TECHNISCHE UNIVERSITÄT MÜNCHEN

Munich-Centre for Advanced Photonics (MAP)

Photocatalysis at surfaces

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Outline:

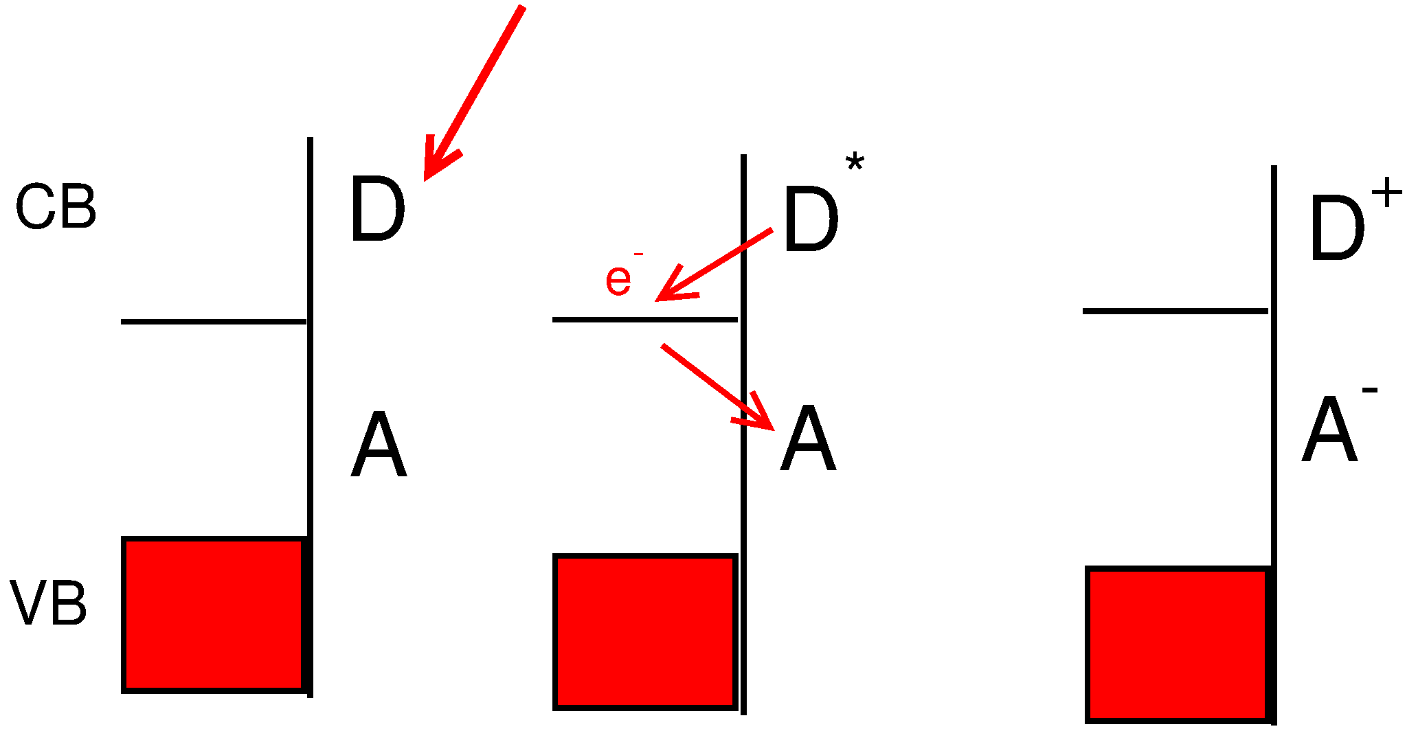
1. Introduction (basic concepts)
2. Water splitting on TiO_2
3. Substrate modifications

   + Examples

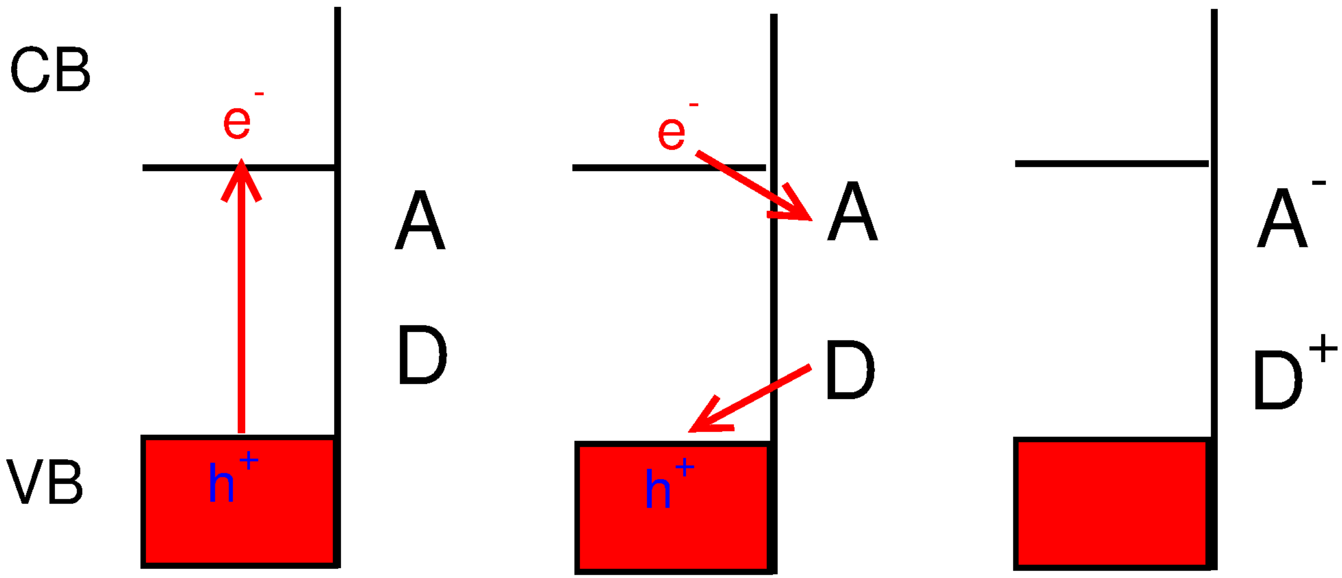
Photocatalysis:

- Catalytic reactions taking place under the action of light
- Catalysis of a photochemical reaction
- Catalysis of a reaction using a photoexcited catalyst
- Wide variety of phenomena ... systematic order needed

Catalized Photoreaction @ Semi-Conductor

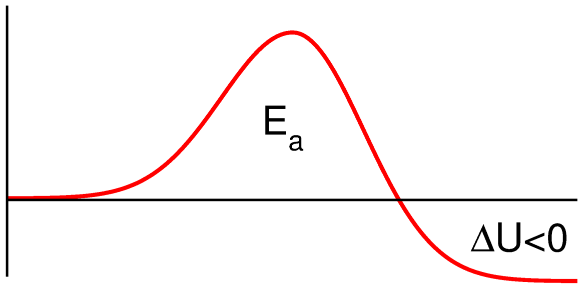


Sensitized Photoreaction/Redox-Reaction @ Semi-Conductor



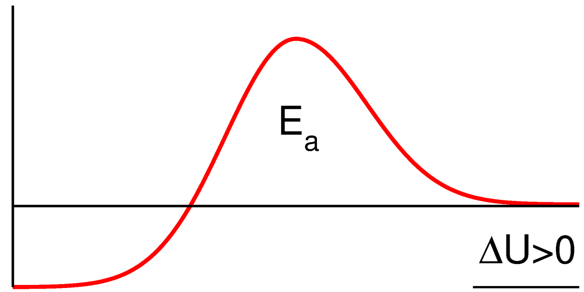
Introduction

'Downhill' reaction



- Degradation of organic compounds / waste
- $CH_3COOH \rightarrow CH_3\cdot + CO_2$

'Uphill' reaction



- Converting Light → Chemical Energy
- $2\ H_2O \rightarrow O_2 + 2\ H_2$

Gibbs Free Energy: $\Delta G = \Delta U + p\Delta V - T\Delta S$

Water Splitting

Redox-Reaction:

$$\begin{array}{rcl} 2\,H^+ + 2\,e^- & \rightarrow & H_2 \\ H_2O & \rightarrow & \frac{1}{2}\,O_2 + 2\,H^+ + 2e^- \\ \hline H_2O & \rightarrow & \frac{1}{2}\,O_2 + H_2 \end{array}$$

Reduction of hydrogen: cathode reaction

Oxidation of oxygen: anode reaction

Energetics from standard electrode potentials:
ΔE : 'electromotive force' (V)
F : Faraday constant = 96485 C/mol

ΔE = E(cathode) - E(anode) = -1.23 V

ΔG = -nFΔE = +237 kJ/mol

Beware: "Reduction/Oxidation of water"

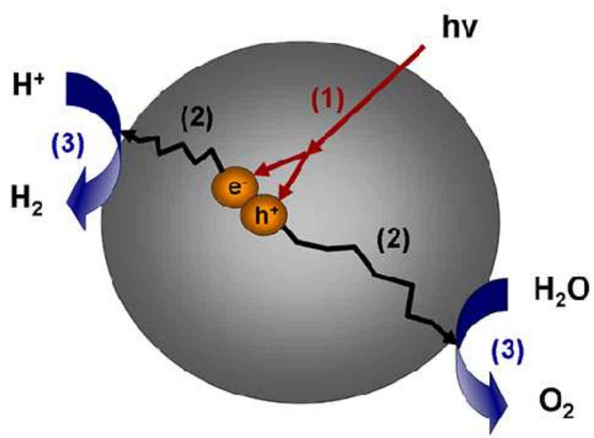
Standard Electrode Potentials (V)

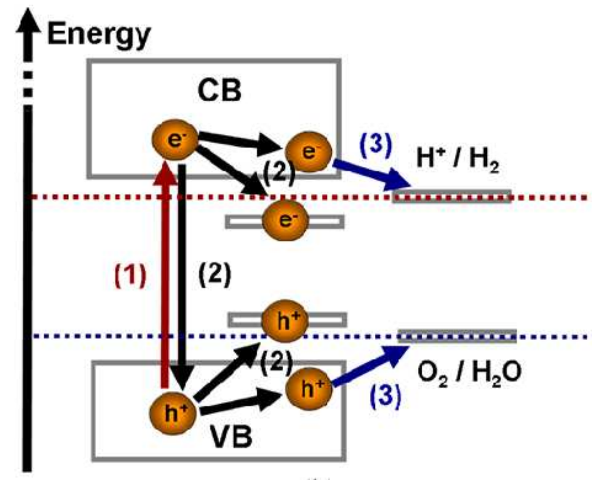
(Half reactions, reductions)

$$\begin{array}{rcll} Li^+ + e^- & \rightleftharpoons & Li & -3{,}05 \\ Zn^{2+} + 2e^- & \rightleftharpoons & Zn & -0{,}76 \\ Ni^{2+} + 2e^- & \rightleftharpoons & Ni & -0{,}25 \\ 2H^+ + 2e^- & \rightleftharpoons & H_2 & 0{,}00 \\ Cu^{2+} + 2e^- & \rightleftharpoons & Cu & 0{,}34 \\ Ag^+ + e^- & \rightleftharpoons & Ag & 0{,}80 \\ Pt^{2+} + 2e^- & \rightleftharpoons & Pt & 1{,}20 \\ \frac{1}{2}O_2 + 2H^+ + 2e^- & \rightleftharpoons & H_2O & 1{,}23 \end{array}$$

Water Splitting

Fujishima, Honda: Colloidal TiO_2 for water splitting 1972





1. Exciton creation
2. e^-/h^+ diffusion
3. Chemical reaction

Akimov, Neukirch, Prezhdo, Chem. Rev. **113**, 4496 (2013)

CB min $>$ LUMO of oxidizer

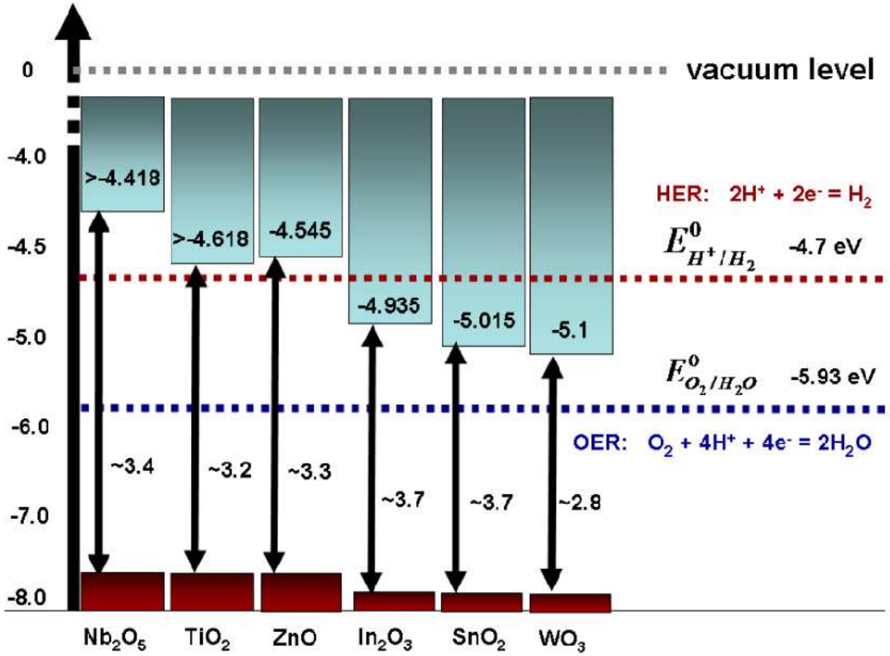
VB max $<$ HOMO of reduced species

Losses:

- Recombination
- Trapping (e.g. defects)
- e^- Solvation

Water Splitting

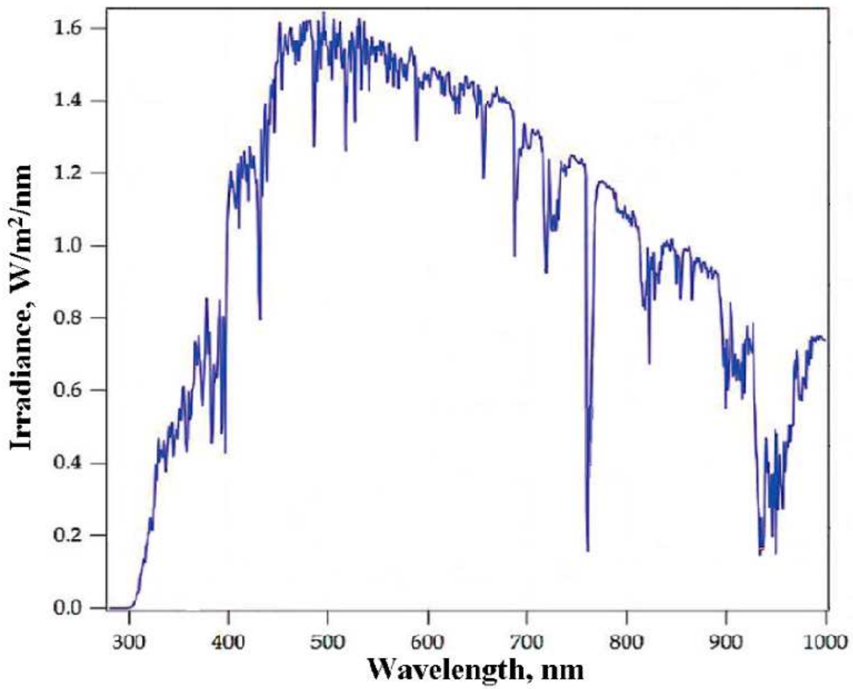
Excitation: Valence band maxima / Conduction band minima



- Two energy scales
- Nb_2O_5, TiO_2, ZnO reduce H^+
- In_2O_3, SnO_2, WO_3 do not reduce H^+
- All: oxidize O_2
- Band gaps: 2.8 - 3.4 eV $\rightarrow$ 460 - 380 nm
  $\Rightarrow$ Modification of band structure

Water Splitting

Solar Radiance:



Water Splitting: ΔE = -1.23 V $\rightarrow \lambda \approx$ 1010 nm

SC band gaps: 2.8 - 3.4 eV $\rightarrow$ 460 - 380 nm

Diffusion:

$$j = -D\vec{\nabla}n \qquad j: \text{ current}; \qquad n: \text{ carrier density}$$

Diffusion coefficient:

$$D = wk_BT$$

Charge carrier mobility: w (mean free path model, ab initio)

Ideal timescale for 10 nm TiO_2 nano-particles:

$$\tau = \frac{R^2}{D\pi^2} = 400 \text{ fs} \ldots 2 \text{ ps}$$

Defects: nano- to micro-seconds

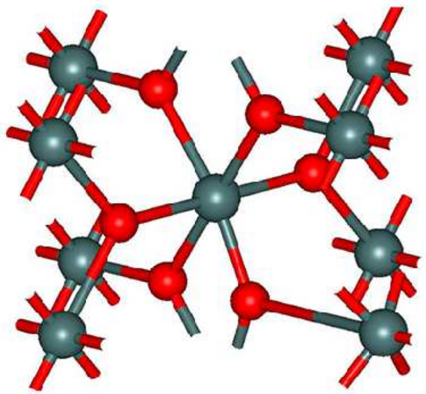
Effective masses:

$$m_e^* \approx 10\ m_e \qquad m_h^* \approx 0.8\ m_e \qquad \frac{1}{m} = \frac{1}{\hbar^2}\frac{d^2\epsilon_n(k)}{dk^2}$$

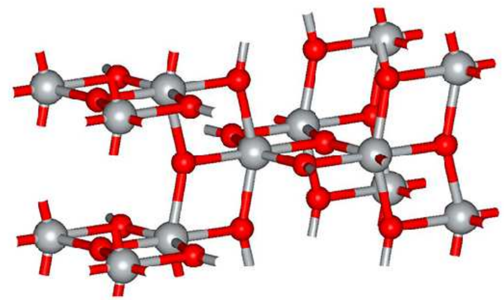
Water Splitting

Structures of TiO_2:

Rutile



Anatase



Enthalpie of formation: $\Delta G_f^0 =$ -212.6 kJ/mol

Band gap: 3.0 eV

Enthalpie of formation: $\Delta G_f^0 =$ -211.4 kJ/mol

Band gap: 3.2 eV

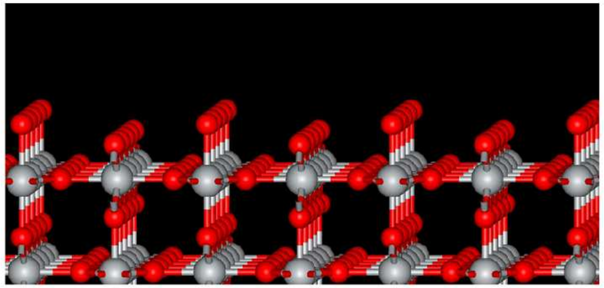
Rutile Ti: octahedral O coordination, O: trigonal-planar Ti coordination

Anatase: Same, less symmetry

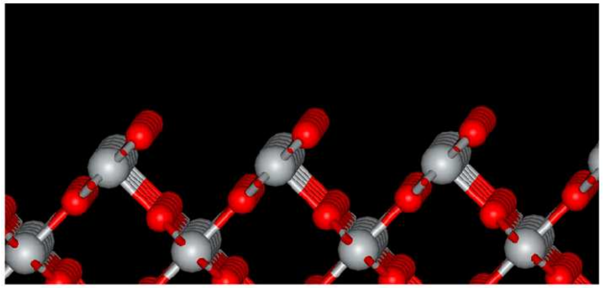
Reality: Mixture, grain boundaries

Idealized Surfaces:

Rutile (110)



Rutile (100)



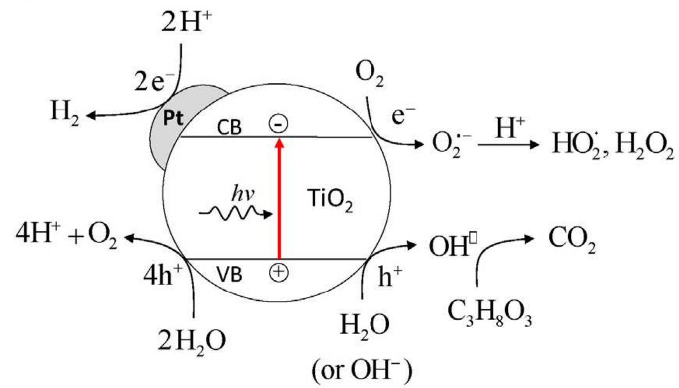
Other metal oxides (SnO_2, CrO_2, NbO_2, PbO_2, WO_2, TaO_2) also rutile structures

Ideal surfaces only in UHV → strong modification in solution

Gas phase: Small coverage → chemisorption → dissociation
High coverage → physisorption

Rutile TiO_2 (110) surface band gap: 2.0 eV ... 2.6 eV reported

Water Splitting



Hydrogen Evolution Reaction (HER):

(acidic environment)

Mechanism 1:

$$H^+ + e^{-*} \rightarrow H^{\cdot *}$$
$$H^+ + H^{\cdot *} + e^{-*} \rightarrow H_2$$

Mechanism 2:

$$H^+ + e^{-*} \rightarrow H^{\cdot *}$$
$$2\ \ H^{\cdot *} \rightarrow H_2$$

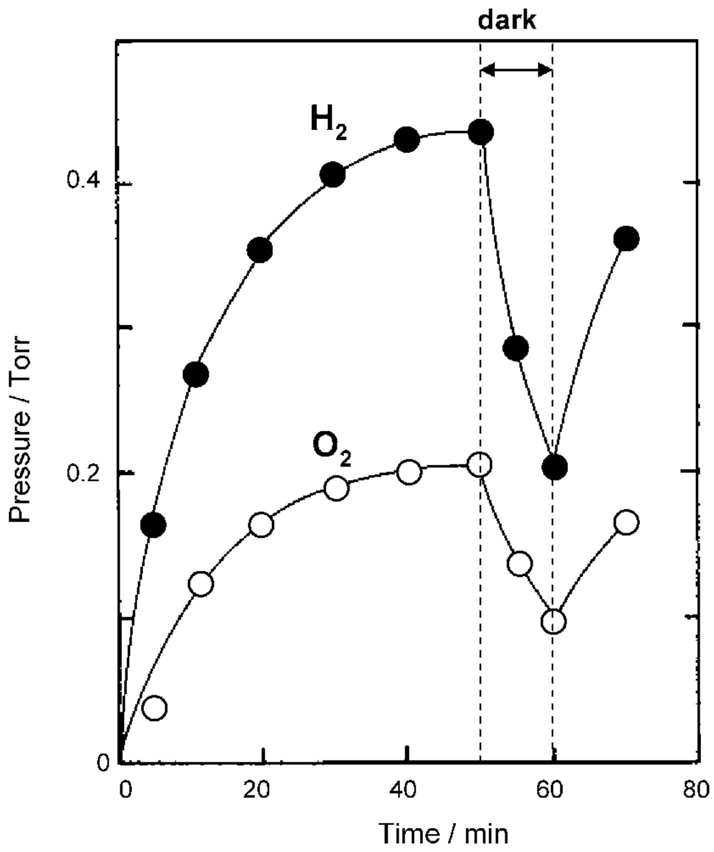
Asterisk: binding site

- H adsorption sites: Pt (Rh, Ir, Re)
- Cheaper: La_5Ni, WC
- Criteria: Weakly bound
- space charge layers beneficial
- First principles: band structure, adsorption energy
- Competing reactions, byproducts

P. Panagiotopoulou et al., Chem. Today **209**, 91 (2013).

Water splitting

Experiment: (Masuoka et al. Cat. Today **122**, 51 (2007))



Minutes 0-50: light driven H_2 production, saturation

Minutes 50-60: dark, backreaction

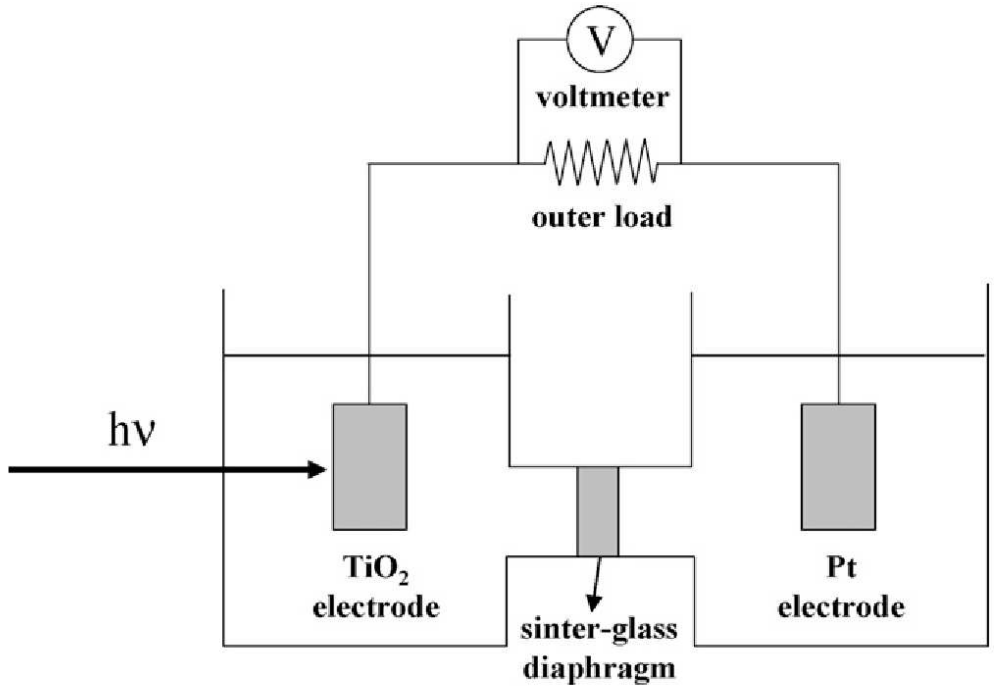
Catalysts do not change equilibrium

Efficiencies : $\approx$ 1-100 μmol/(g h)

Mixture of H_2, O_2

Water Splitting

Separate H_2/O_2 evolution: Photo-electrochemical cell



Matsuoka et al. Cat Today **122**, 51 (2007)

Substrate modifications

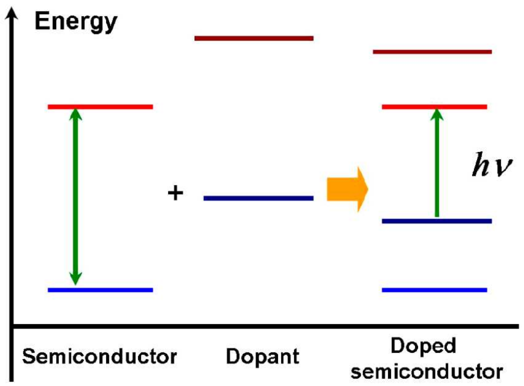
Designing more effective catalysts: Absorption of visible light

- Doping
- Sensitizing with chromophores
- Quantum size effects
- Z-schemes

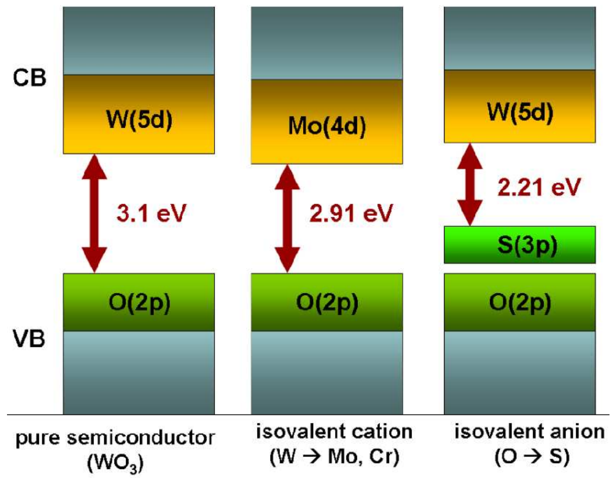
Substrate modifications

Doping:

Scheme



Examples

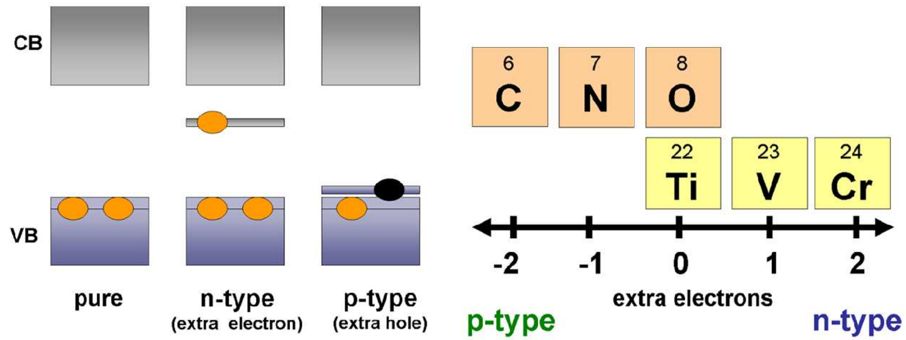


- Both band gaps large, but shifted
- Resulting band gap smaller
- Isovalent doping vs. n/p doping

- S2p higher than O2p
- Mo4d lower than W5d
- d(Mo)≈d(W), but d(S)>d(O)
  → lattice and band structure

Substrate modifications

n-p-codoping

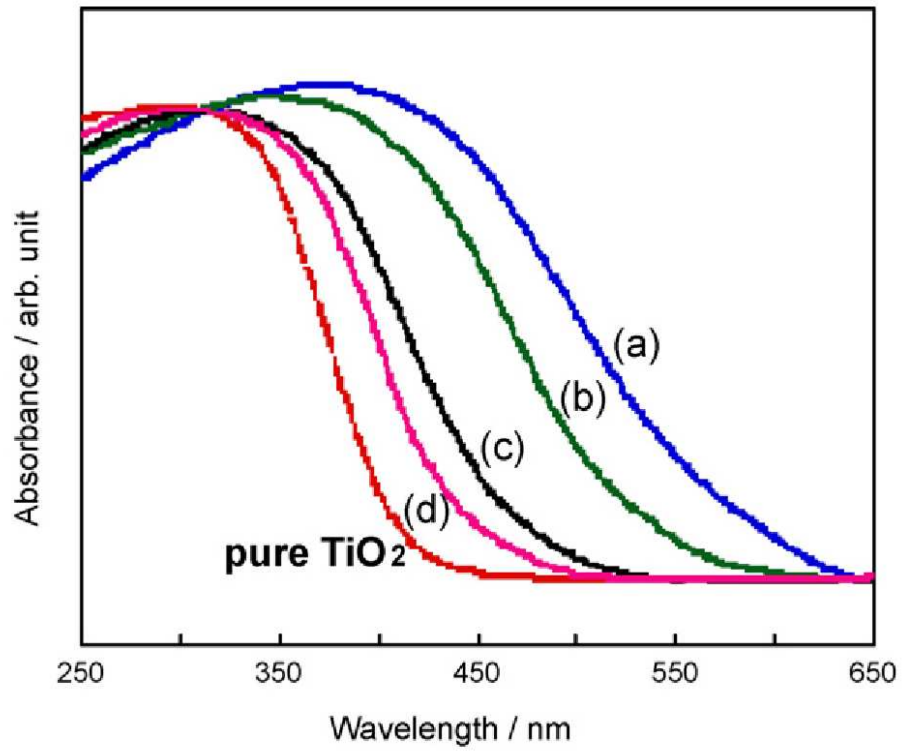


- n- or p-doping: reduces band gap
- n-doping: localized d-states $\rightarrow$ recombination
- p-doping: delocalized p-states
  nitrogen: successfully used
  but: solubility thermodynamically limited
- $\Rightarrow$ Codoping

- n-p coulomb attraction: stabilization
- band gap reduction
- (non)compensation
- combinatorial increase in possibilities
- lots of work to be done, systematic?

Substrate modifications

Absorption Spectra of doped TiO_2

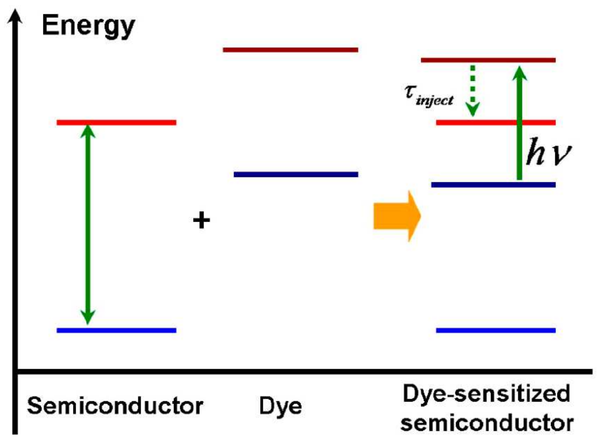


a) V, b) Cr, c) Fe, d) Ni with 1.33 μmol/g

Matsuoka et al. Cat Today **122**, 51 (2007)

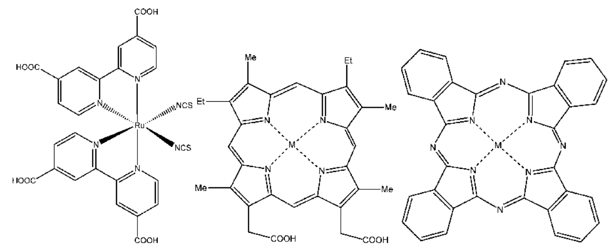
Substrate modifications

Sensitizers



- no change in sc band gap
- attachment of small gap chromophore
- injection into sc
- excitation HOMO → CB very rare
- Grätzel cell: dye-sensitized solar cell

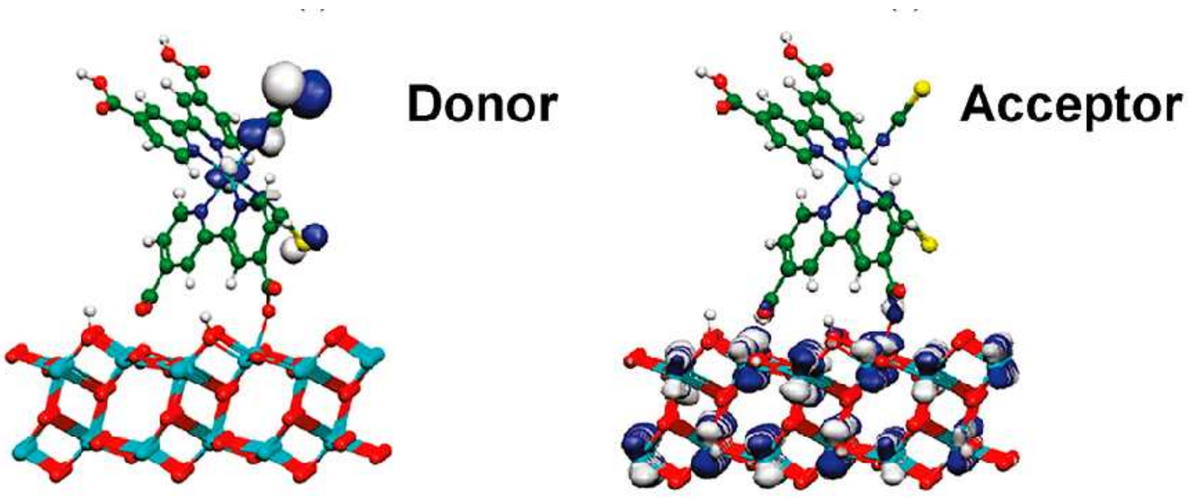
Metallo-organic sensitizers



- metal d-orbital → ligand CT
- N3 dye: Grätzel
- Ru expensive
- (b) porphyrin: chlorophyll
- light-harvesting
  photo-to-current efficiency
  coupling with CB

Substrate modifications

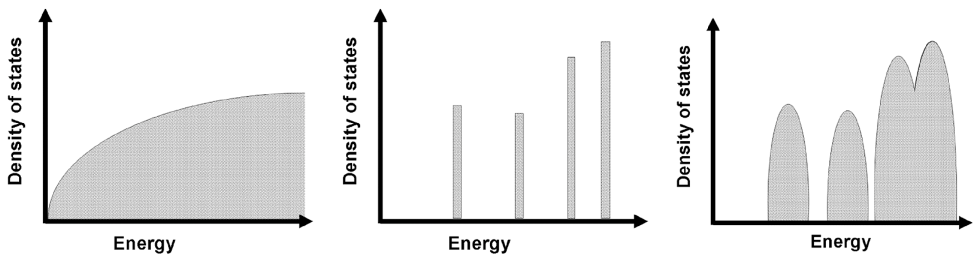
Injection:

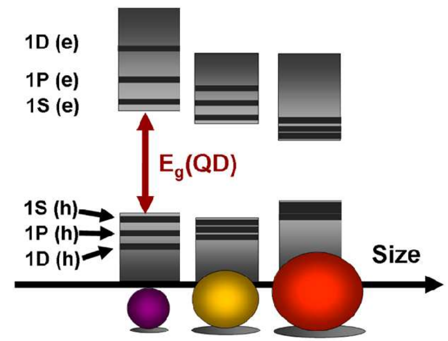


N3 dye at TiO_2

Substrate modifications

Quantum Dot Sensitizers: Confinement





- e^- structure between molecules $\leftrightarrow$ solid
- Small gap semi-conductors
  CdS, CdSe, InP, ...
- Advantages:
  - Tuning band gap via shape, size
  - High visible absorbance
  - Suppression of recombination by space charge layers

- Model: Particle in a sphere + effective masses

$$E_{n,e} = E_{\mathrm{CB}} + \frac{\pi^2\hbar^2}{2m_e^* L^2} n^2$$

$$E_{n,h} = E_{\mathrm{VB}} - \frac{\pi^2\hbar^2}{2m_h^* L^2} n^2$$

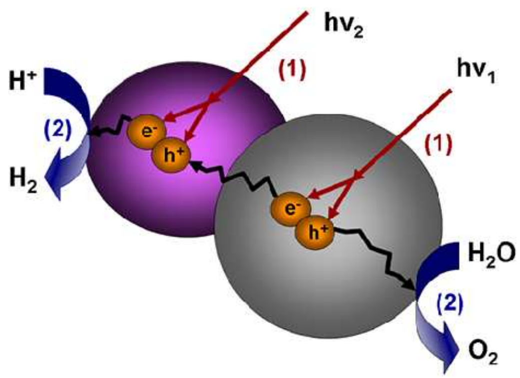
- Reality ZnO:

$$E_g(L) = 3.30\ eV + \frac{0.293\ eV}{L} + \frac{3.94\ eV}{L^2}$$

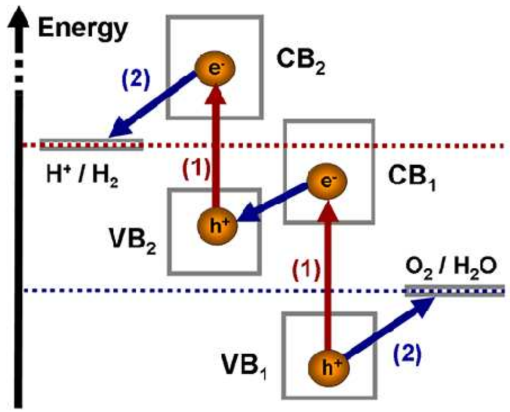
Substrate modifications

Z-scheme: (here: water splitting)

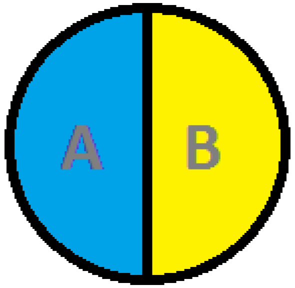
Space



Energy



Realization e.g. as Janus particle:

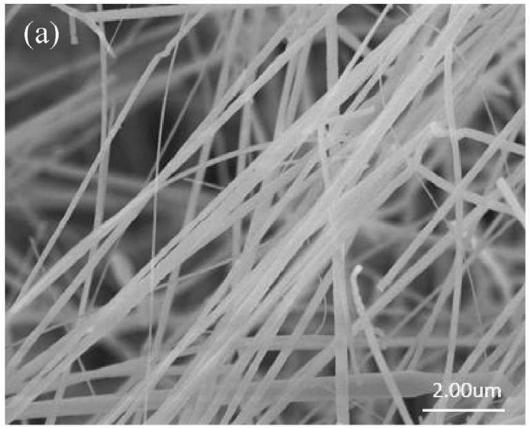


- Composite system
- "A" can drive hydrogen reduction (only)
- "B" can drive oxygen oxidation (only)
- 2 photons required
- maybe different parts of spectrum

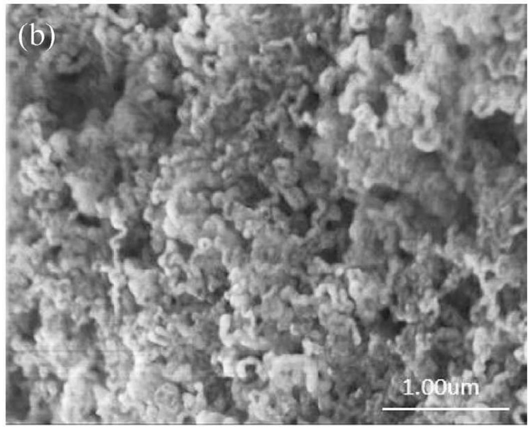
Possible 'mediator', to prevent intra-particle e^--h^+ recombination

Example: SiC

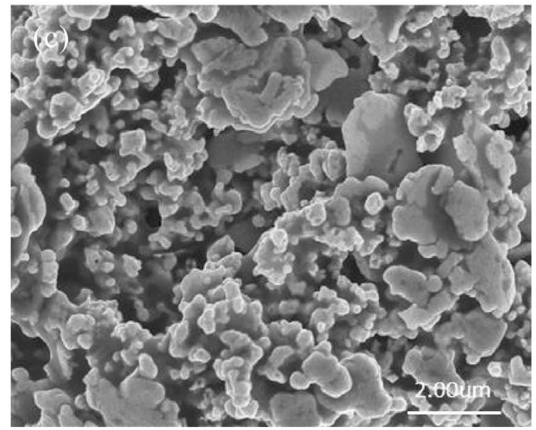
Effect of morphology: SiC



Fibers



Wires

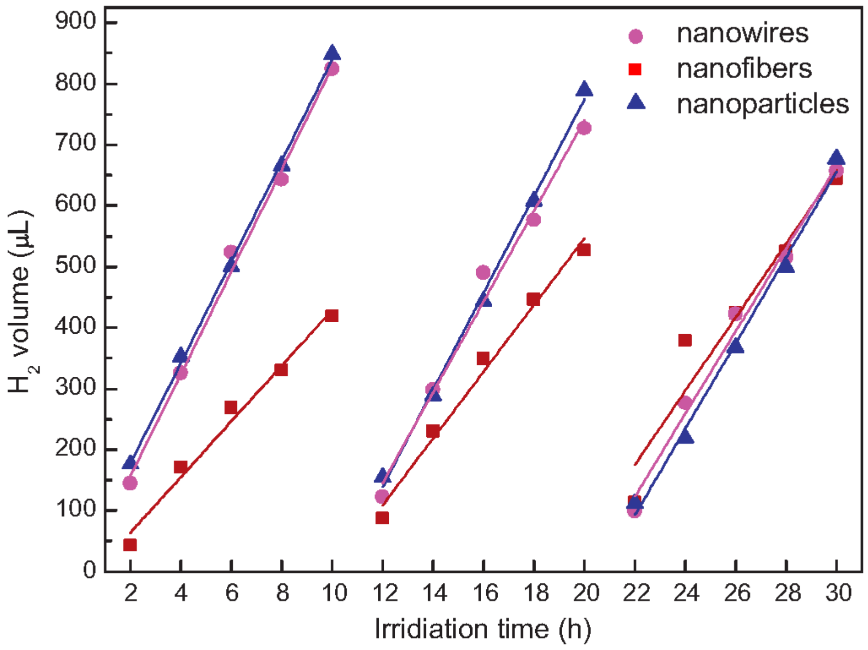


Nano-Particles

	Fibers	Wires	Particles
Surface Area (m^2/g)	45	52	81

Stacking fault densities, absorption spectra, ...

Effect of morphology: SiC



- 3 runs of 10 hours
- no degradation
- fibers seem to improve
- visible light irradiation
- factor 2 better than commercial SiC

Introduction