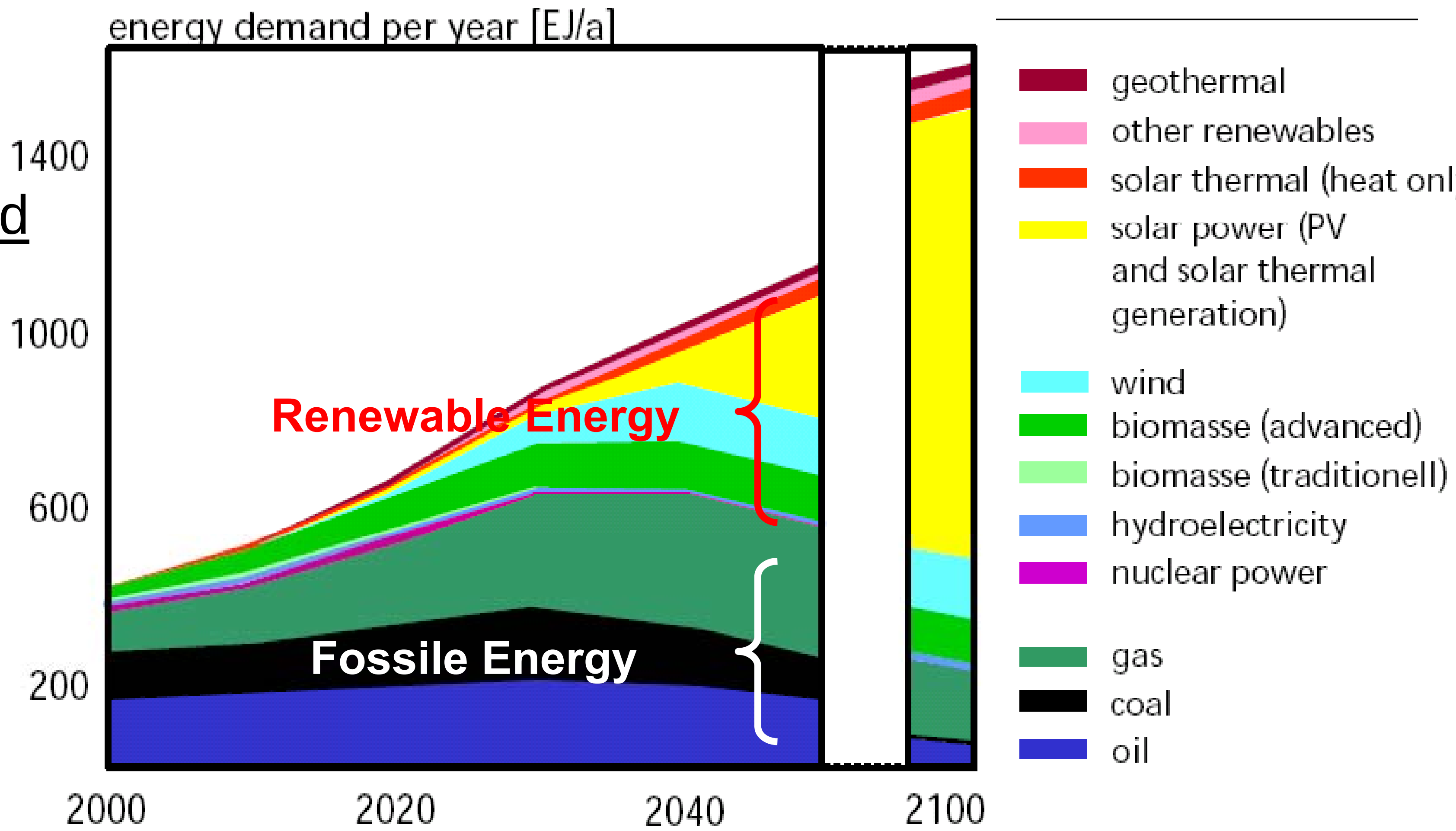


Energy Resources used „Today“



Energy scenarios

World energy demand



(Wissenschaftlicher Beitrat der Bundesregierung Globale Veränderungen, 2003, www.wbgu.de)

Energy scenarios

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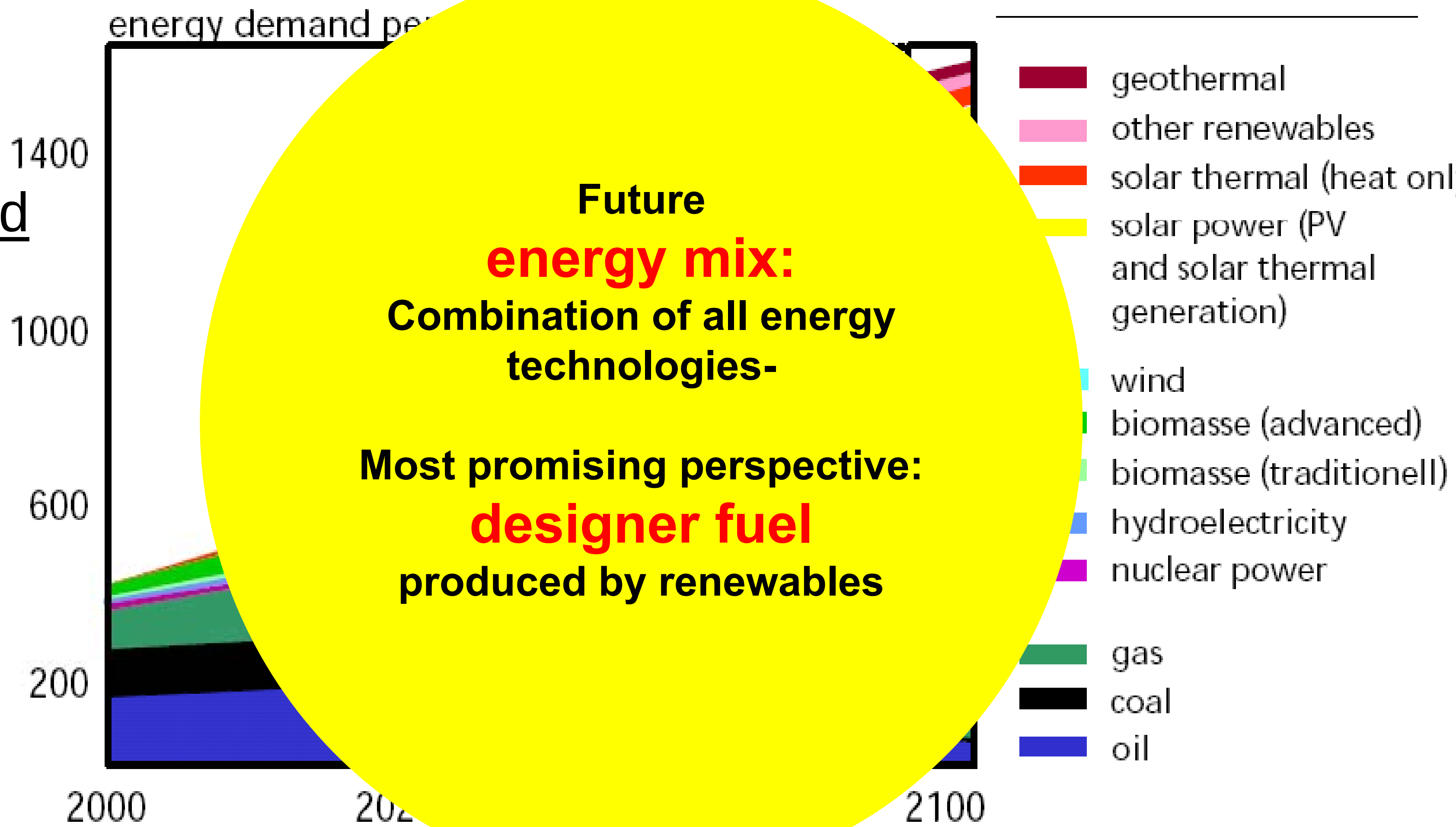
World energy demand



Future

energy mix:

Combination of all energy technologies-

Most promising perspective:

designer fuel

produced by renewables

(Wissenschaftlicher Beitrat der Bundesregierung Globale Veränderungen, 2003, www.wbgu.de)

Designer Fuel Cycle: H_2 or CH_3OH or ...

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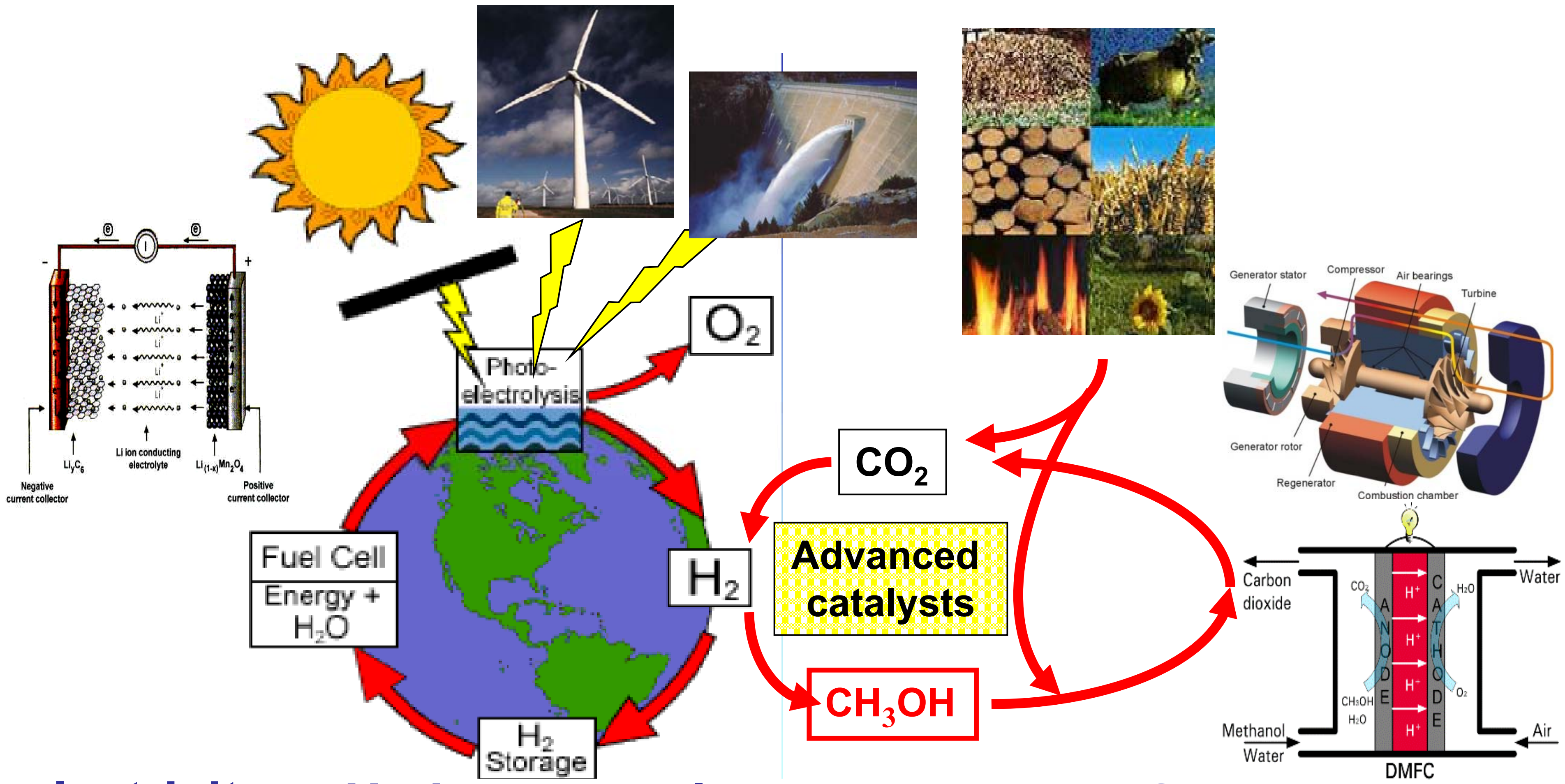
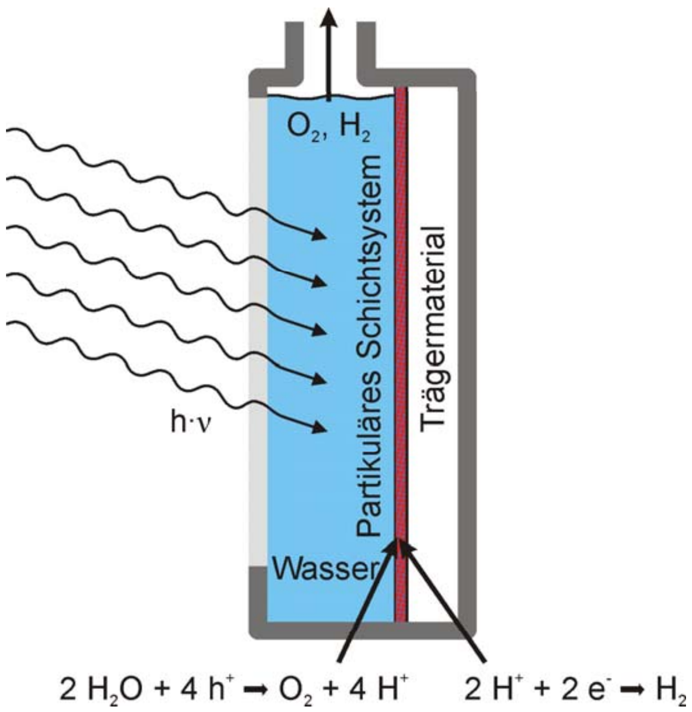


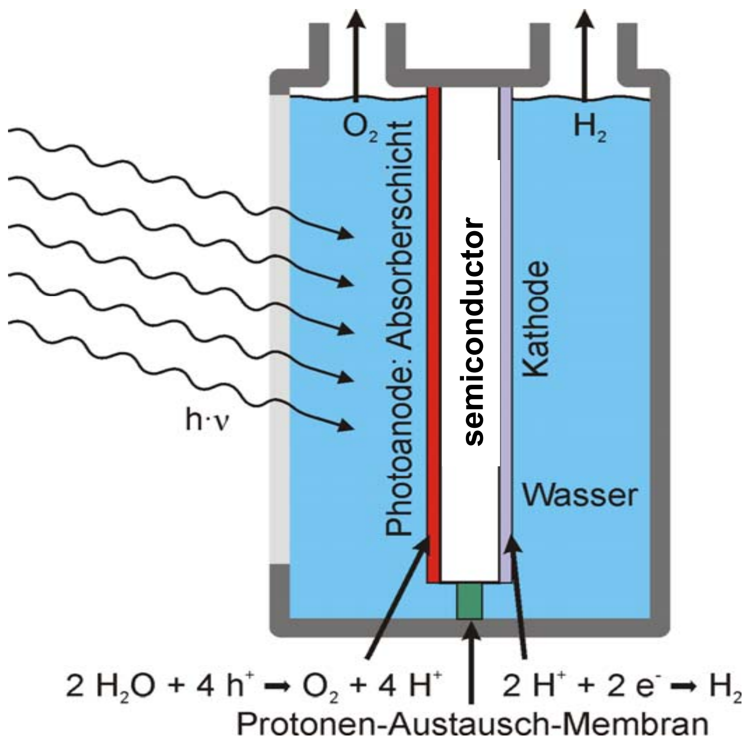
electricity **Hydrogen cycle** **Designer fuel cycle**

Basic Device Structure for Photoelectroytic H_2-Production

▪Direct hydrogen production by photoelectrolysis

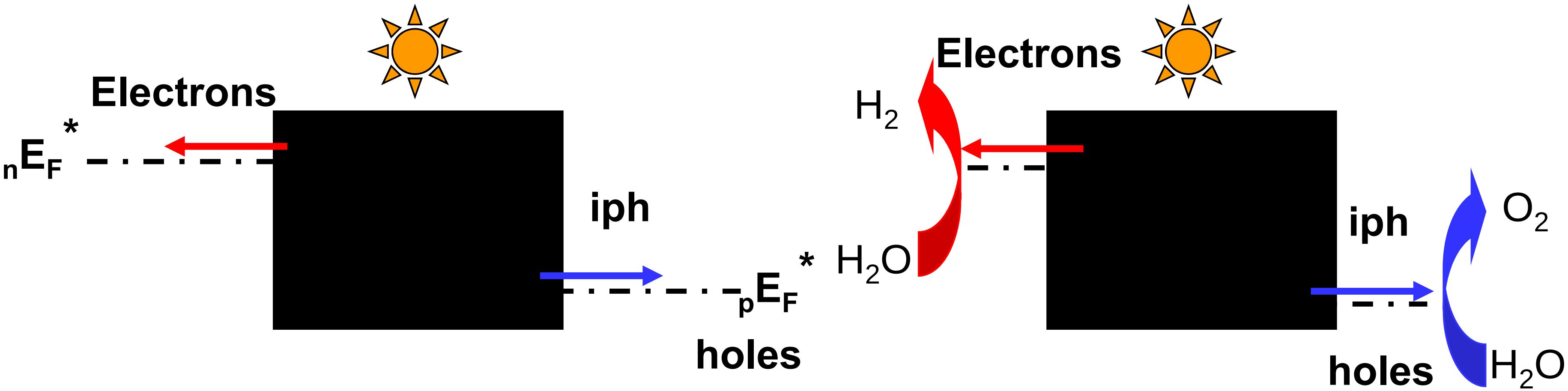


„Photocatalytic“ device PC
based on oxide particles



Photoelectrochemical device PEC
based on semiconductor electrode

Photovoltaic converter requirements (Black box approach)



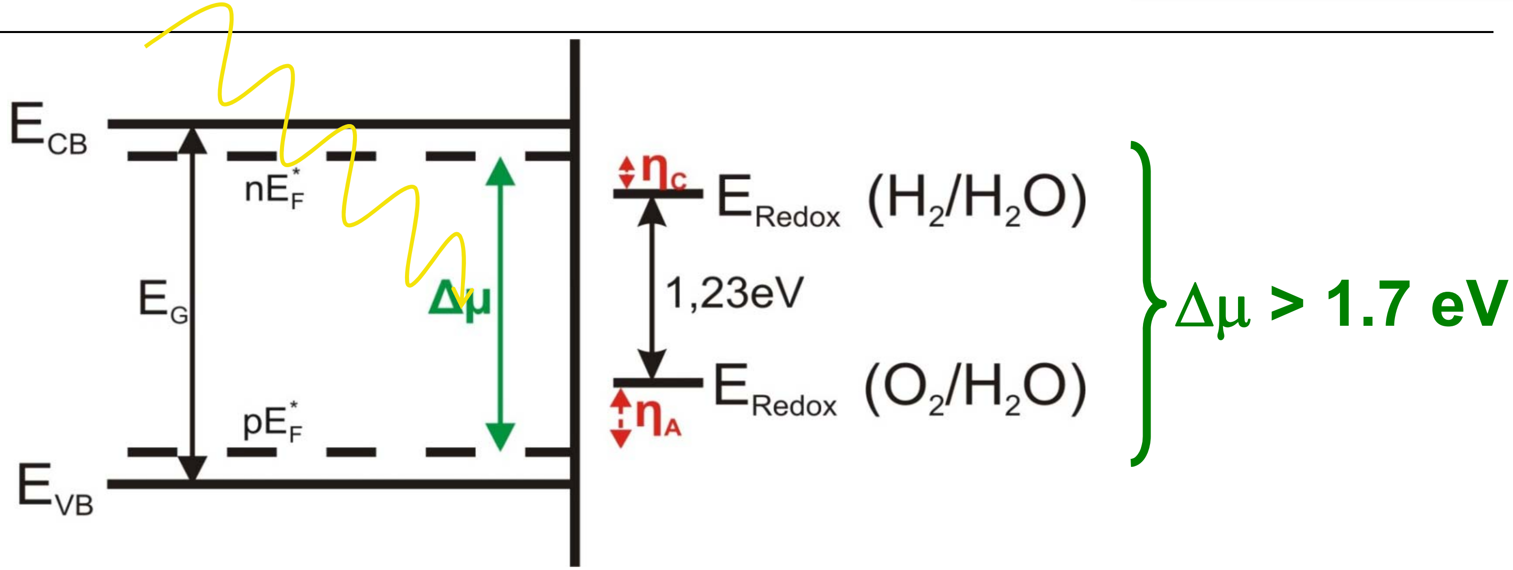
Optimisation of performance:

- **Maximize photovoltage $U_{ph} < {}_nE_F^* - {}_pE_F^*$**
- **Maximize photocurrent i_{ph}**

Optimisation of performance:

- **Minimum photovoltage $U_{ph} > E_{red} - E_{ox}$**
- **Maximize photocurrent i_{ph}**
- **Minimize overvoltage h**

Thermodynamic conditions for water splitting



- Photovoltage Uph equivalent to chemical potential of electron-hole pairs $\Delta\mu$ must be larger than difference of H_2O oxidation/reduction potential:

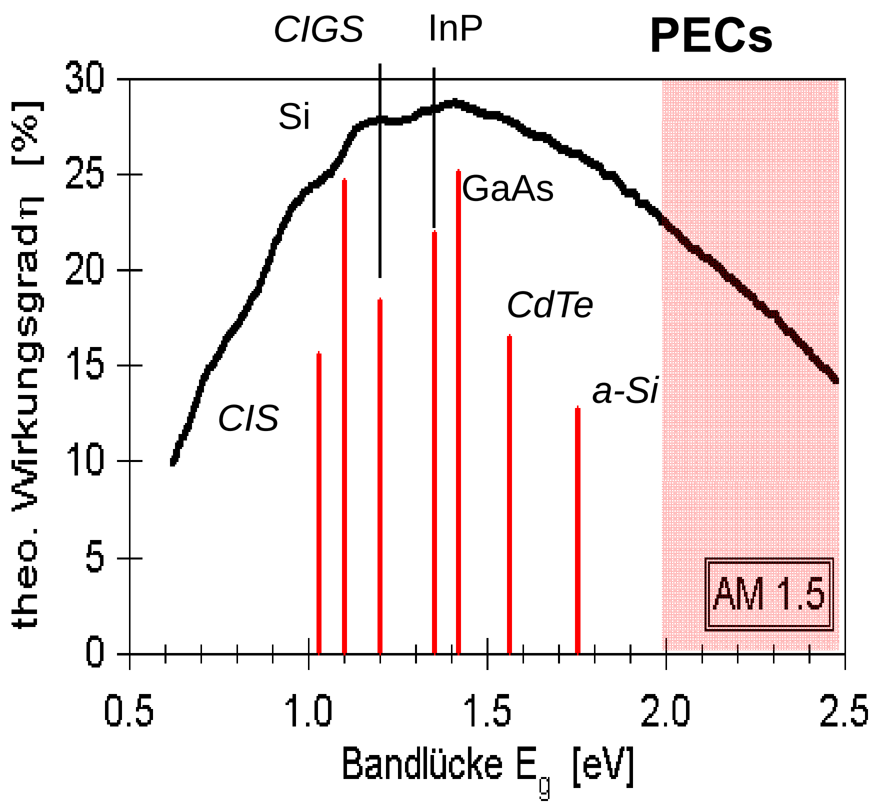
$$\Delta\mu = {}_nE_F^* - {}_pE_F^* = kT \ln n^*p^*/n_i^2$$

- For high rates the cathodic and anodic overvoltages must also be overcome:

cathodic overpotential $\eta_c < 0.1$ V   anodic overpotential $\eta_A < 0.4$ V

empirical rule: $U_{ph} < E_G - 0.4 \rightarrow E_G > 2.2$ eV

Expected PEC conversion efficiencies

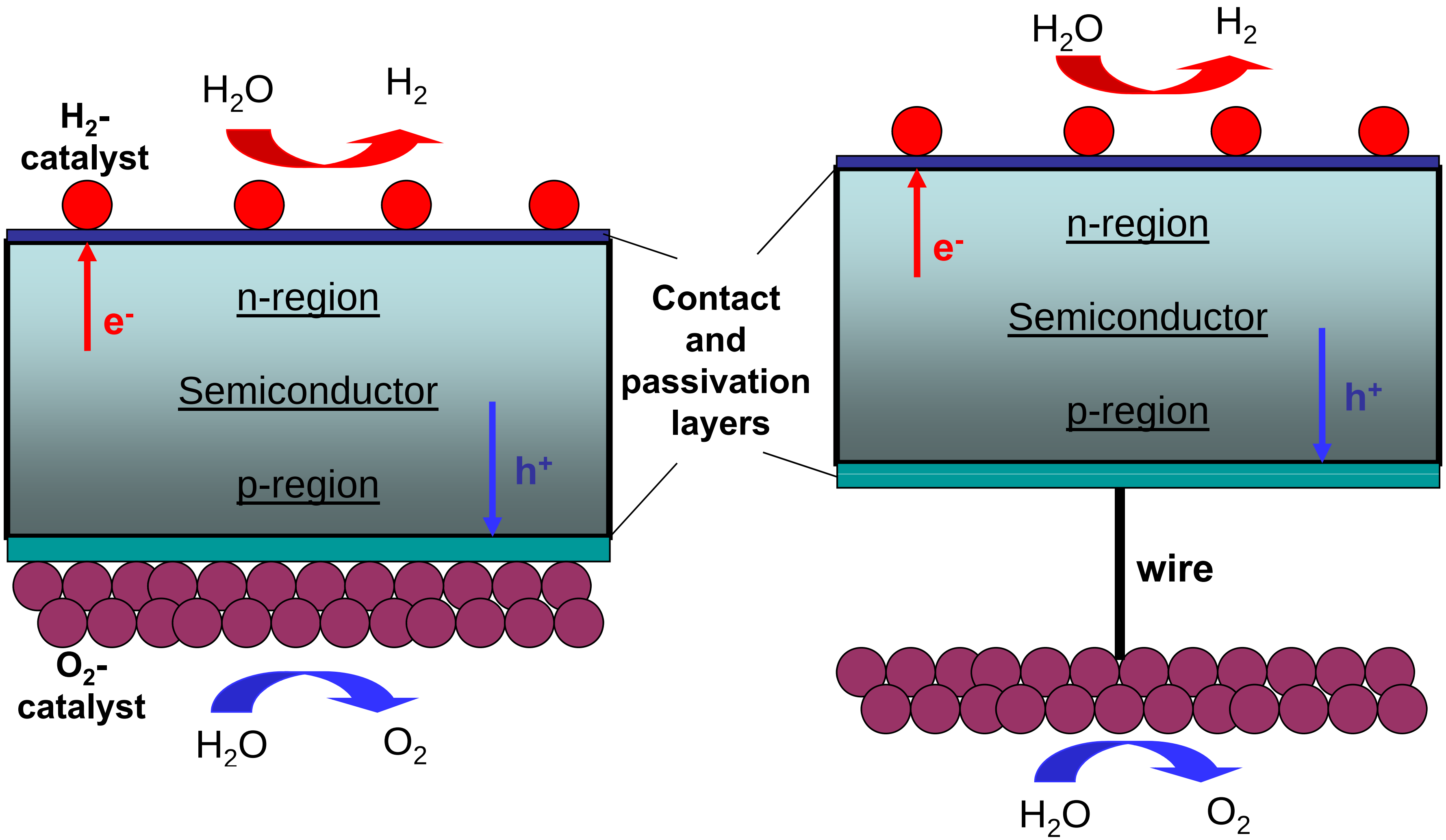


One semiconductor layer:

Bandgap E_G: 2.0 - 2.5 eV
Efficiency η: 22 – 15 %

- ☺ **Water spitting by light using photoelectrochemical solar cells is very promising**
- ☺ **Cheap thin film PV technology seems feasible**
- ☹ **Optimisation of new wide bandgap semiconductors and coupling with advanced catalysts needed**

Possible devices structure: one absorber



Photoelectrolytic solar cell: one semiconductor

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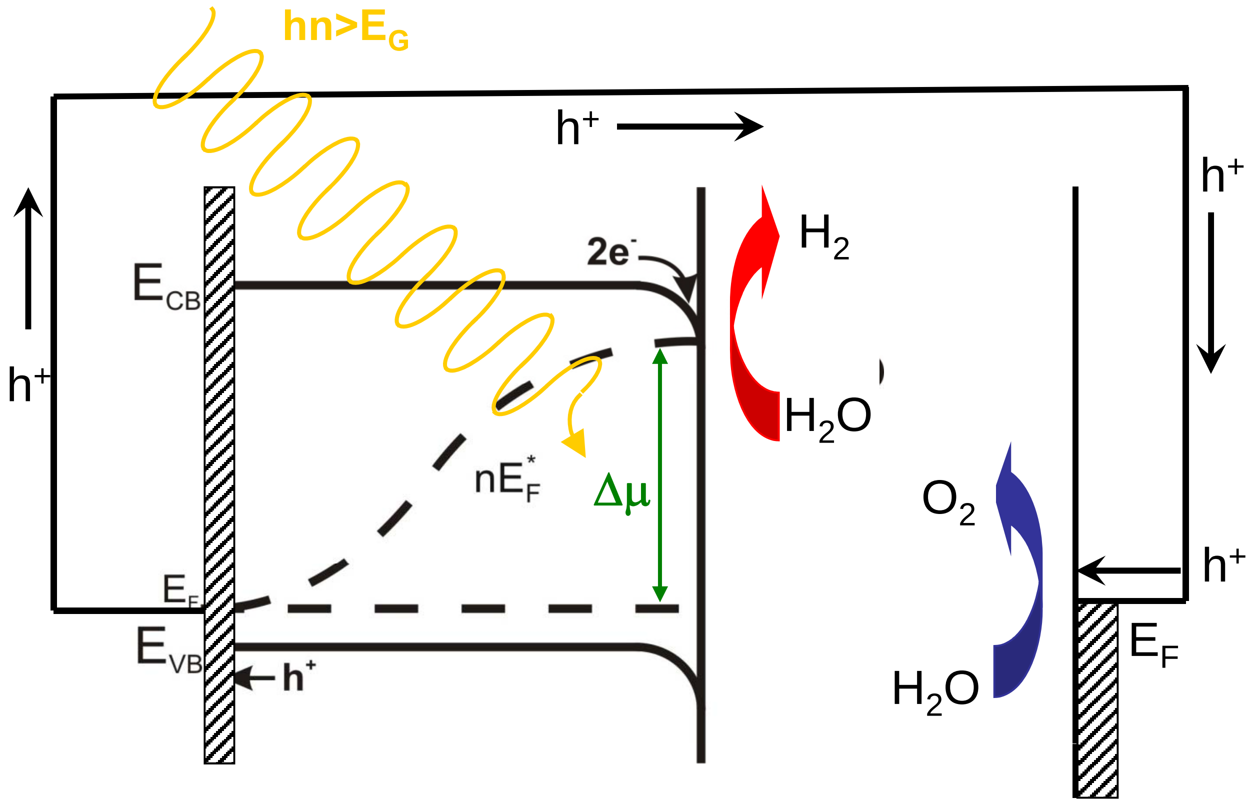
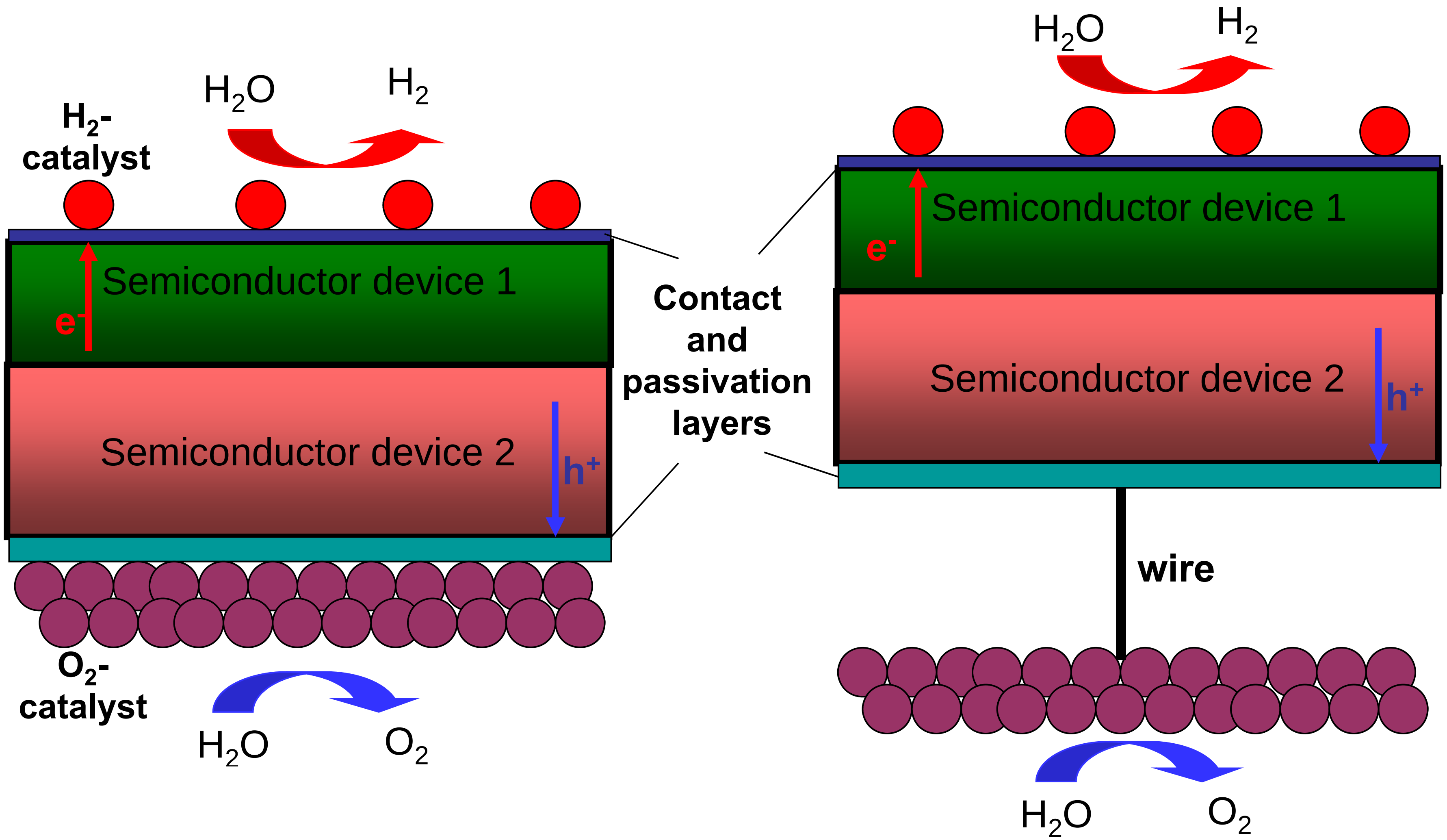
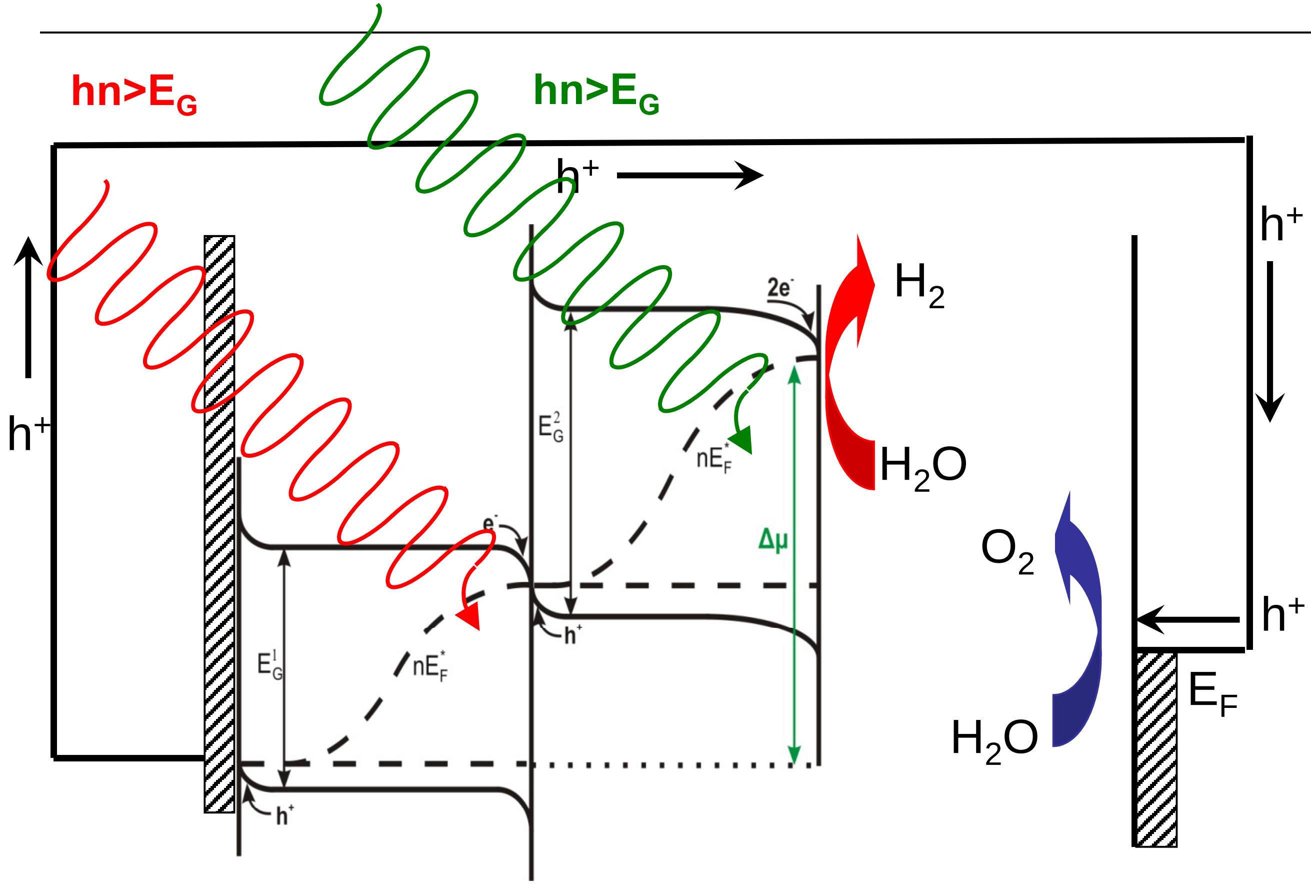


- Bandgap > 2 eV: ZnSe, ZnTe, SiC, GaP, InGaN, …
- Kinetic limits: catalytic metal particles needed
- p-doped SC usually stable
- Counter reaction H_2O oxidation at RuO_2/IrO_2 catalysts

Possible devices structure: two absorbers

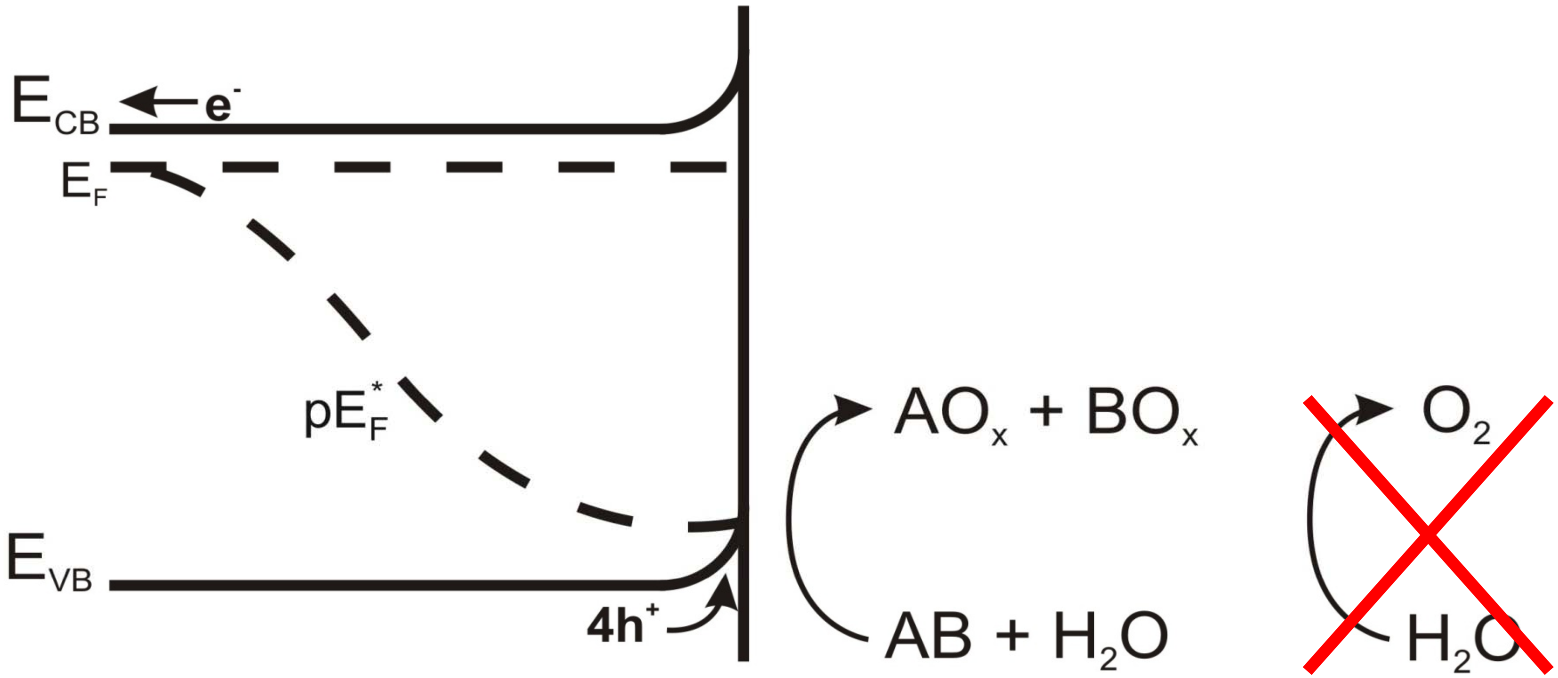


Photoelectrolytic solar cell: two semiconductors



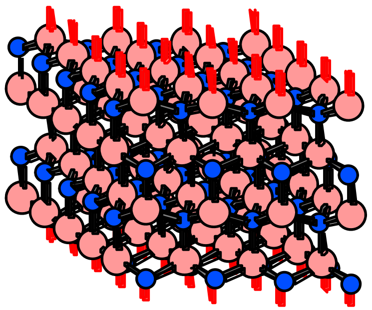
- Bandgap > 1 eV: Si, CdTe, CIS, GaAs, InP,
- Kinetic limits: catalytic metal particles needed
- p-doped SC usually stable
- Counter reaction H_2O oxidation at RuO_2/IrO_2 catalysts

Photoelectrolytic solar cell: n-doped semiconductors

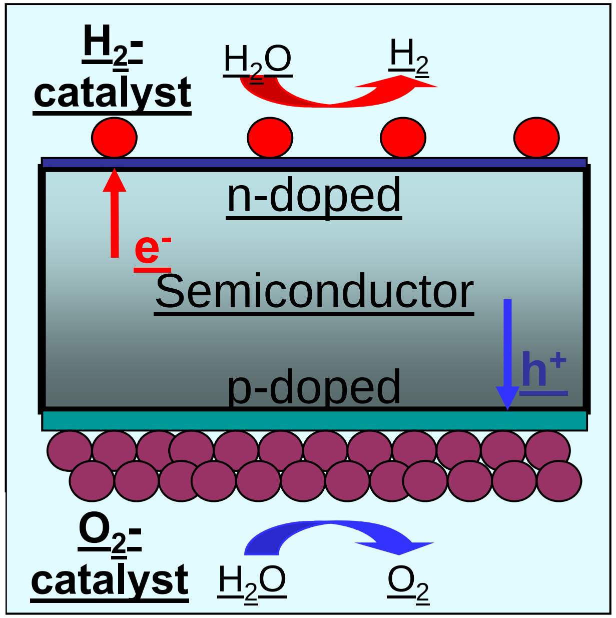


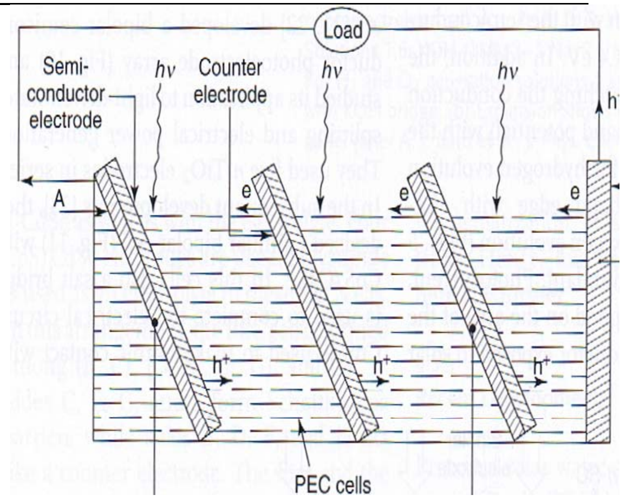
- **Transfer of 4 holes needed for evolution of 1 molecule O_2**
- **Decomposition reaction of semiconductor favoured**

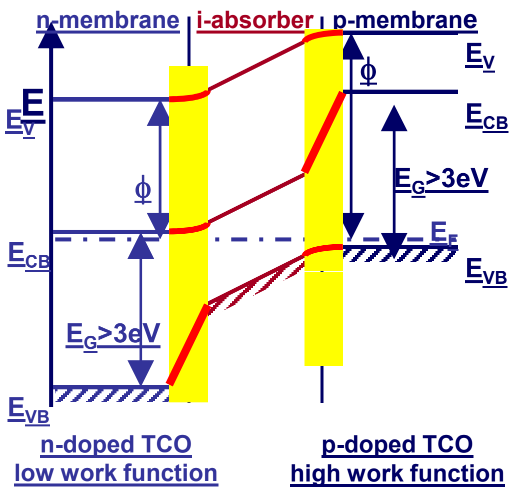
Photoelektrolysezellen

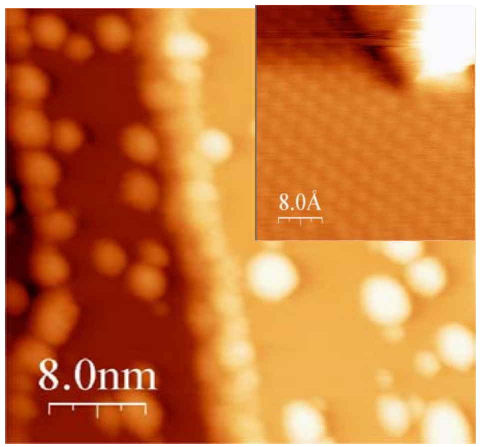


Wide bandgap semiconductors: ZnSe, ZnTe, SiC, GaP, InGaN

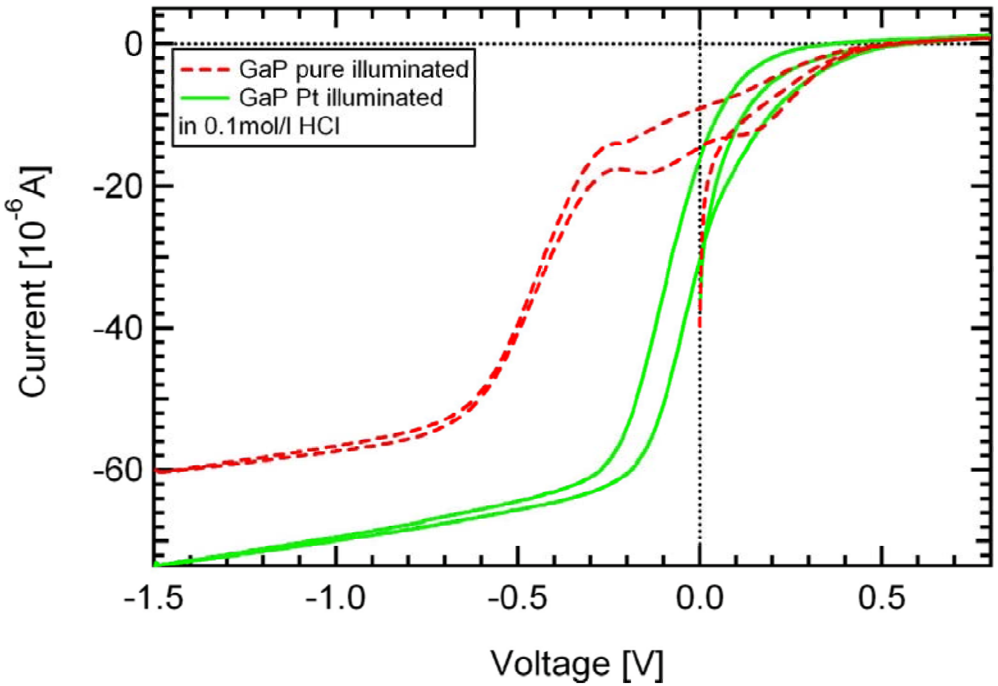


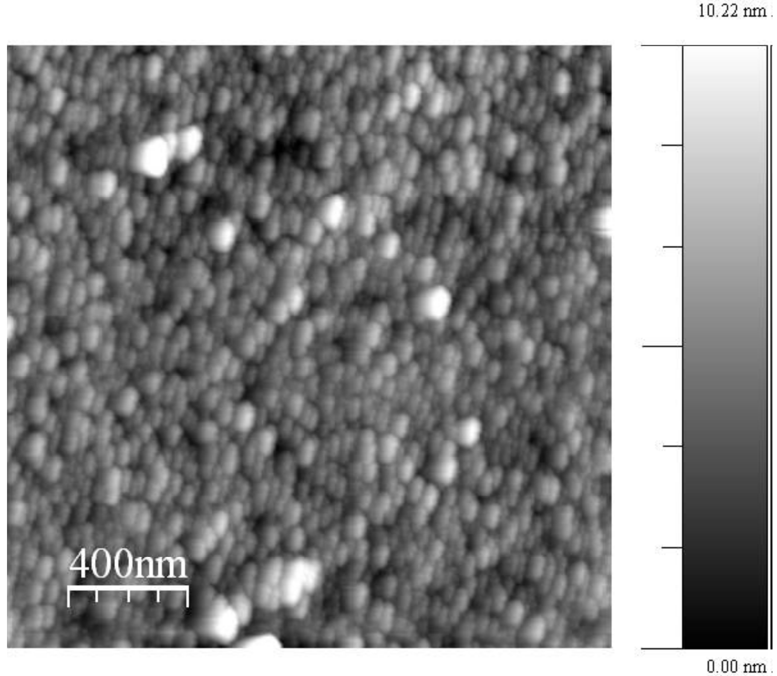




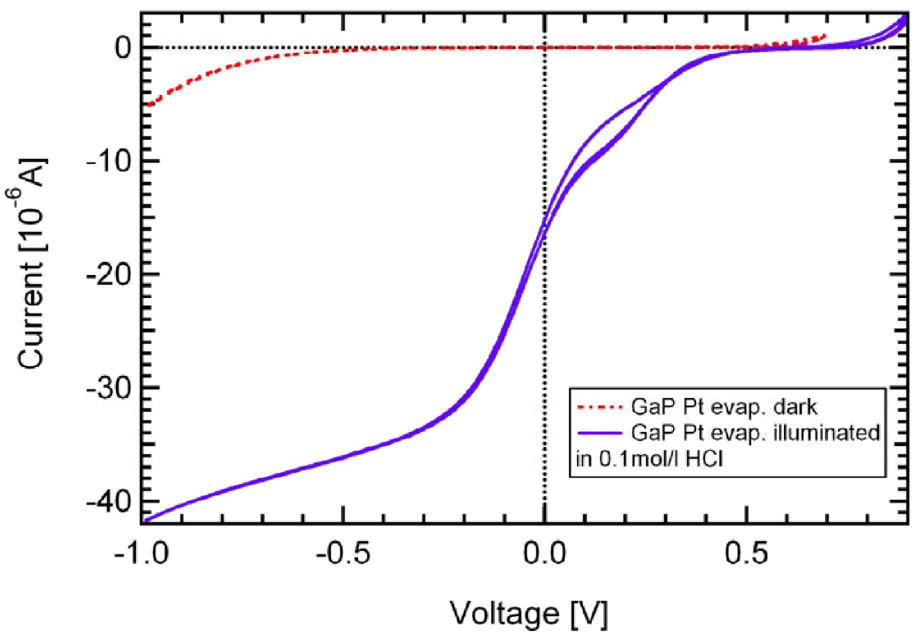


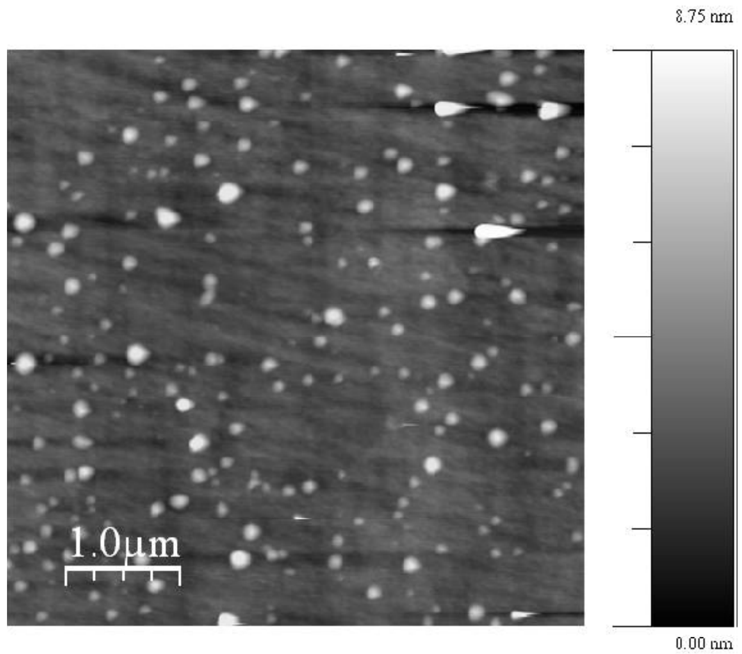
Pt deposition on p-GaP under H_2-evolution, V_D=-2 V, 5 s





PVD of Pt on p-GaP





Status of research

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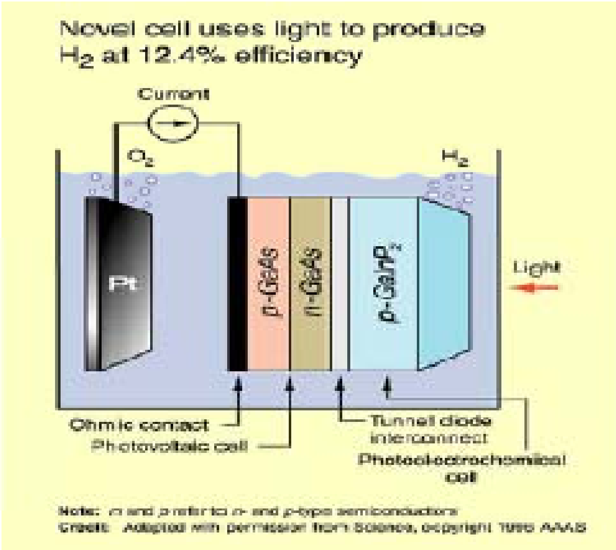
National Renewable Energy Laboratory

World Record Photoelectrolysis Device Science, April 17 1998.



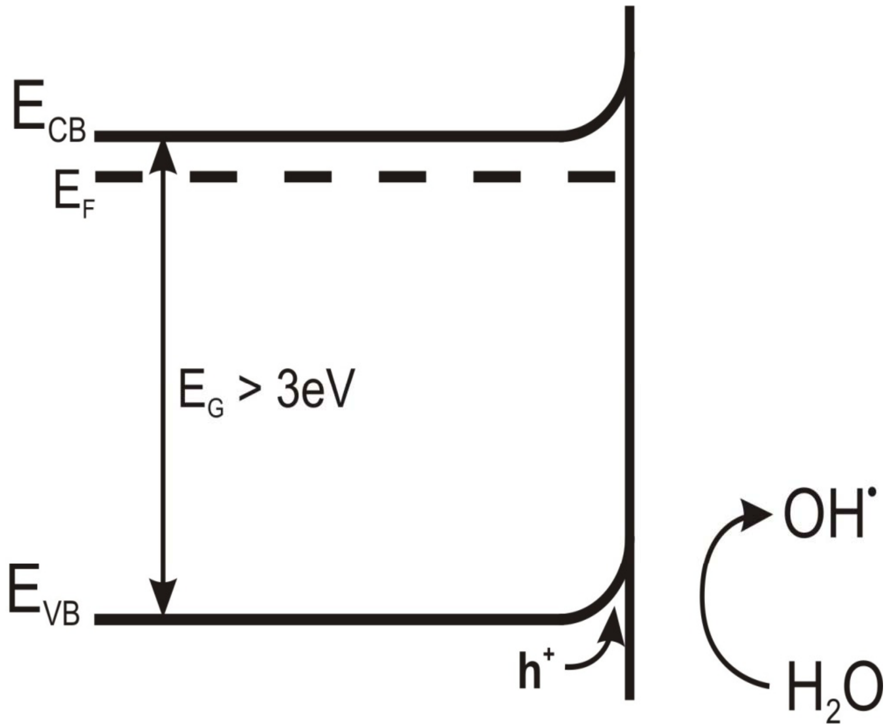
- Direct water electrolysis.
- Unique tandem (PV/PEC) design.
- 12.4% Solar-to-hydrogen

Experimental Cell

Operated for the U.S. Department of Energy by Midwest Research Institute • Battelle • Bechtel

Advantage: high efficiency of 12%
Disadvantage : non-oxide (stability) semiconductor
Expensive H_2Cost: >$13/kg
Looking for cheap and stable materials

Photoelectrolytic solar cell: n-doped oxide semiconductors



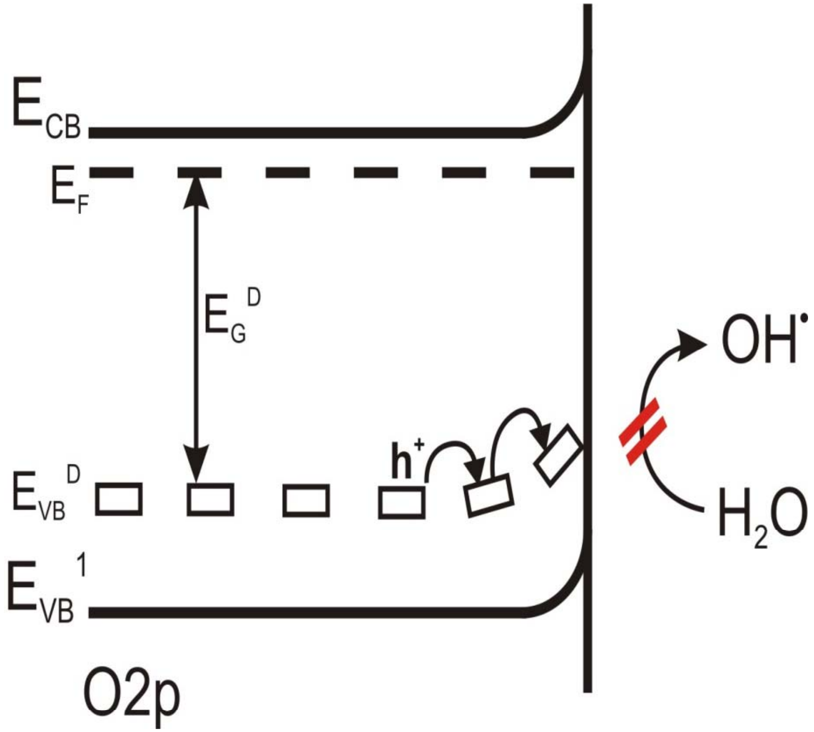
Oxides: TiO_2, $SrTiO_3$,

- **Bandgap > 3 eV:**
  only UV absorption:
  low efficiencies

- **No kinetic limits:**
  E(·OH/H_2O): 2.7 V vs NHE
  E(H_2O_2/H_2O): 1.8 V vs NHE

- **Bandgap engineering needed**

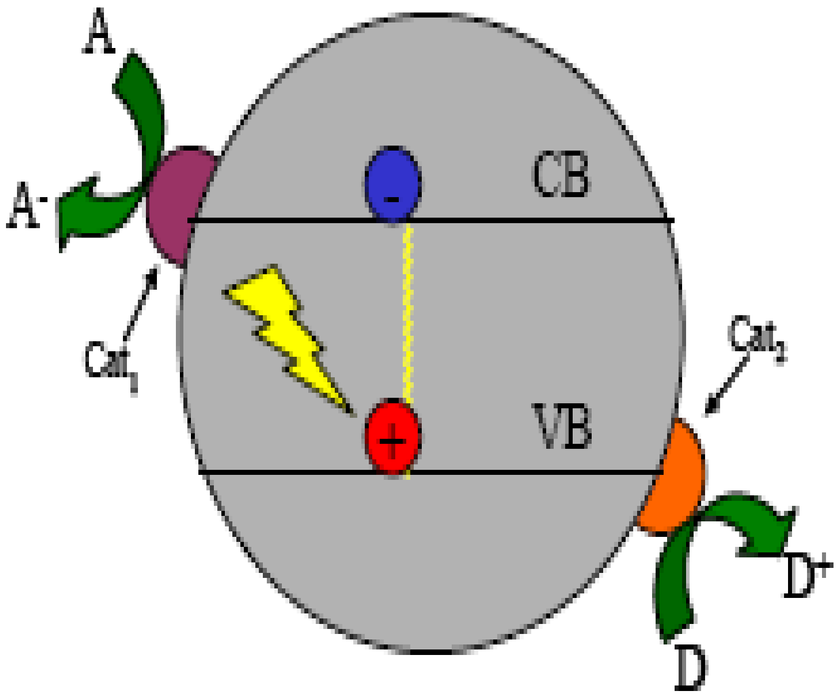
Bandgap engineered oxide semiconductors



- **Bandgap Reduction by Anion and Metal Substitution**
- **Bandgap < 3 eV: absorption in visible region due to localized defect levels**
- **Kinetic limits: E(.OH/H_2O): 2.7 V, vs NHE**
- **Low effciency**
  - **- hopping transport (low mobility)**
  - **- reduces charge carrier separation**

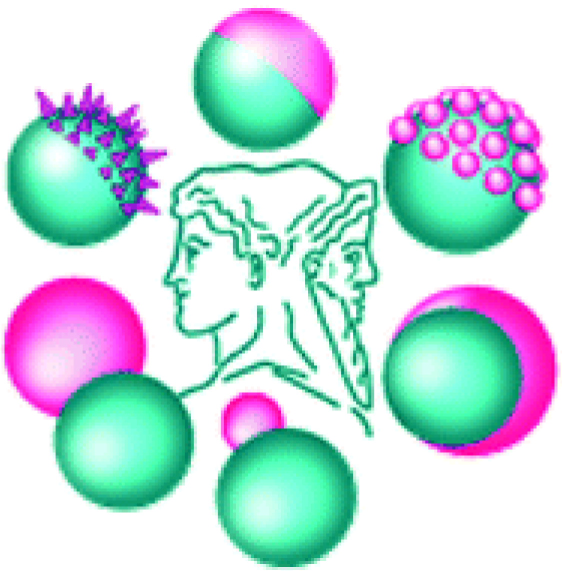
$L_{Diff} = (D\ \tau)^{1/2} = (\mu\ (kT/e)\ \tau)^{1/2}$ ⇒ **for $\mu = 10^{-2}$ cm²/Vs and t = 10^{-8} s L_{Diff} = 15 nm << 3/α**

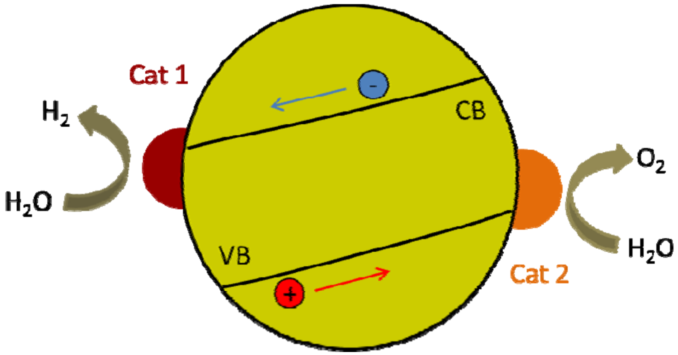
Possible solutions: Oxides nanoparticles

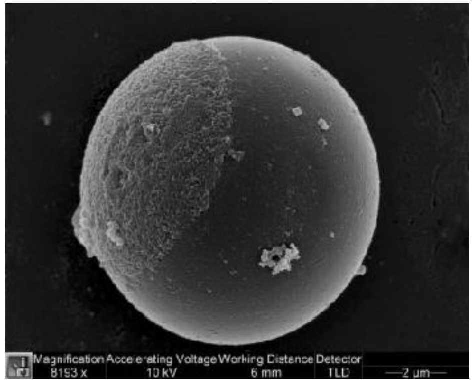


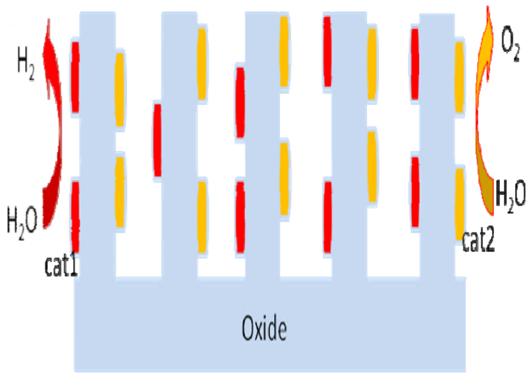
- **Nano-SC-Particles:**
  size smaller than diffusion lengths:<15 nm
- **Bandgap Engineering**
  reduction of bandgaps by additional defect levels (doping)
- **Tranport engineering**
  Engineered diffusion pathways of electron-hole pairs (doping gradients)
- **Nano-Catalysts**
  - efficient H_2 production
  - efficient O_2 evolution

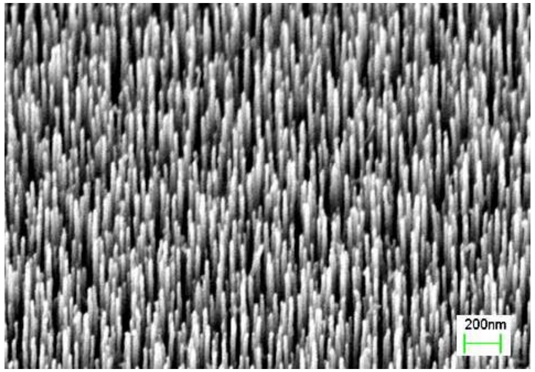
Perspectives of Janus structures



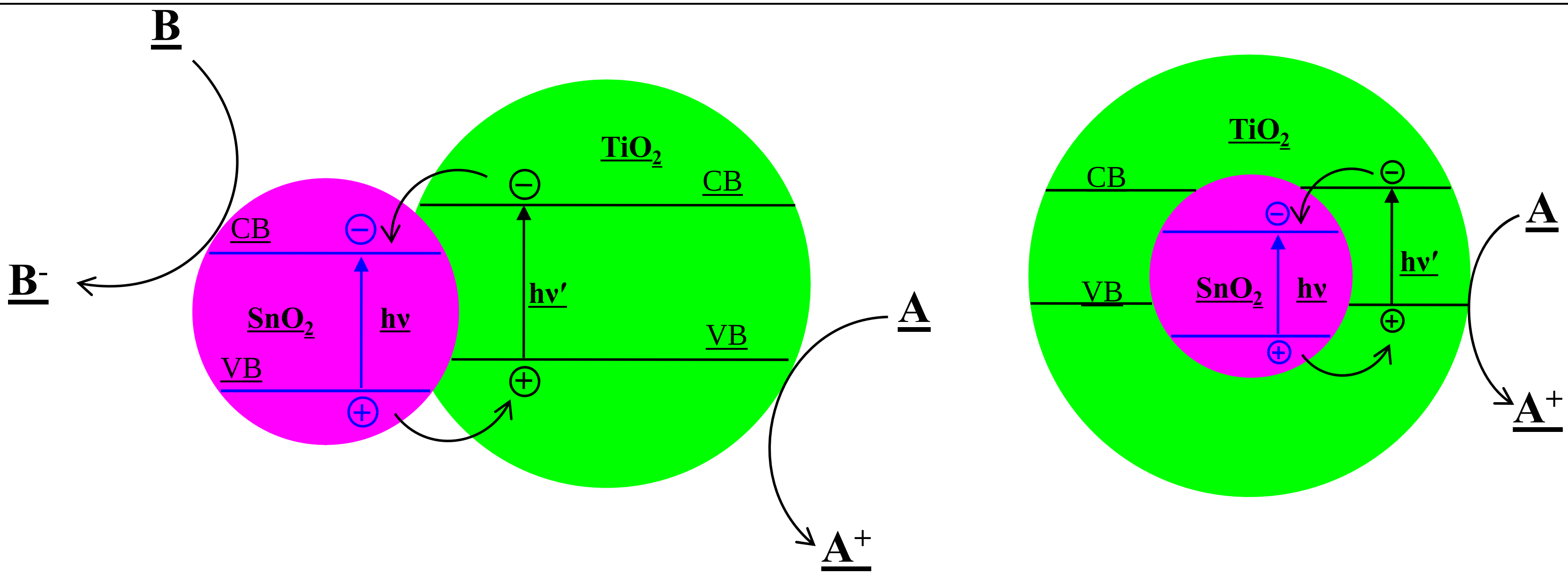








Oxide heterostructures



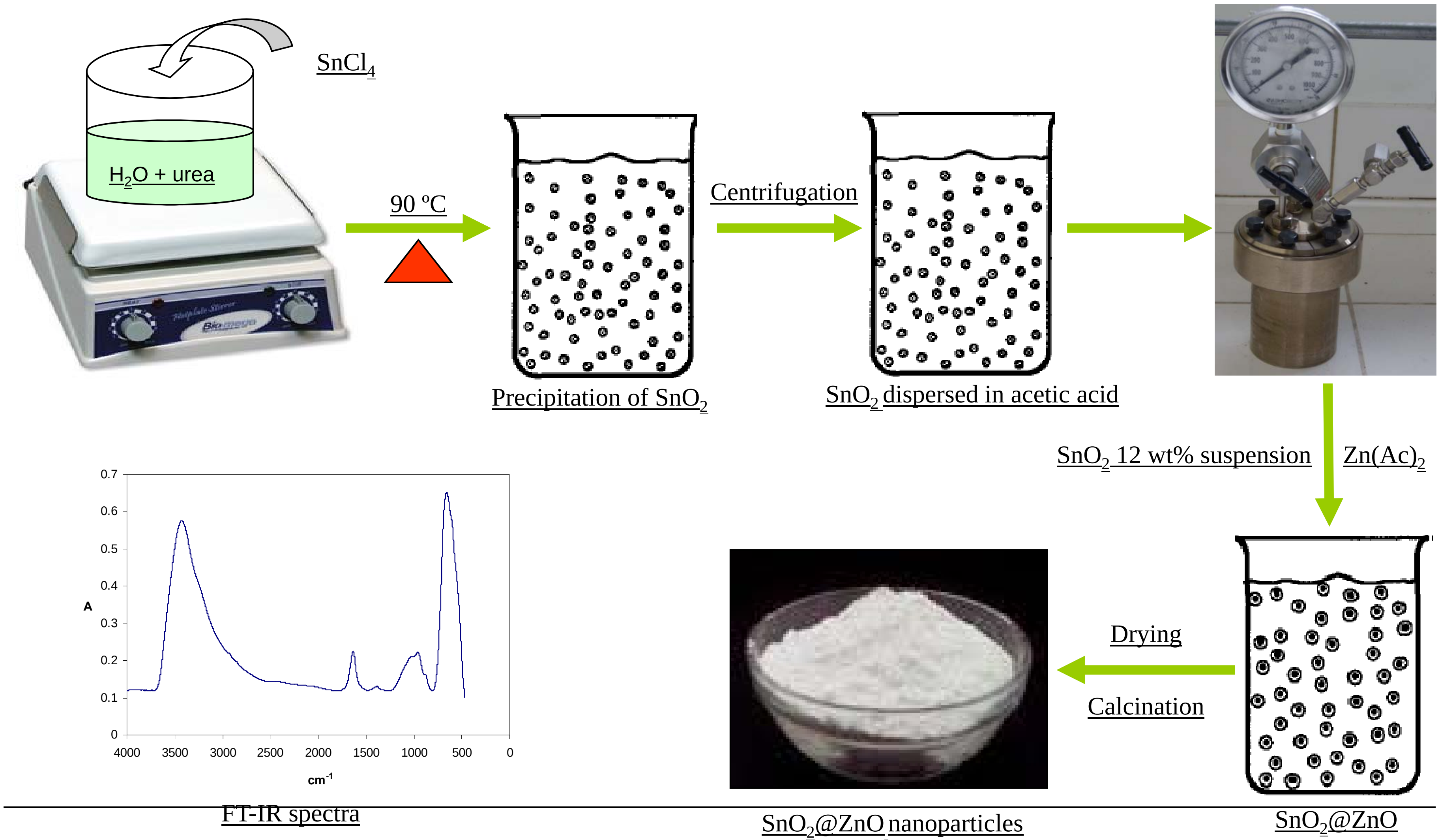
- Both electron and hole are accessible to selective oxidation and reduction processes on their surfaces

- Only one of the charge carriers is accessible at the surface of the core/shell semiconductor system

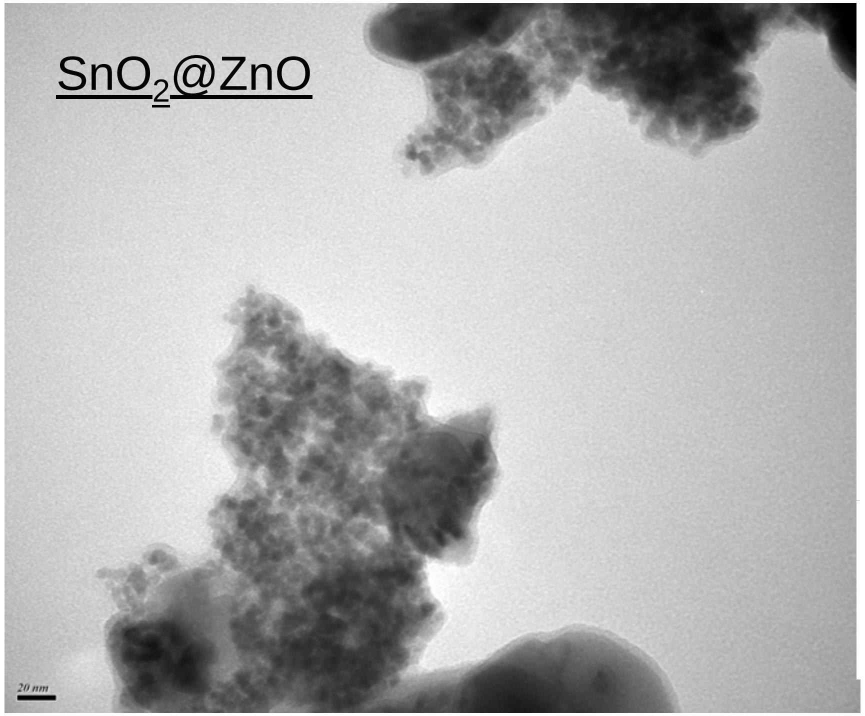
- Selective charge transfer possible at the semiconductor electrolyte interface ?

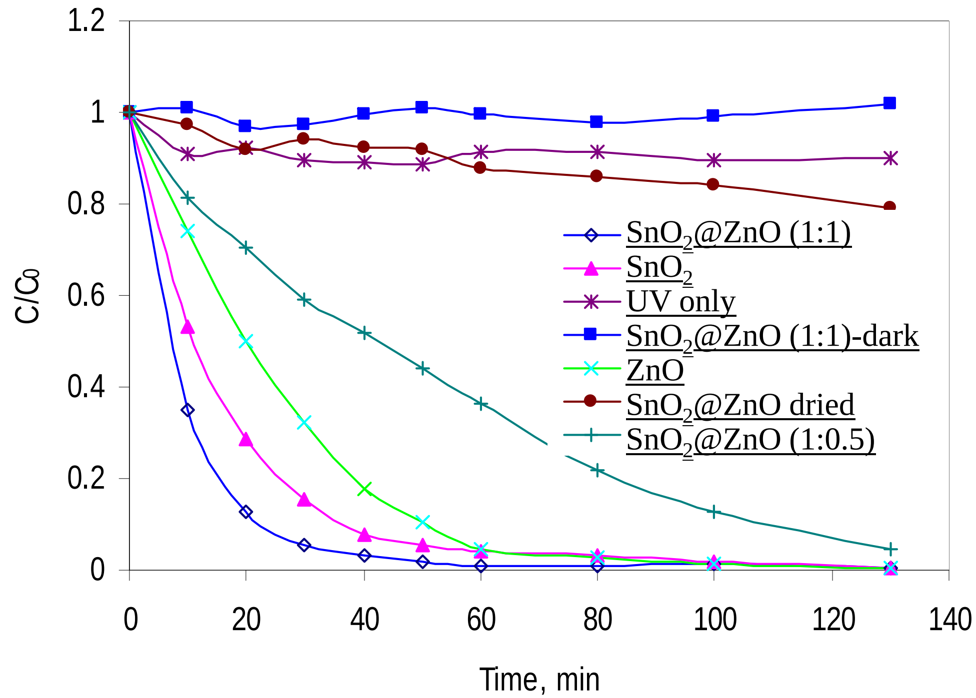
First results: T. Uddin, T. Toupance

Preparation of SnO_2 and SnO_2@ZnO nanoparticles



First results on heterostructures





$SC + h\nu \rightarrow SC\ (h_{VB}^{+} + e_{CB}^{-})$

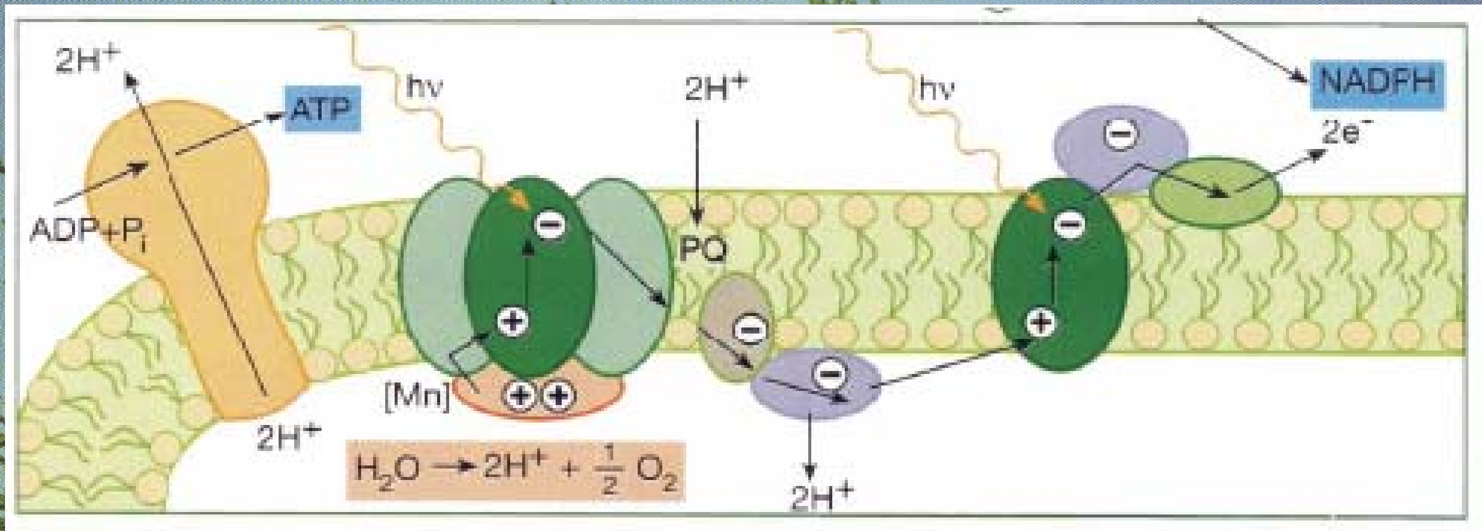
$OH^{-}_{ads} + h_{VB}^{+} = {}^{\cdot}OH_{ads}$

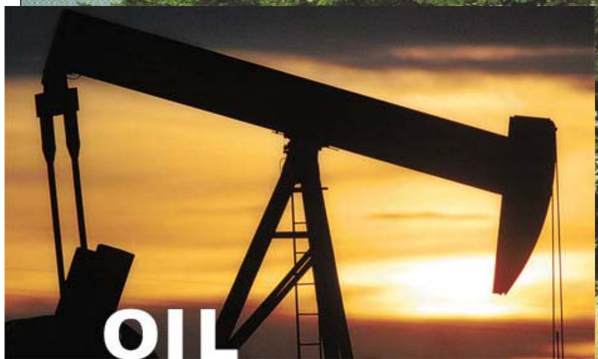
$H_2O_{ads} + h_{VB}^{+} \rightarrow {}^{\cdot}OH_{ads} + H^{+}$

$dye + {}^{\cdot}OH_{ads} \rightarrow {}^{\cdot}dye \rightarrow$ Oxidation of dye

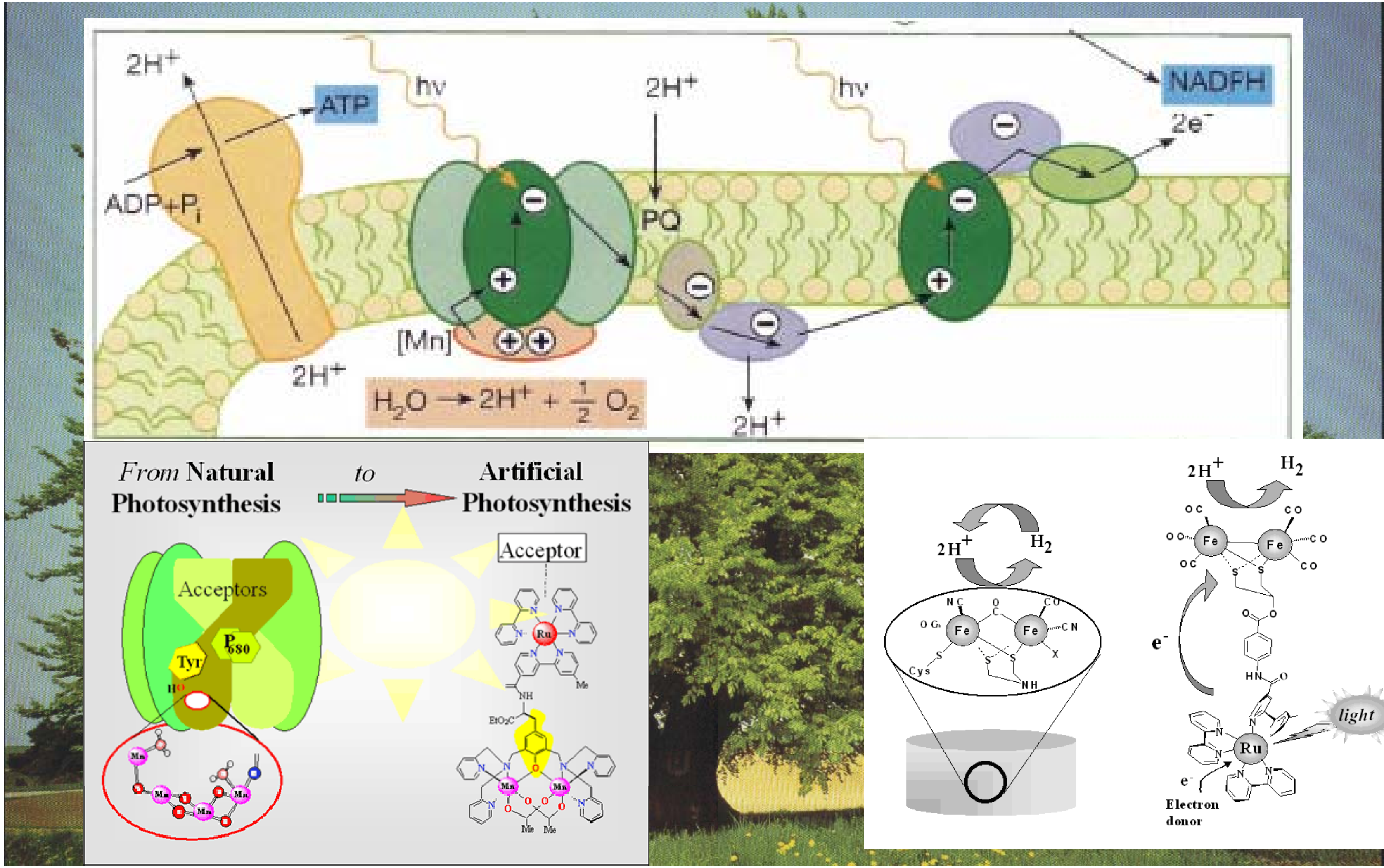
$dye + h_{VB}^{+} \rightarrow {}^{\cdot}dye \rightarrow$ Oxidation of dye

Photosynthesis



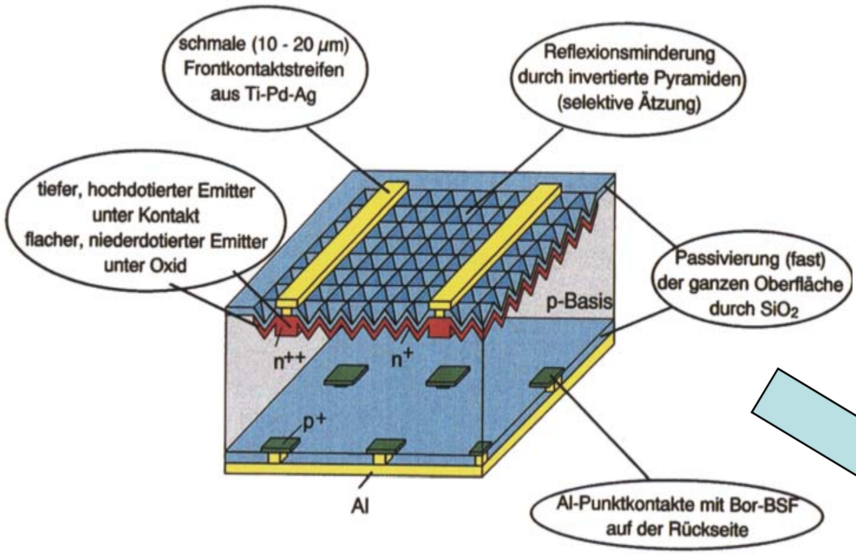


Photosynthesis



Styring, Uppsala

Electrolysis driven by solar cells: Reference technology



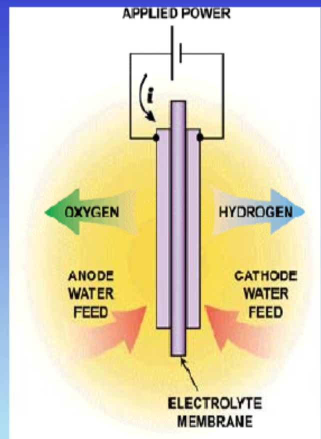
Solar Cell and Electrolyzer

Overall practical efficiency:
η< 8 % (PV:15% x EL:50%)

Overall theoretical efficiency:
η < 15% (PV:20% x EL:70%)

Hydrogen production by electrolysis

$$\text{Anode}: 4\,OH^- \longrightarrow O_2 + 2\,H_2O + 4\,e^-$$
$$\text{Cathode}: 4\,H_2O + 4\,e^- \longrightarrow 2\,H_2 + 4\,OH^-$$
$$\text{Overall}: 2\,H_2O \longrightarrow 2\,H_2 + O_2$$



Electrolyte composition:
Pure water (σ < 5 µS/cm) + 30% KOH

Electrocatalysis: Research needs

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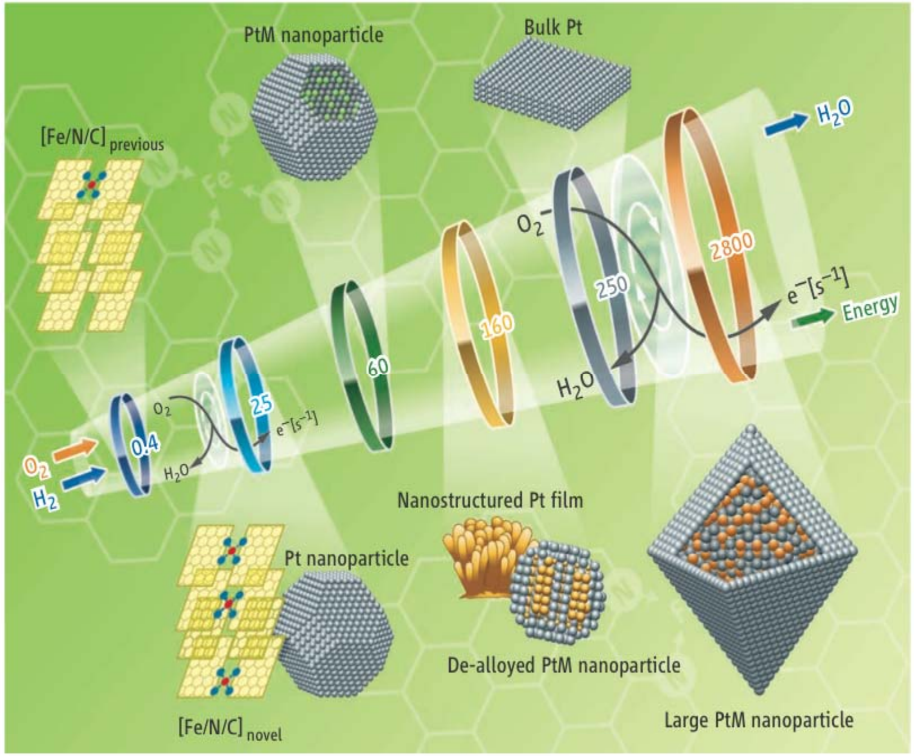
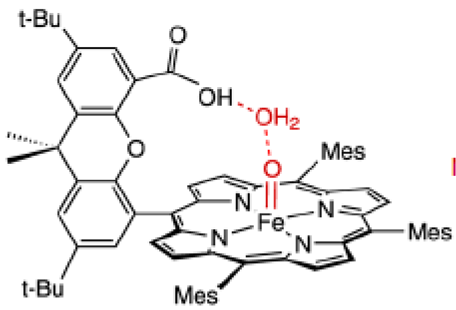
Size and composition effects and catalyst/support interaction



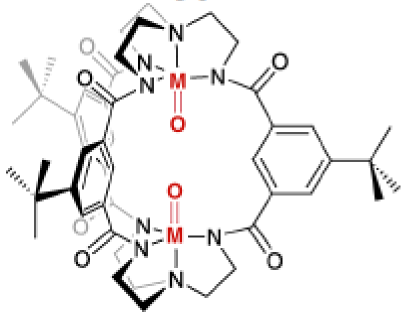
Gasteiger, Markovic, et al

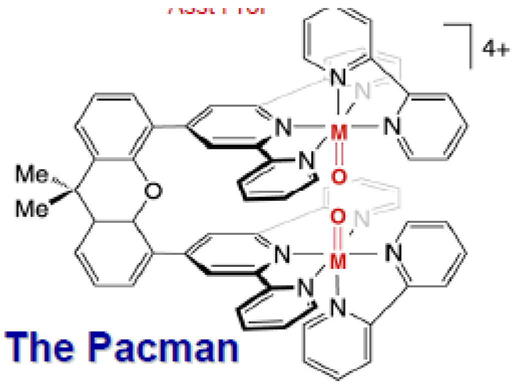
Specifically designed electrocatalysts

The Hangman



The Cryptman





The Pacman

Nocera et al

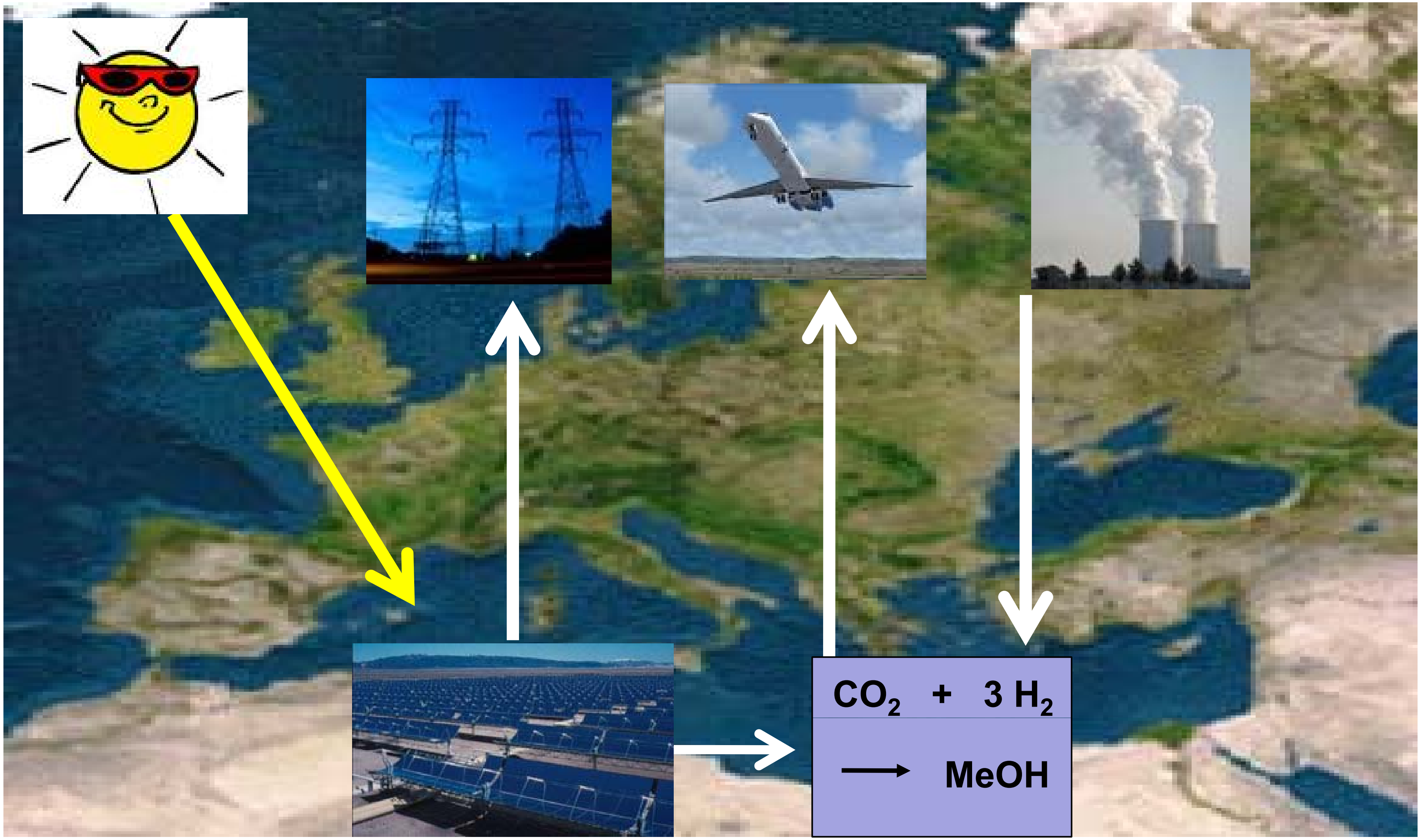
Energie Effizienzen für H_2 Produktion

- Photosynthetische Membran: η < 7% (theoretischer Wert)
- Biomimetische Systeme: η < 1% (praktischer Wert)
- Solarzelle und Elektrolyseur: η < 15% (PV:20% x EL:70%)
- Photoelektrolyseur: η < 20% (theoretischer Wert, E_G>1.8eV
  η < 15% (?, erhoffter realistischer Wert)

Aber

H_2 braucht effiziente Speicherung: Umwandlung zu CH_3OH

Solare Brennstoffe (Desertec)



Zusammenfassung und Schlussfolgerungen

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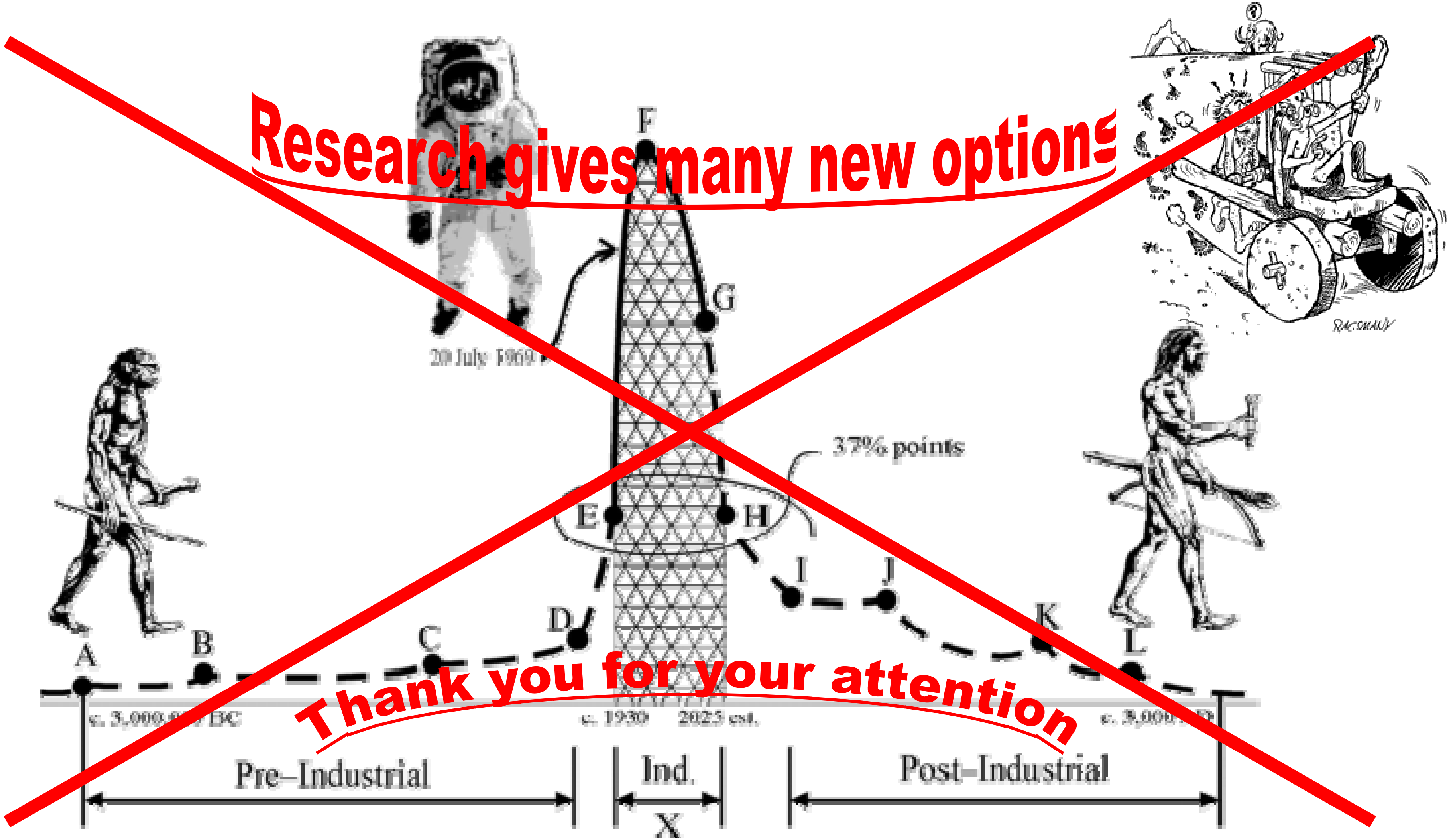
- SolarFuels ergo Brennstoffe aus erneuerbaren Primärenergiequellen sind eine vielversprechende Perspektive für eine nachhaltige Energiewirtschaft
- Biomimetische Ansätze weisen (noch?) zu geringe Wirkungsgrade auf
- Photoelektrolyse mit anorganischen Photovoltaik-Systemen weisen die besten Perspektiven auf
- Es gibt noch maßgebliche materialwissenschaftliche und bauelementbezogenen Herausforderungen, die einen interdisziplinären Forschungsansatz benötigen


Research gives many new options
Thank you for your attention
F
G
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A
B
C
D
37% points
20 July 1969
Pre–Industrial
Ind.
Post–Industrial
X
c. 1930
2025 est.