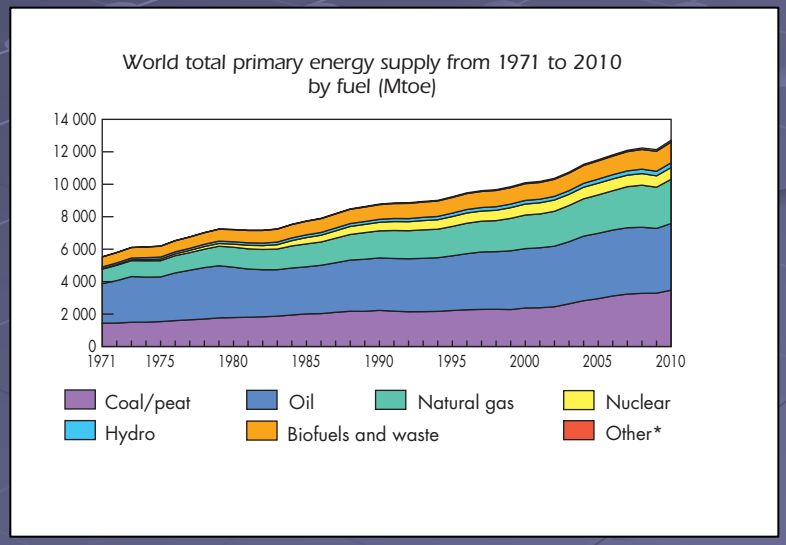
Characterization of photoelectrochemical processes for energy conversion through computer simulations

Nicola Seriani

The Abdus Salam International Centre for Theoretical Physics,
Strada Costiera 11, 34151 Trieste, Italy

The energy challenge

- Sustainably providing clean energy for the needs of tomorrow is one of the key challenges humankind has to face



World Energy Statistics, International Energy Agency

- Shift towards renewable energy sources

Solar energy

- Solar energy is abundant
- Source is irregular → importance of energy storage (batteries, solar-to-fuel, hydrogen storage,...)
- So far, mainly photovoltaics: but electricity is difficult and expensive to store
- Moreover, some applications need storage at high energy density: liquid fuels for airplanes
- Solar fuels: the goal is to use solar energy to produce fuels (hydrogen, hydrocarbons, methanol,...)

Solar fuels

- Solar fuels: the goal is to use solar energy to produce fuels (hydrogen, hydrocarbons, methanol,...)

- Three main routes:

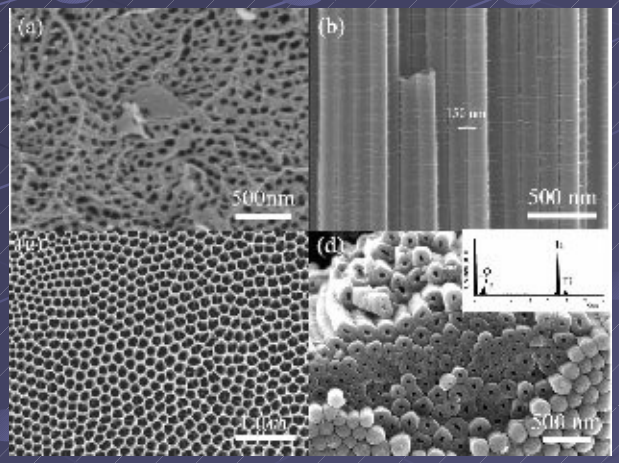
    1. Solar thermal

    2. Photovoltaics + electrocatalysis

    3. Photo(electro)catalysis

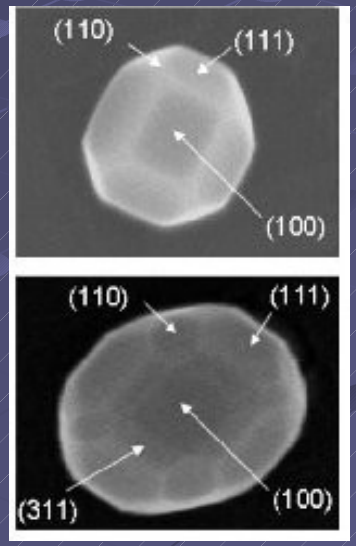
Nanostructures for energy applications

- Ability to control, manipulate and understand materials at the nanoscale could lead to major advancement in the field of energy conversion and storage
- Properties at the nanoscale different from bulk



TiO_2 nanotubes as anode material for dye-sensitized solar cells

Li et al., Chem. Mater. 22, 5707 (2010)



Platinum nanoparticles for fuel cells

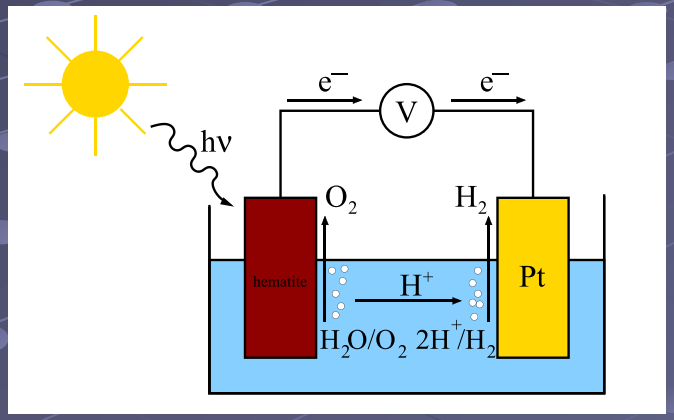
Komanicky et al., Electrochim. Acta 55, 7934 (2010)

Silicon nanowires as anode for Li batteries

Chang et al., Adv. Funct. Mater. 20, 4364 (2010)

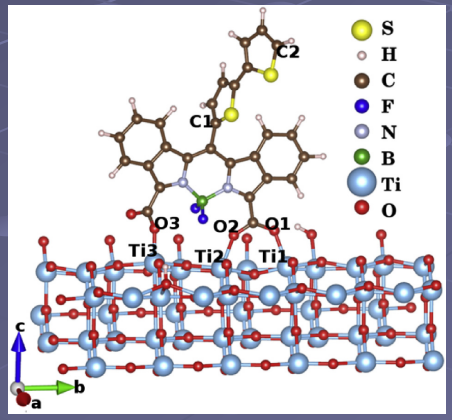
Understanding functional materials at the atomic level

Photocatalysis for solar fuels



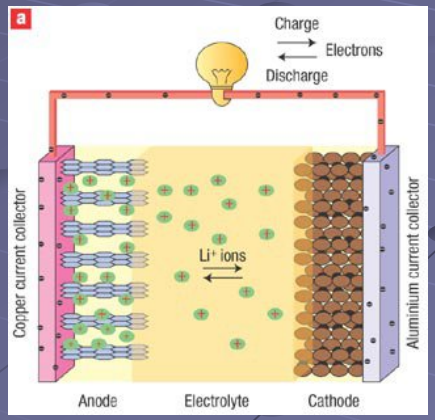
N. Seriani, J. Phys.: Condens. Mat. 29, 463002 (2017)

Photovoltaics



Songkhao et al., Dyes and Pigments 142, 558 (2017)

Batteries



B. Scrosati, Nature Nanotechnology 2, 598 (2007)

Complex composition: defects, dopants,...
Complex environment affecting composition and interfaces
Complex processes: photoabsorption, charge dynamics, interface reactions

Computational materials science for sustainable energy

Environment
(pressure, temperature, applied voltage, pH,...)

↓

Properties
(atomic structure, stability, electronic properties,...)

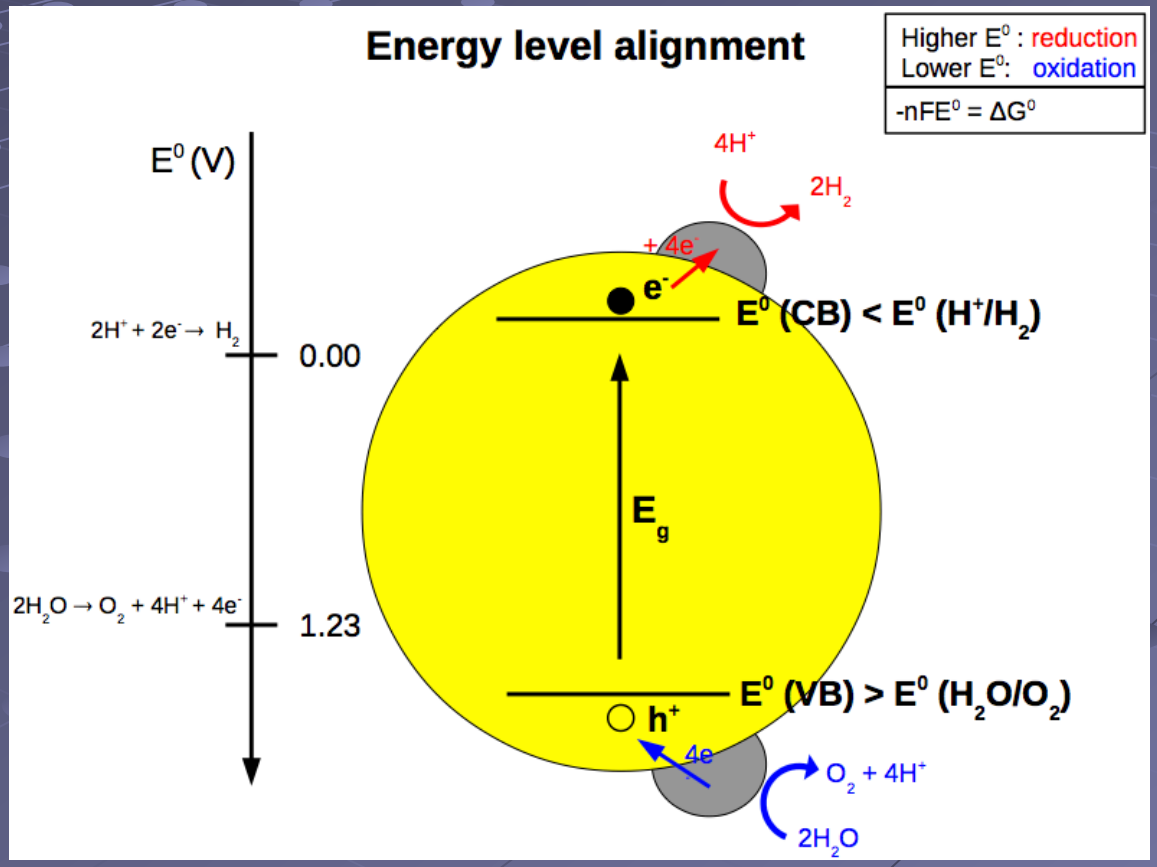
↓

Function
(photocatalytic activity, lithium storage capacity,...)

↑ Materials design

Density functional theory and high-performance computing

Photocatalysis



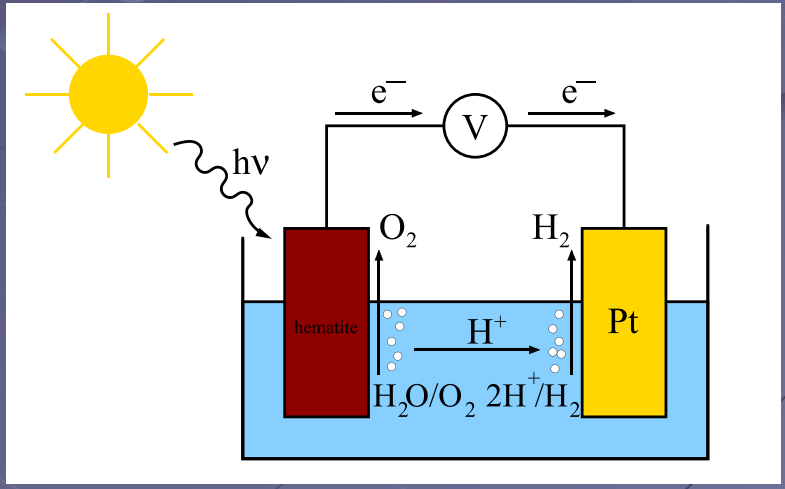
Photoelectrocatalysis

Overall: $2H_2O \rightarrow O_{2,g} + 2H_{2,g}$

At the anode: $2H_2O \rightarrow O_{2,g} + 4H^+_{aq} + 4e^-$

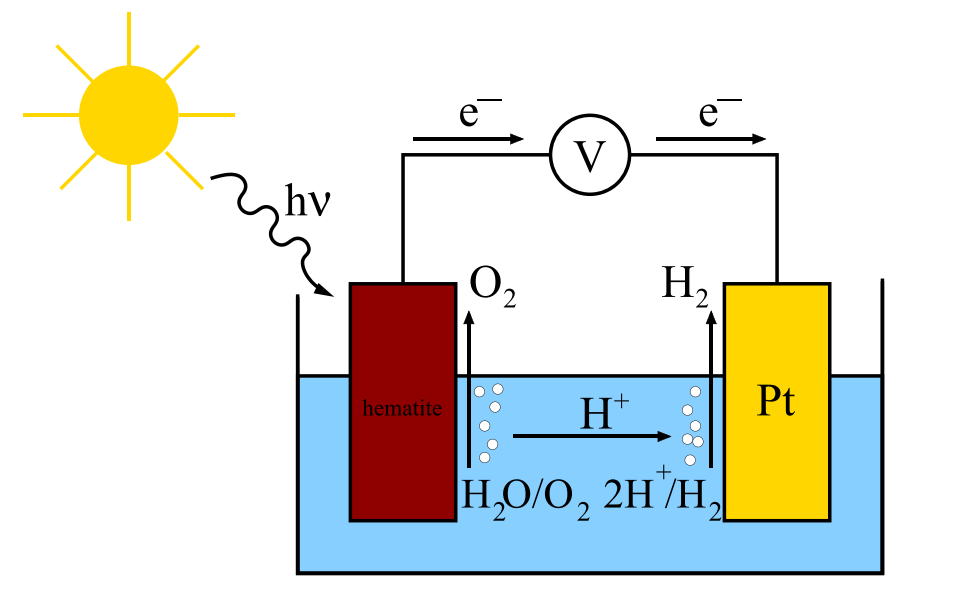
At the cathode: $4H^+_{aq} + 4e^- \rightarrow 2H_{2,g}$

Acidic conditions...

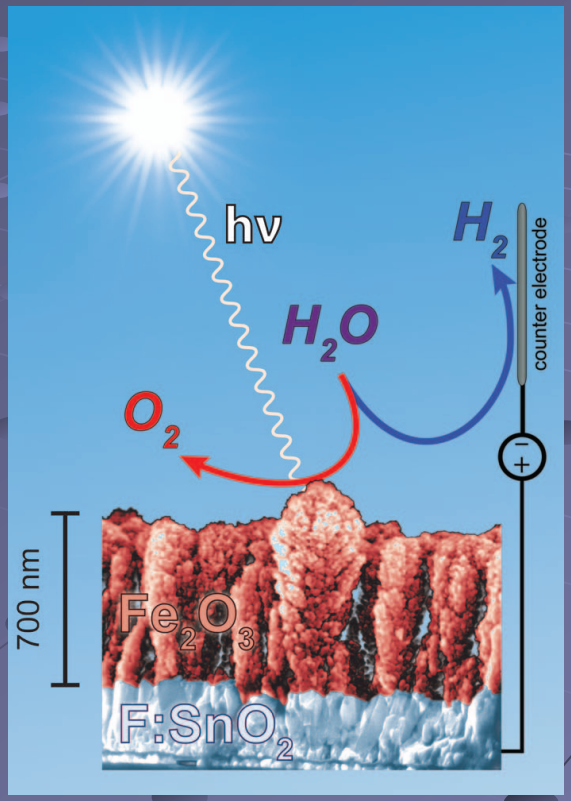


N. Seriani, J. Phys.: Condens. Mat. 29, 463002 (2017)

Photoelectrochemical cells for solar-fuel production



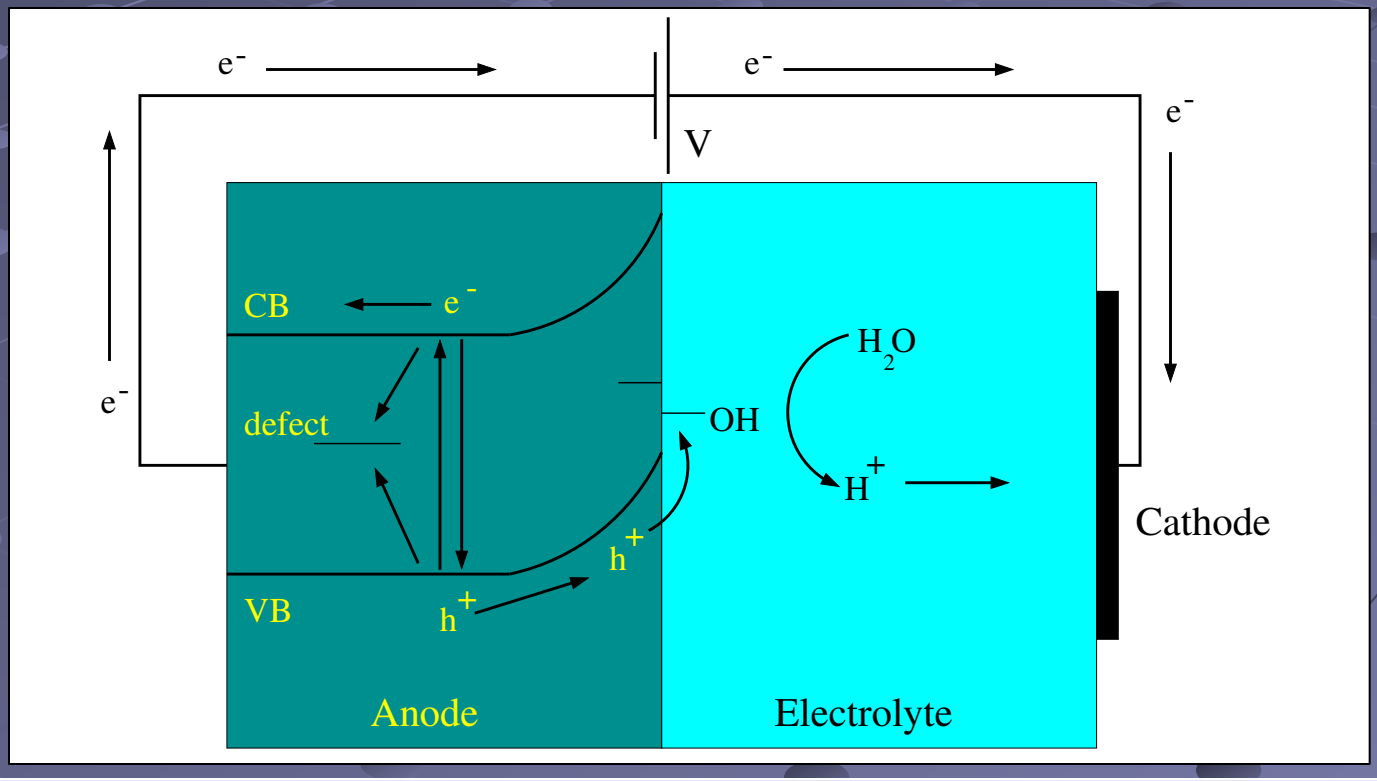
N. Seriani, J. Phys.: Condens. Mat. 29, 463002 (2017)



K. Sivula et al., ChemSusChem 4, 432 (2011)

Complex (photo-)physics and (photo-)chemistry

- Photoabsorption, recombination, charge separation, charge transfer, adsorption, proton-coupled electron transfer, ...

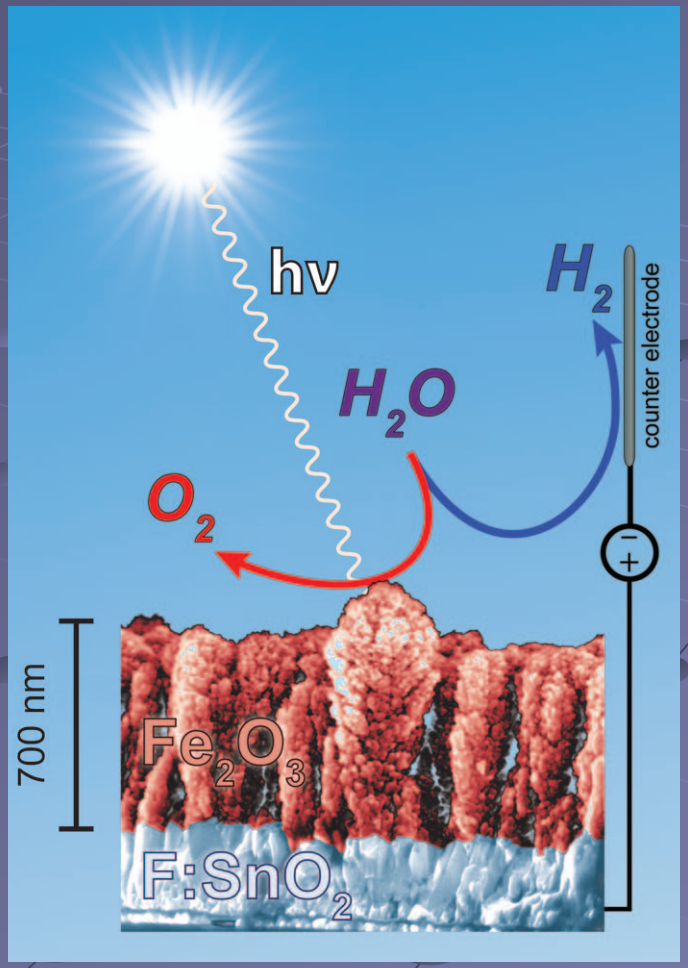


Titania as a photocatalyst

- The material of choice is TiO_2, for its wide availability, safety, stability, and activity
- It has a gap of ~3 eV, it absorbs in the UV range
- This accounts for less than 5% of the energy in the visible range
- Need to find other materials (hematite), to modify the titania photocatalyst and to understand the mechanisms of the photocatalytic process

Hematite

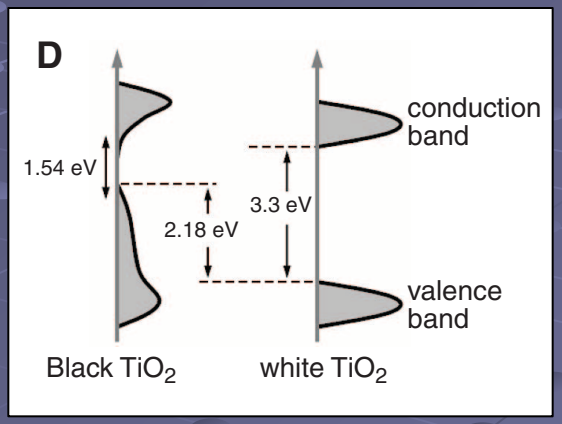
- α–Fe_2O_3 (hematite) is a promising material as photoanode for photo-electrocatalytic water splitting.
- Gap ~2 eV
- Problem of charge transport and recombination
- Charge transport problem is less important for nanostructured materials
- Some progress, but not definitive
- Need to characterize material and processes

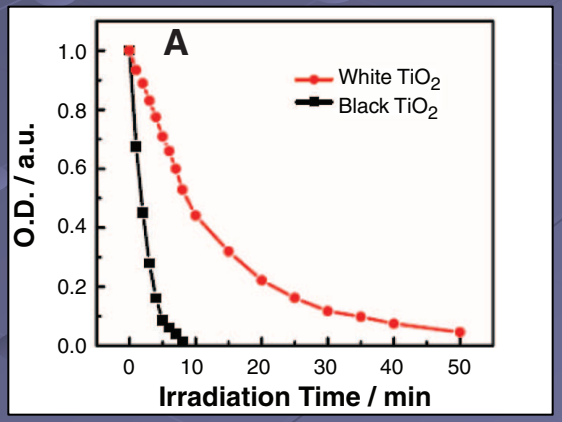


K. Sivula et al., ChemSusChem 4, 432 (2011)

Black hydrogenated titania

Hydrogenation improves photoabsorption and photocatalytic activity



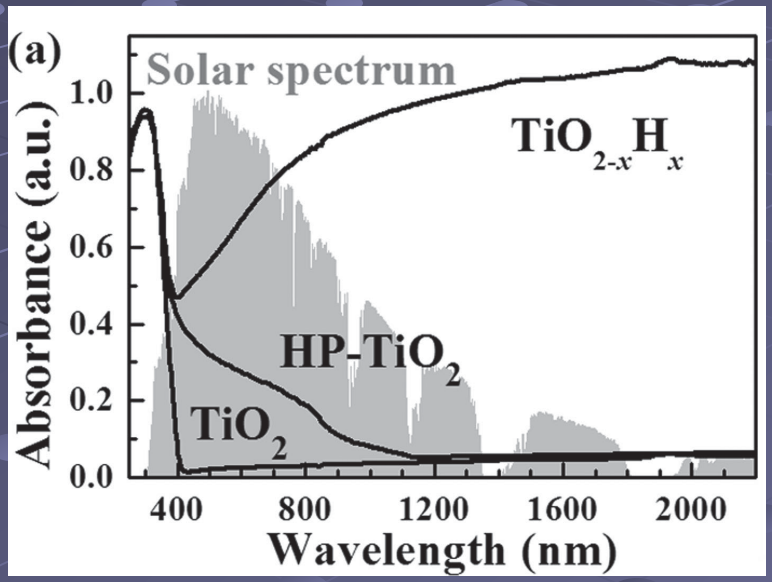


Optical density of methylene blue solution as function of time

X. Chen et al., Science 331, 746 (2011)

Black hydrogenated titania

Optical absorption spectrum depends on hydrogenation method:



HP-TiO_2 by high-pressure thermal treatment

$TiO_{2-x}H_x$ by plasma treatment

X. Chen et al., Science 331, 746 (2011)
Z. Wang et al., Adv. Funct. Mater. 23, 544 (2013)

Computational details

- Density functional theory: PBE + U
- Plane waves
- Norm-conserving pseudopotentials

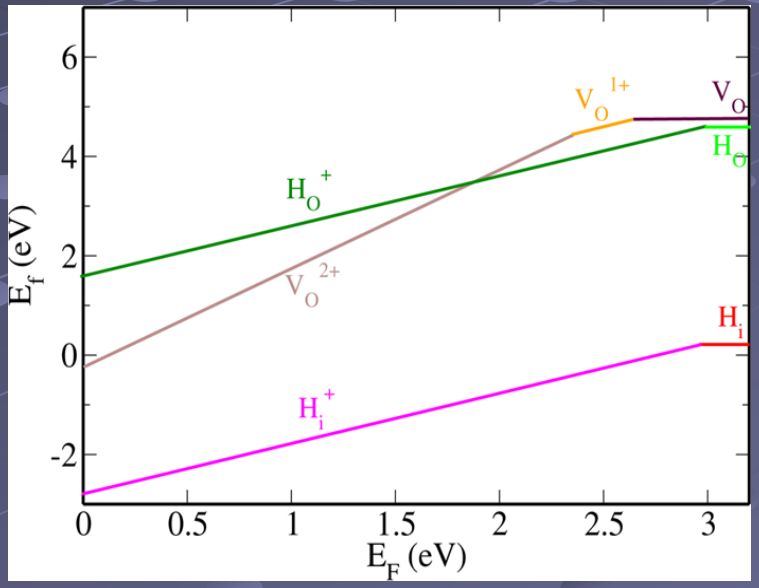
- GW + Bethe-Salpeter Equation
- G_0W_0
- Plasmon pole approximation

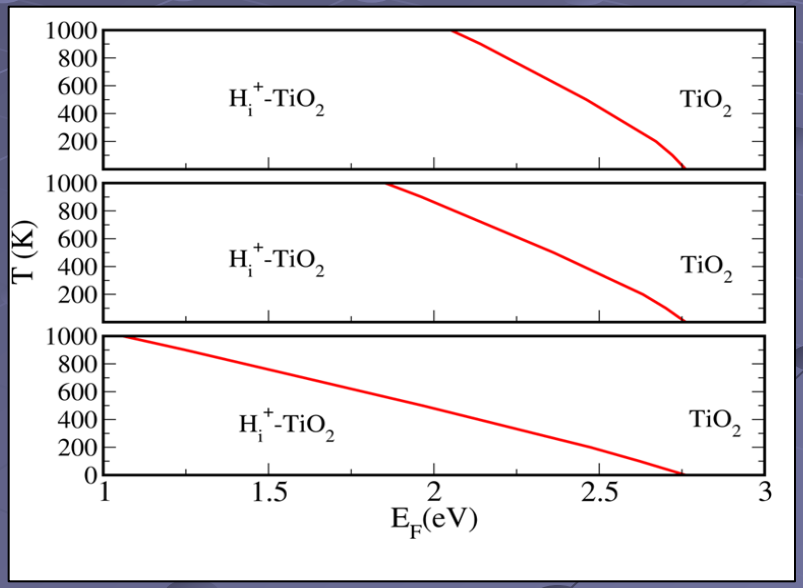
http://www.quantum-espresso.org

http://www.yambo-code.org

Hydrogenated titanium dioxide: thermodynamics

-) H_i: interstitial hydrogen
-) H_O: hydrogen in oxygen vacancy
-) V_O: oxygen vacancy





p_{H2}=1atm

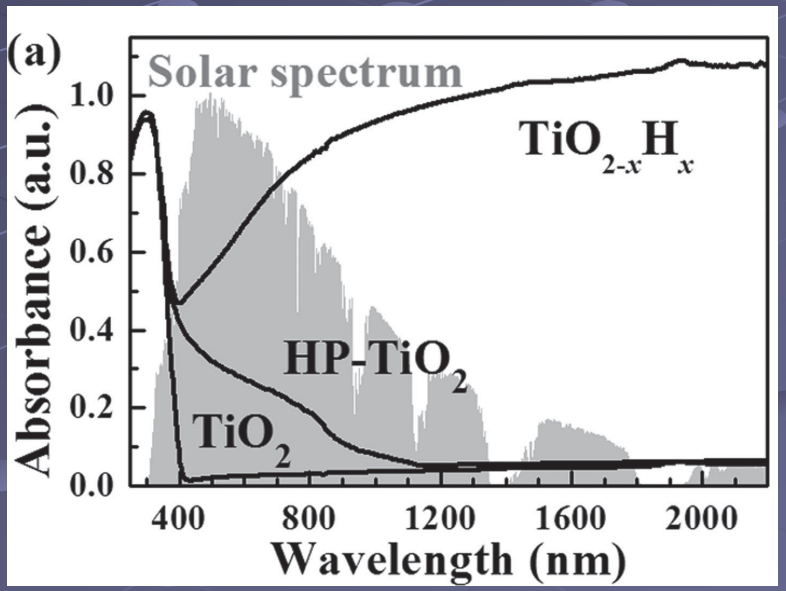
p_{H2}=0.01 atm

p_{H2}=10^{-10} atm

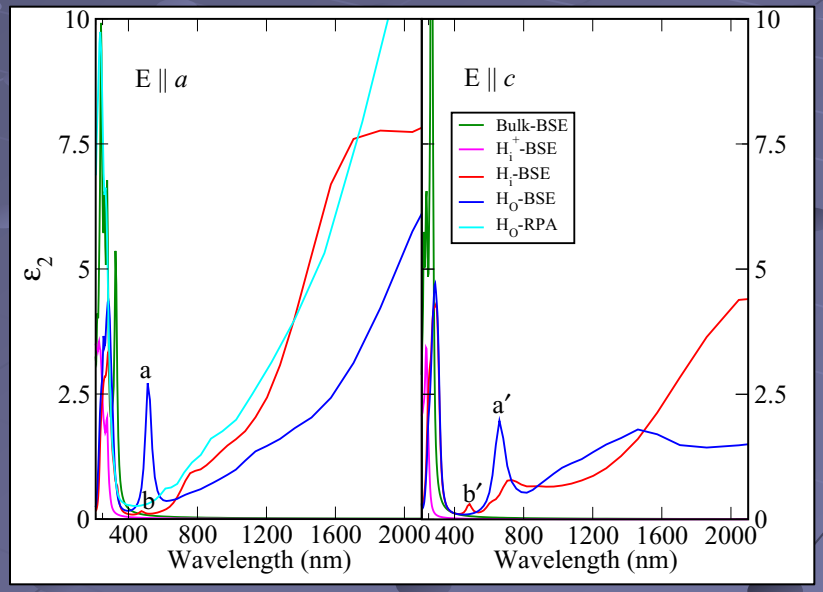
S. S. Ataei, M. R. Mohammadizadeh, N. Seriani, JPCC 120, 8421 (2016)

Hydrogenated titanium dioxide: optics

-) Neutral hydrogen defects lead to adsorption in visible and IR
-) Proton defects barely influence photoabsorption
-) HP-TiO_2 spectrum is reproduced in presence of disordered Ti-H and O-H (L. Liu et al., PRL 111, 065505 (2013))



Z. Wang et al.,
Adv. Funct. Mater. 23, 544 (2013)
X. Chen et al., Science 331, 746 (2011)



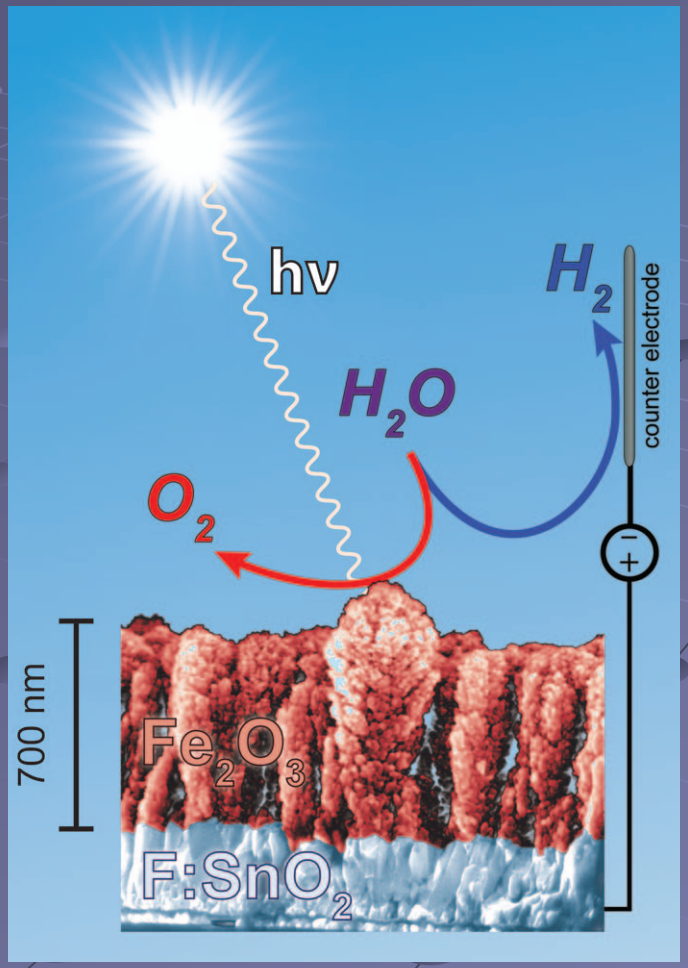
S. S. Ataei, M. R. Mohammadizadeh, N. Seriani,
PRB 95, 155205 (2017)
S. S. Ataei, M. R. Mohammadizadeh, N. Seriani,
JPCC 120, 8421 (2016)

Hydrogenated titania: conclusions

- Hydrogenated TiO_2 has an improved photoabsorption and photocatalytic activity
- The photoabsorption spectrum depends heavily on the hydrogenation conditions (high pressure vs. plasma treatment)
- First-principles simulations show that neutral hydrogen defects lead a photoabsorption spectrum compatible to that of plasma treated H-TiO_2
- Charged H defects show only marginal differences with respect to defect-free titania

Reactions at the surface of the photocatalyst

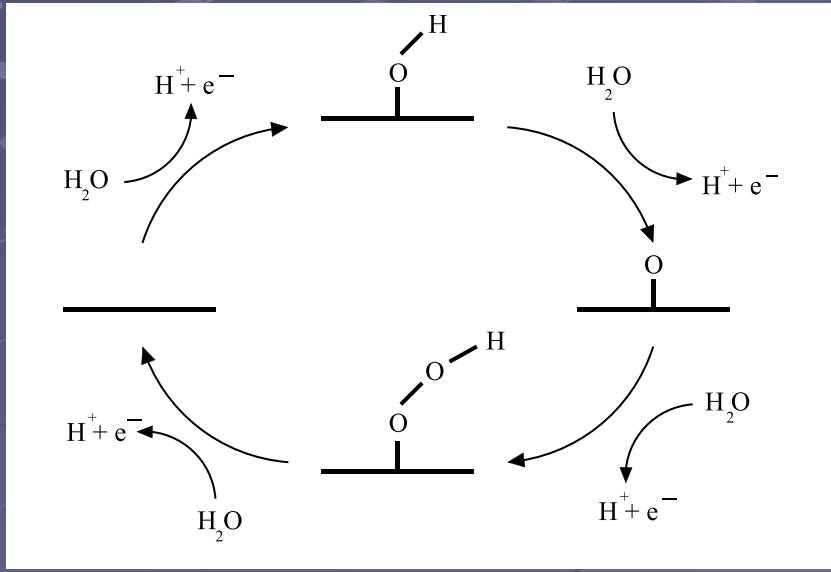
- Oxygen evolution takes place at the interface between the photocatalyst and the electrolyte
- Important to characterize thermodynamics and kinetics chemical reactions, and of charge transfer



K. Sivula et al., ChemSusChem 4, 432 (2011)

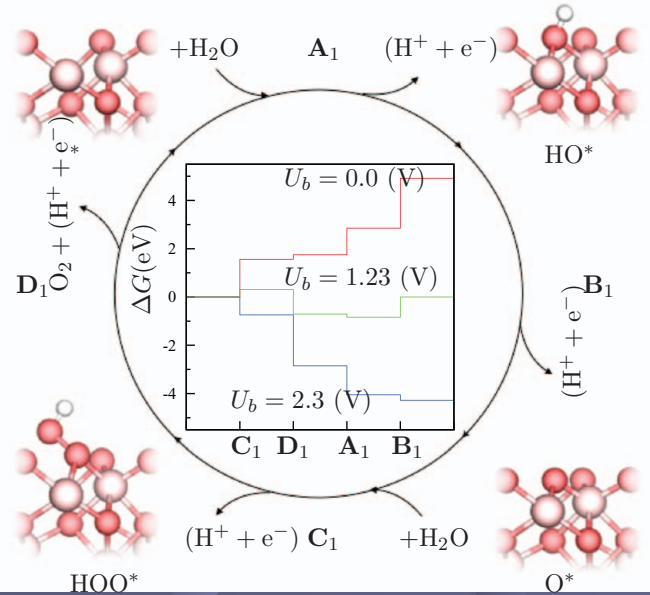
Water oxidation at the photoanode

At the anode: $2H_2O \rightarrow O_{2,g} + 4H^+_{aq} + 4e^-$



At the surface of the photoanode, the reaction proceeds through 4 elementary steps (proton coupled electron transfers)
This takes place however in a complex environment

Thermodynamics of water splitting at the (0001) surface of hematite



Nguyen et al., J. Chem. Phys. 140, 064703 (2014)

Seriani, J. Phys.: Condens. Mat. 29, 463002 (2017)

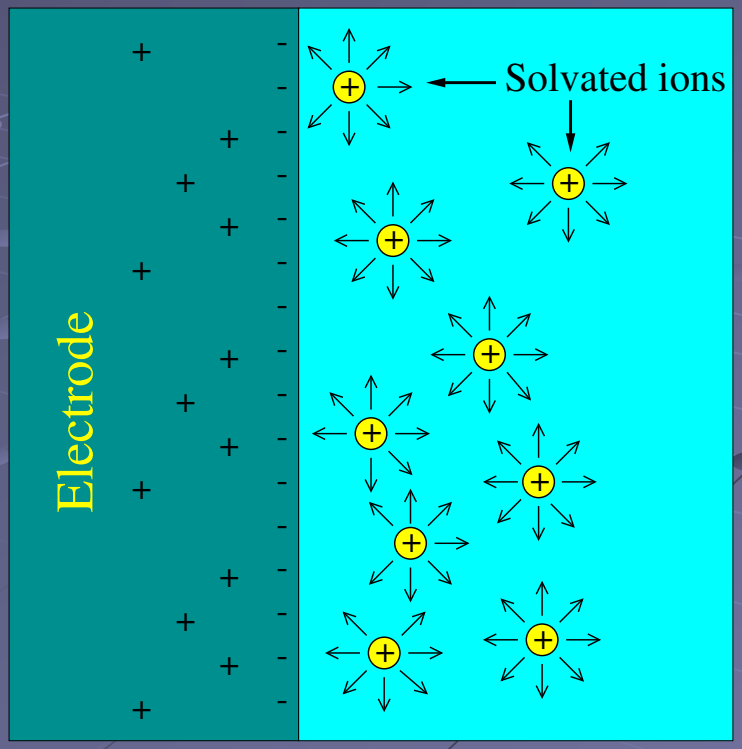
Crucial to take into account the photoelectrochemical conditions (in water, under illumination)

We find an overpotential of 0.8 V for photo-driven water oxidation, in fair agreement with experiments

The electrochemical interface

A crucial role is played by the electrochemical interface, specially for charge dynamics:

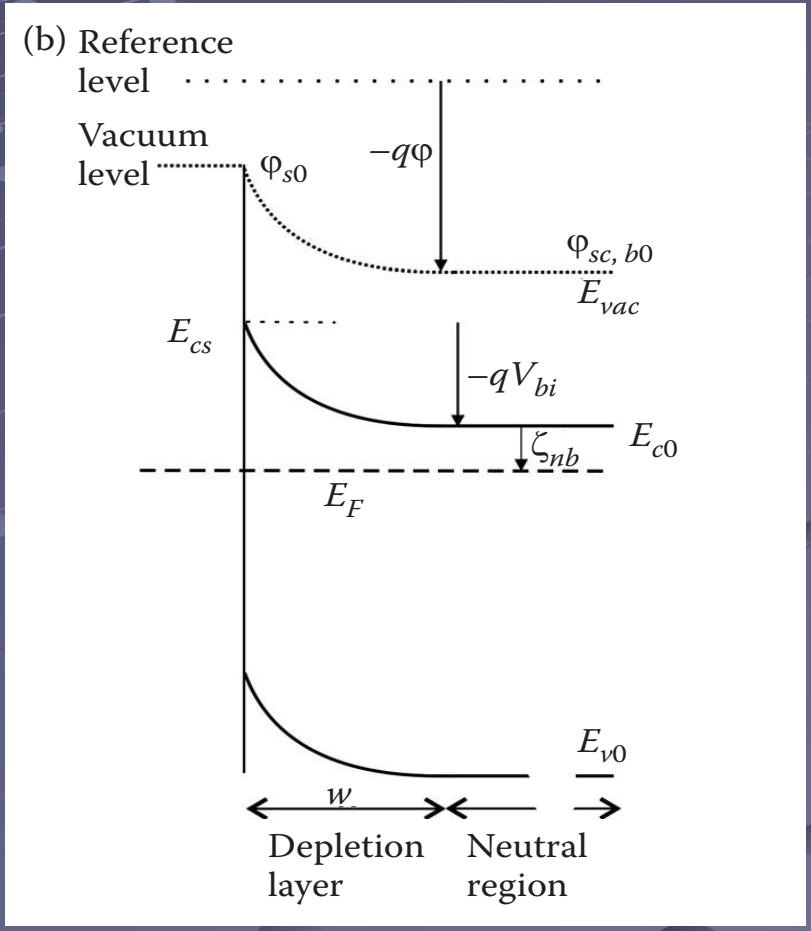
space charge layer,
double layer,
ions,
electric field,
illumination,
hole transfer



Goal is to take a second look (with new tools) at old models** of the interface and of the double layer

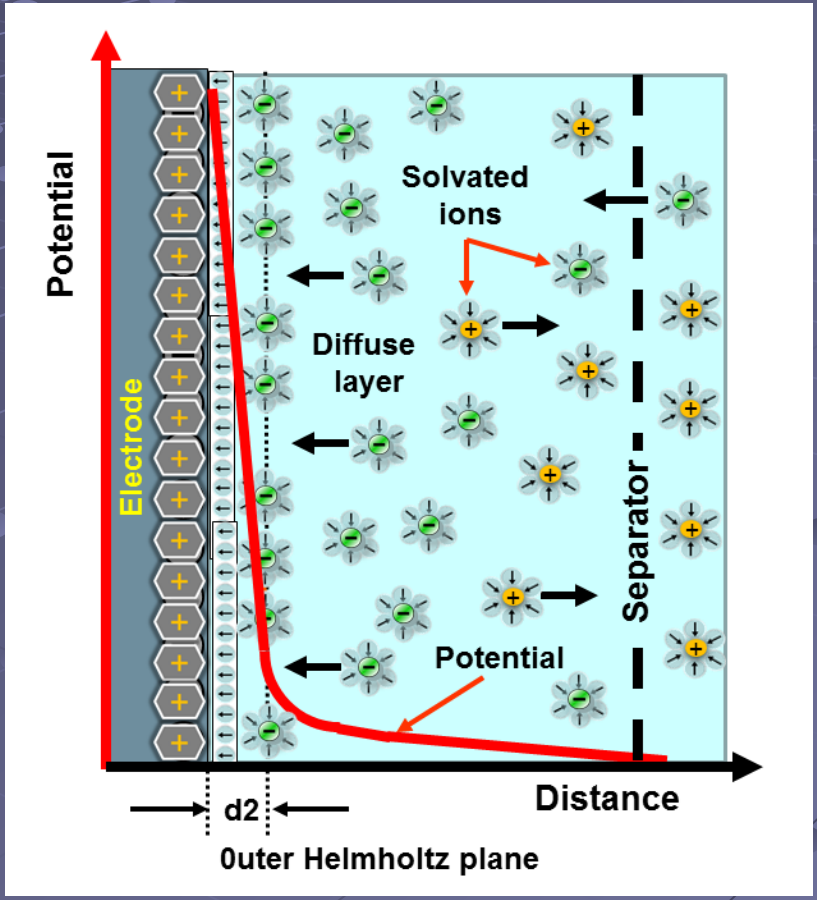
** Stern, Z. Electrochem., 30, 508 (1924)
** Gouy, J. Phys. 9, 457 (1910)

On the semiconductor side: the space charge layer



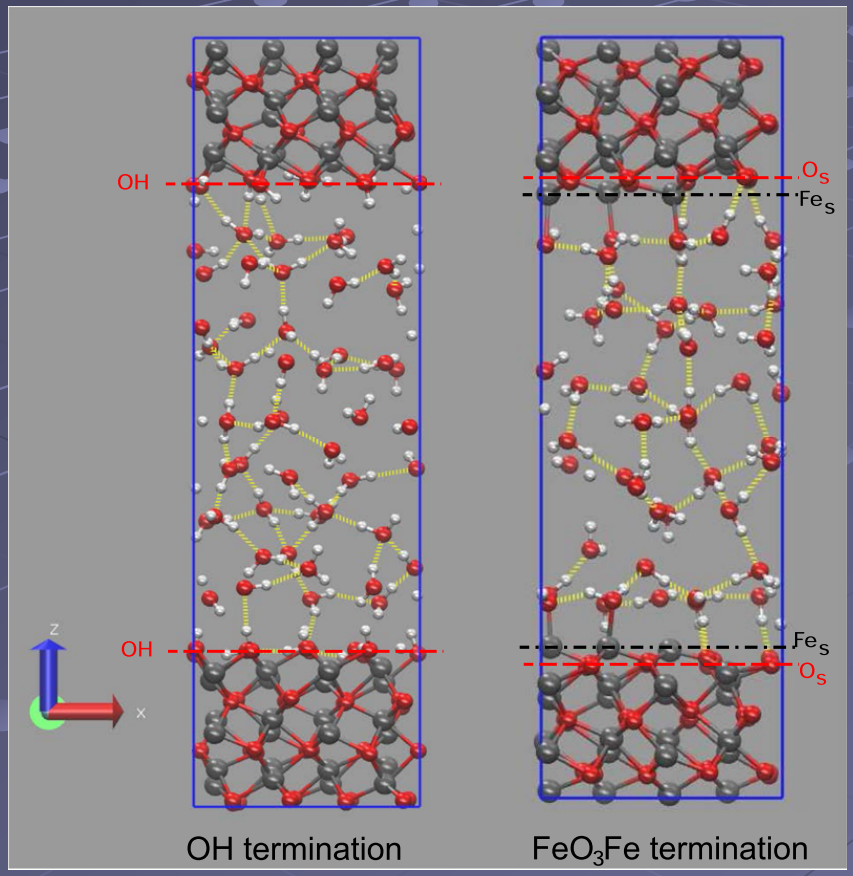
J. Bisquert, Nanostructured energy devices (CRC Press)

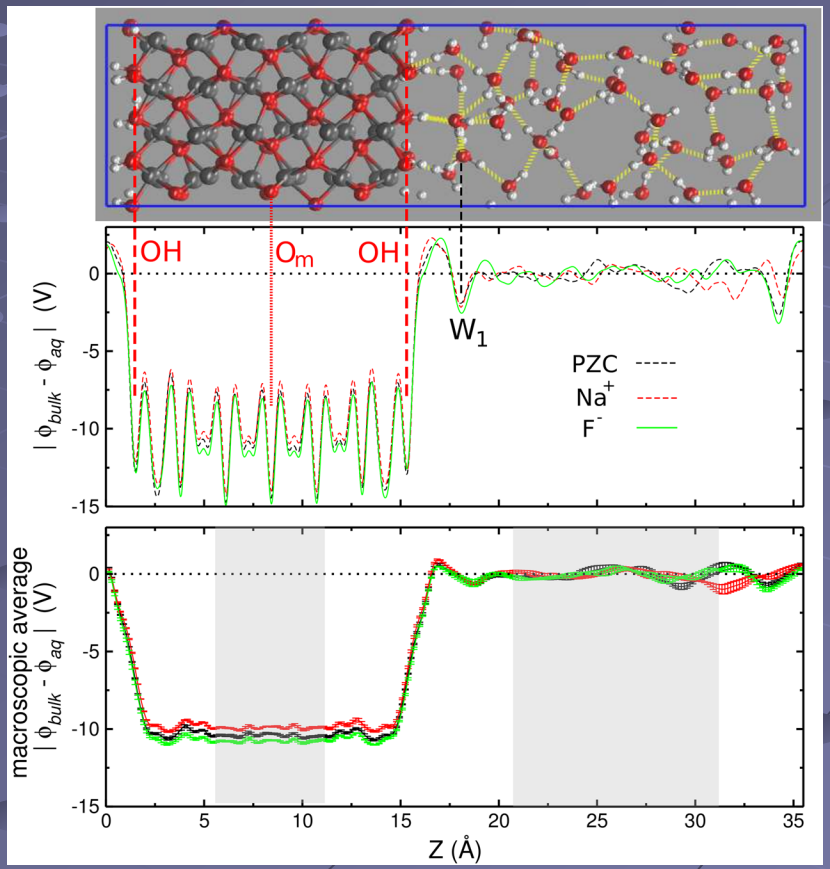
On the electrolyte side: the double layer



By Elcap - Own work, CC0, https://commons.wikimedia.org/w/index.php?curid=25771148

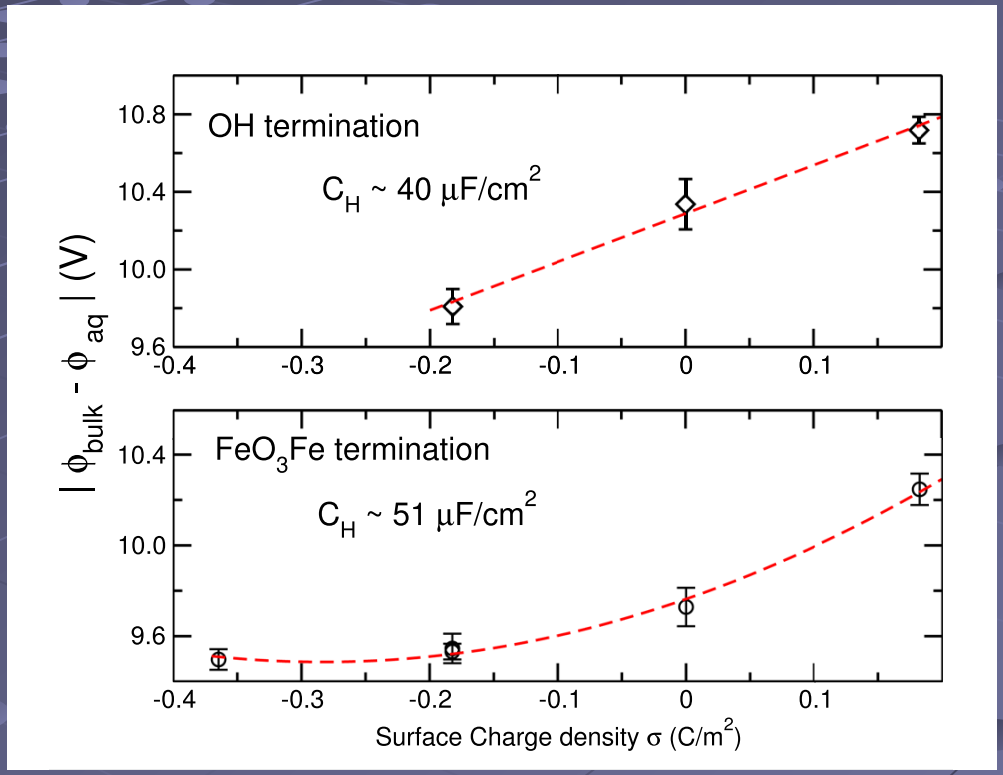
The double layer at the (0001) hematite surface





Ulman, Poli, Seriani, Piccinin, Gebauer, J. Chem. Phys. 150, 041707 (2019)

The capacitance of the double layer



Ulman, Poli, Seriani, Piccinin, Gebauer,
J. Chem. Phys. 150, 041707 (2019)

The capacitance of the double layer

TABLE I. The estimates of various capacitances for the hematite water interface under different pH conditions reported by various experiments. The values reported by Lucas and Boily[42,43] are converted to μF/cm^2 by area normalization assuming a cross-sectional area of a micro-electrode ~491 μm^2. Capacitance $\tilde{C}_{bulk}$[57,59] effectively amounts to capacitance of C_{SC} and C_H in series.

Reference	C_{SC} (μF/cm^2)	C_H (μF/cm^2)	C_{dl} (μF/cm^2)	C_{SS} (μF/cm^2)	Surface	pH	Experimental technique and model
Boily, Chatman, and Rosso[35]	...	31–73	...	...	(001)	0–14	OCPM and 1-pK/2-pK BSM
Chatman, Zarzycki, and Rosso[36]	... ...	30–88 20–88 59–80	18–35 18–60 12–68	... ...	(001) (012) (113)	3–11	OCPM and TLM
Hwang and Lenhart[37]	...	56–156	-	...	...	5–10	OCPM and TLM
Shimizu and Boily[39]	C_{int} ~ 0.50 and 0.55			...	(001)	11 and 4.3	CV
	...	0.2–2.0	0.5–0.6	...	(001)	4–12	GEIS
Shimizu and Boily[41]	10^{-8} 10^{-9}	0.2–0.6 3–35	0.2–0.6 1–10	... ...	(001) (012)	3–13	GEIS
Lucas and Boily[42]	... ...	12.6 75.1	1.46 9.06	... ...	(001) (012)	5.9	GEIS
	... ...	44–124 53–180	2–63 2–53	... ...	(001) (012)	5.9	LEIS
Lucas and Boily[43]	... ...	117 212.8 149.3	4.75 10.84 5.33	... ...	(001)	5 (NaCl) 5 ($NaHCO_3$) 5 (NH_4Cl)	LEIS
	... ...	144 176.2 243.4	1.06 2.93 1.42	... ...	(012)	5 (NaCl) 5 ($NaHCO_3$) 5 (NH_4Cl)	LEIS
	... ...	192 368.4 298.8	6.27 7.33 8.94	... ...	(001)	9 (NaCl) 9 ($NaHCO_3$) 9 (NH_4Cl)	LEIS
	... ...	227.5 237.7 331	2.01 2.12 2.24	... ...	(012)	9 (NaCl) 9 ($NaHCO_3$) 9 (NH_4Cl)	LEIS
Iandolo *et al.*[56]	...	...	...	10–90	...	12.9	EIS under Illumination (ECM2)
Klahr *et al.*[57]	$\tilde{C}_{bulk}$ ~1–4		...	20–160 10–100	...	6.9 13.3	EIS under Illumination (ECM2)
Klotz *et al.*[59]	3.98	126	...	...	...	14	EIS under Illumination (ECM1)
	$\tilde{C}_{bulk}$ ~ 3.86		...	125	...	14	EIS under Illumination (ECM2)

Experimental data fall in a broad range

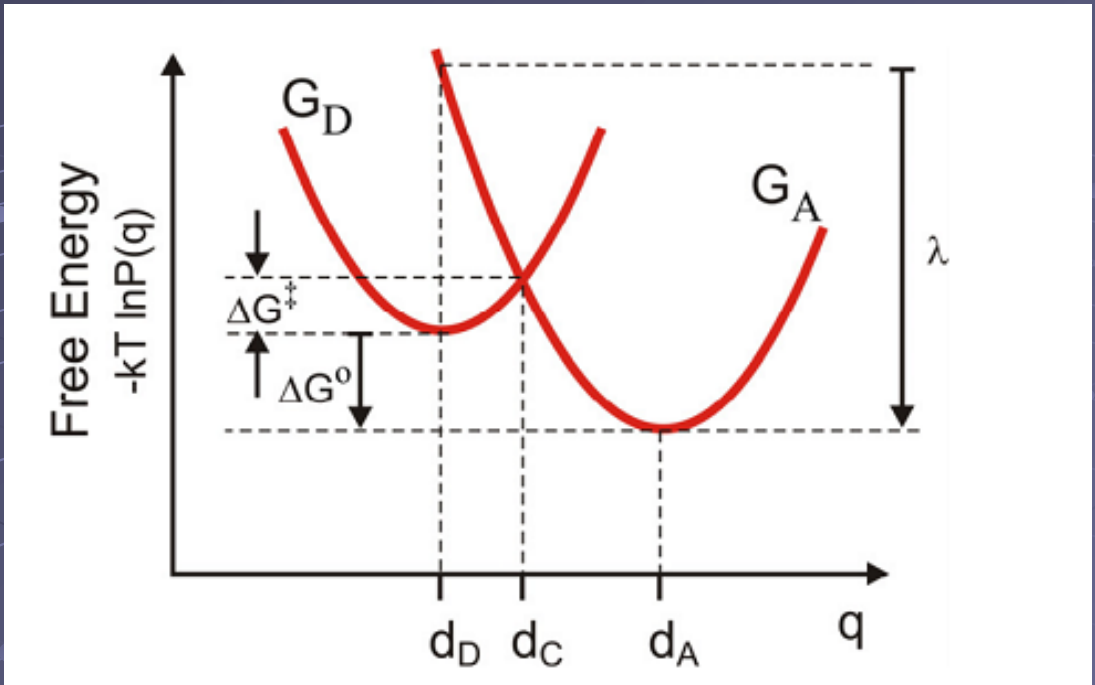
Ulman, Poli, Seriani, Piccinin, Gebauer, J. Chem. Phys. 150, 041707 (2019)

Charge transfer kinetics at the interface

Transient absorption spectroscopy and intensity-modulated photocurrent spectroscopy indicate a very slow hole transfer at the interface, in the millisecond-to-second regime

Getting an insight into this process could be important

Marcus theory of electron transfer



ΔG^0: reaction free energy
ΔG^+: reaction barrier
λ: reorganization energy

$$k_{\mathrm{ET}} = \frac{2\pi}{\hbar} \frac{\langle |H_{ab}|^2 \rangle_T}{\sqrt{4\pi k_{\mathrm{B}} T \lambda}} \exp\left[-\frac{(\lambda + \Delta A)^2}{4 k_{\mathrm{B}} T \lambda} \right]$$

Marcus rates from constrained density functional theory

$$k_{\mathrm{ET}} = \frac{2\pi}{\hbar} \frac{\langle |H_{ab}|^2 \rangle_T}{\sqrt{4\pi k_{\mathrm{B}} T \lambda}} \exp\left[-\frac{(\lambda + \Delta A)^2}{4 k_{\mathrm{B}} T \lambda} \right]$$

ΔA: reaction free energy
λ: reorganization energy
H_{ab}: matrix element, electronic coupling

Constrained DFT allows to perform molecular dynamics while keeping the charge either in the initial or in the final state (CP2K code)

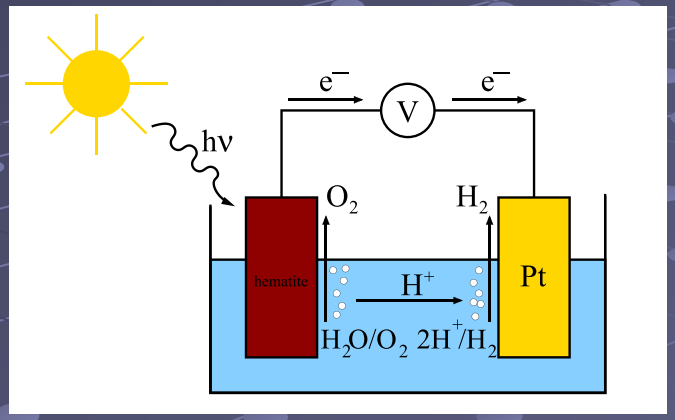
Marcus theory of electron transfer: preliminary results

With one hole at the surface: $k_{et} \approx 3*10^{-7}\ s^{-1}$

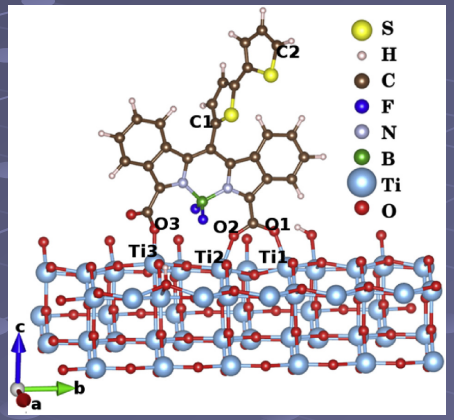
With two holes at the surface: $k_{et} \approx 2*10^{3}\ s^{-1}$

Experiments: timescale in the ms-to-s range

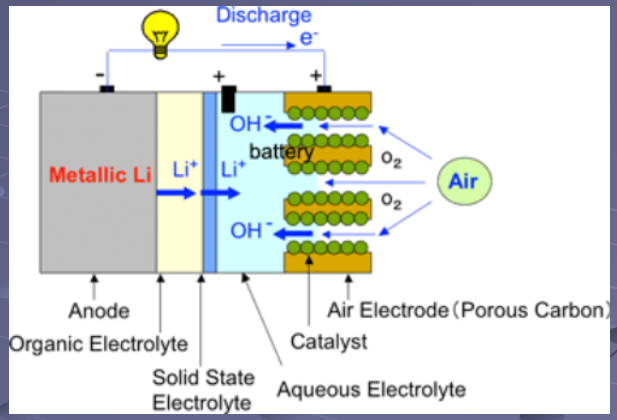
The road travelled...



Photocatalysis for solar fuels



Photovoltaics



Batteries

In some cases we are able to understand some effects of the environment on properties and functionality:

-) simplified models of environment

-) only some properties: photoabsorption, thermodynamics of reactions

Open scientific issues

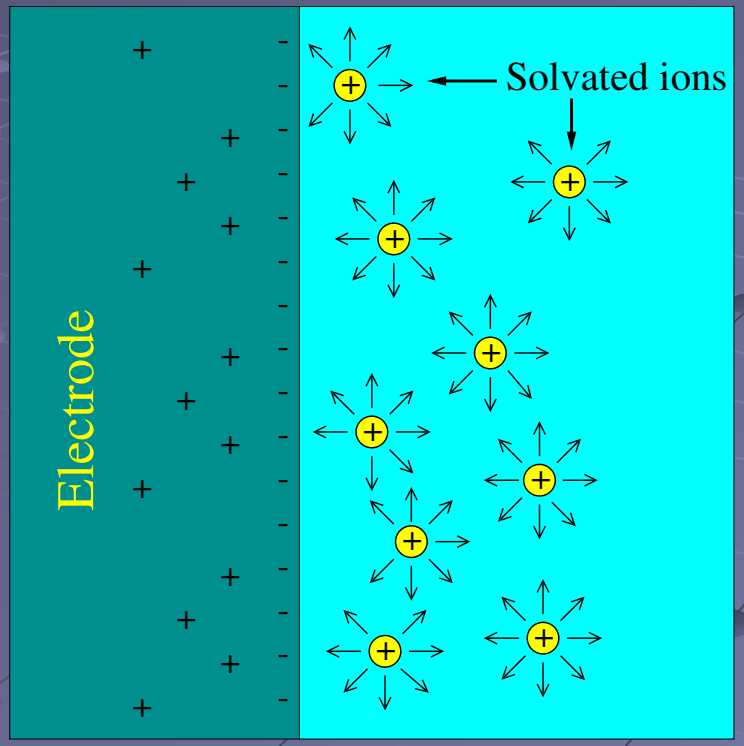
Which species are involved in the rate-limiting charge transfer?

How does their atomic configuration and dynamics depend on the structure of the interface?

Is it possible to engineer the interface to circumvent or change the nature of the rate-limiting step?

Interaction with experimentalists will be crucial

Use of advanced computational methods will be essential



Conclusions

- Titania and hematite is an interesting photocatalyst for water oxidation
- DFT simulations can provide insight into important processes: photoabsorption, chemical reactions, charge transfer
- Black hydrogenated titania
- Processes at the hematite/water interface

Acknowledgements

- M.-T. Nguyen (PNNL)
- K. Ulman (NUS)
- N. Ansari, E. Poli, N. Kumar, R. Gebauer (ICTP)
- S. Piccinin, M. Farnesi Camellone (CNR-IOM)
- S. S. Ataei, M. R. Mohammadizadeh (University of Tehran)

Financial support: ICTP

Computational resources: ICTP and CINECA

Density functional theory

- Method to reduce the many-electron Schrödinger equation to equations for one-electron wavefunctions (Kohn-Sham equations)

Schrödinger equation

$$[-\sum_i^N \frac{\hbar^2}{2m}\nabla_i^2 + \sum_i^N V(\vec{r}_i) + \sum_{i<j} U(\vec{r}_i, \vec{r}_j)]\Psi(\vec{r}_1, ..., \vec{r}_N) = E\Psi(\vec{r}_1, ..., \vec{r}_N)$$

$$[-\frac{\hbar^2}{2m}\nabla_i^2 + V(\vec{r}_i) + \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} + V_{xc}[n(\vec{r})]]\phi_i(\vec{r}) = \varepsilon_i\phi_i(\vec{r})$$

Kohn-Sham equation

Approximations necessary for V_{xc}

H in TiO_2: Density functional theory (DFT)

- Density functional theory: PBE + U
- Hubbard U(Ti3d) = 3.5 eV; U(O2p) = 3.5 eV
- Plane waves
- Norm-conserving pseudopotentials
- E_{cut} = 100 eV
- 6 x 6 x 2 k-points

- E_{gap} = 3.27 eV

GW + Bethe-Salpeter Equation

- GW + Bethe-Salpeter Equation
- G_0W_0
- Plasmon pole approximation
- E_{cut} = 7 Ry for the correlation part of self-energy
- 6000 plane waves for the exchange self-energy
- $\hbar\omega_p$ = 3.94 eV for the Drude term
- 4 occupied and 22 empty states for BSE

Hematite: calculation details

- PBE+U
- U = 4.2 eV for Fe 3d states
- Plane waves
- Ultrasoft pseudopotentials
- Energy cutoff 40 Ry
- Quantum-ESPRESSO

Nørskov's approach

***Finite V*:**

V=0 $\mu(H^+) + \mu(e^-) = 1/2\mu(H_2)$

$V \neq 0$ $\mu(e^-) \rightarrow \mu(e^-) - eV$

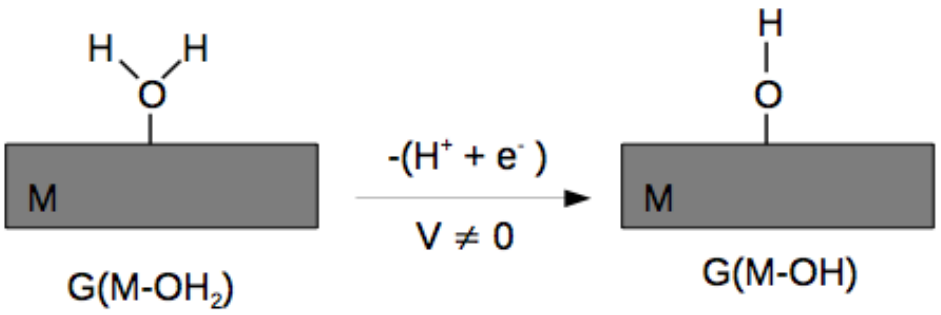
$\mu(H^+) + \mu(e^-) = 1/2\mu(H_2) - eV$

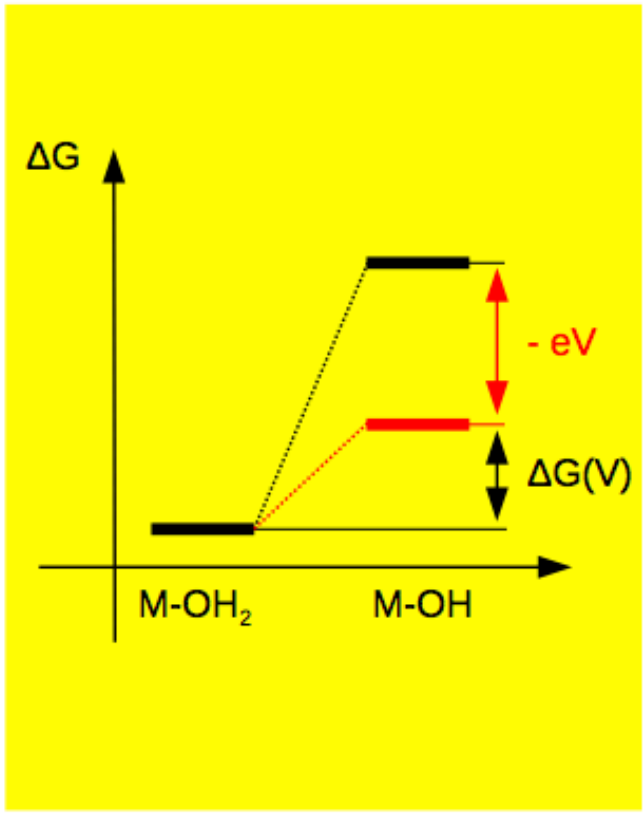
All other effects of the bias V are neglected in this approach

Nørskov's approach

Example: $V \neq 0$

$M\text{-}OH_2 \rightarrow M\text{-}OH + H^+ + e^-$





$\Delta G(V) = G(M\text{-}OH) + \mu(H^+) + \mu(e^-) - G(M\text{-}OH_2)$

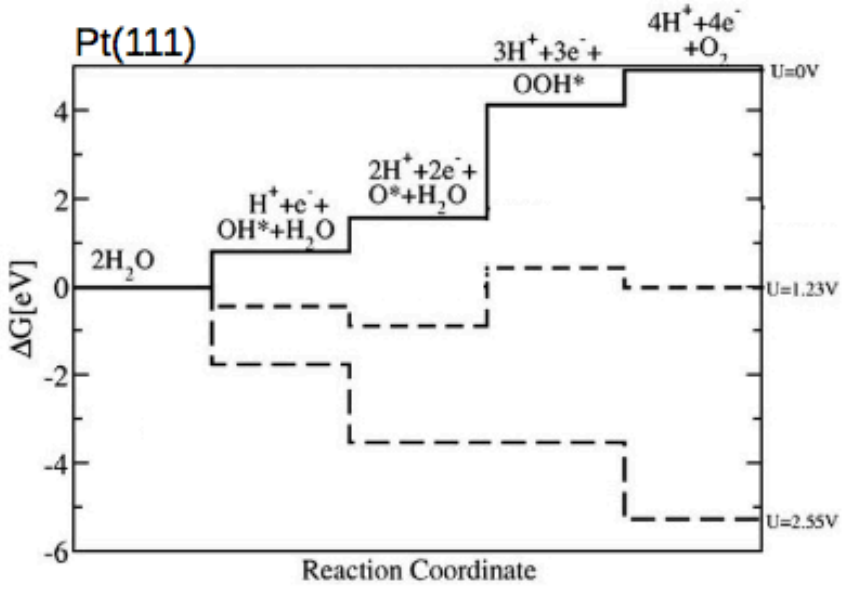
$= G(M\text{-}OH_2) + 1/2\mu(H_2) - eV - G(M\text{-}OH)$

$= \Delta G(V=0) - eV$

The relative energies of the intermediates depend linearly on the bias V

Nørskov's approach

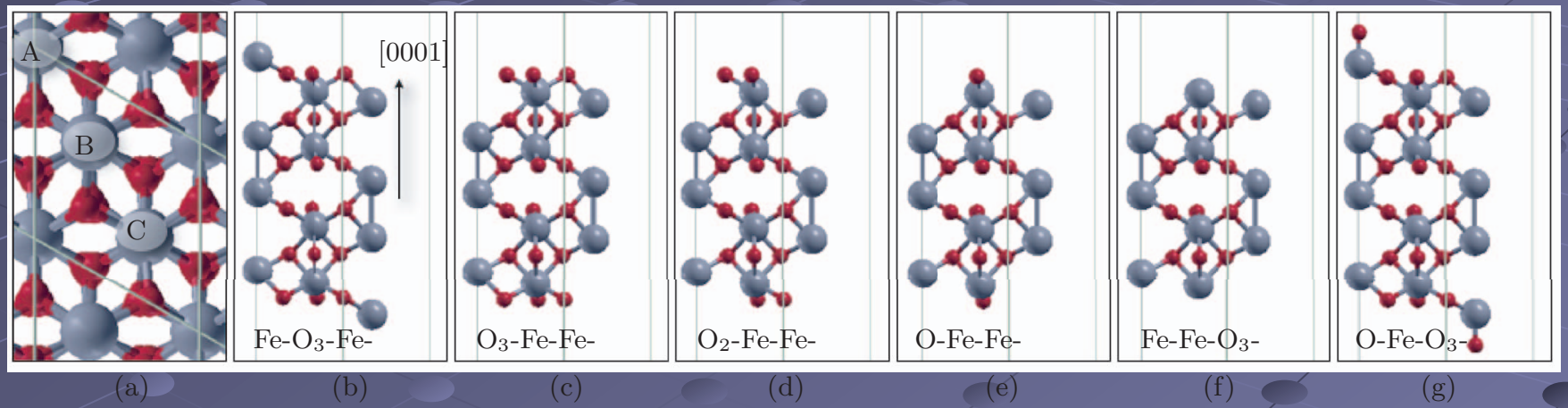
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $\quad \Delta G^0 = 4.92$ V



- U = 1.23 V is not sufficient to oxidize water on Pt(111): OOH* is too weakly bound compared to O*
- At U =2.55 V all steps are downhill in energy
- The overpotential of Pt(111) is 2.55-1.23 = 1.32 V

Rossmeisl *et al.* Phys. Chem **319**, 178-184 (2005)

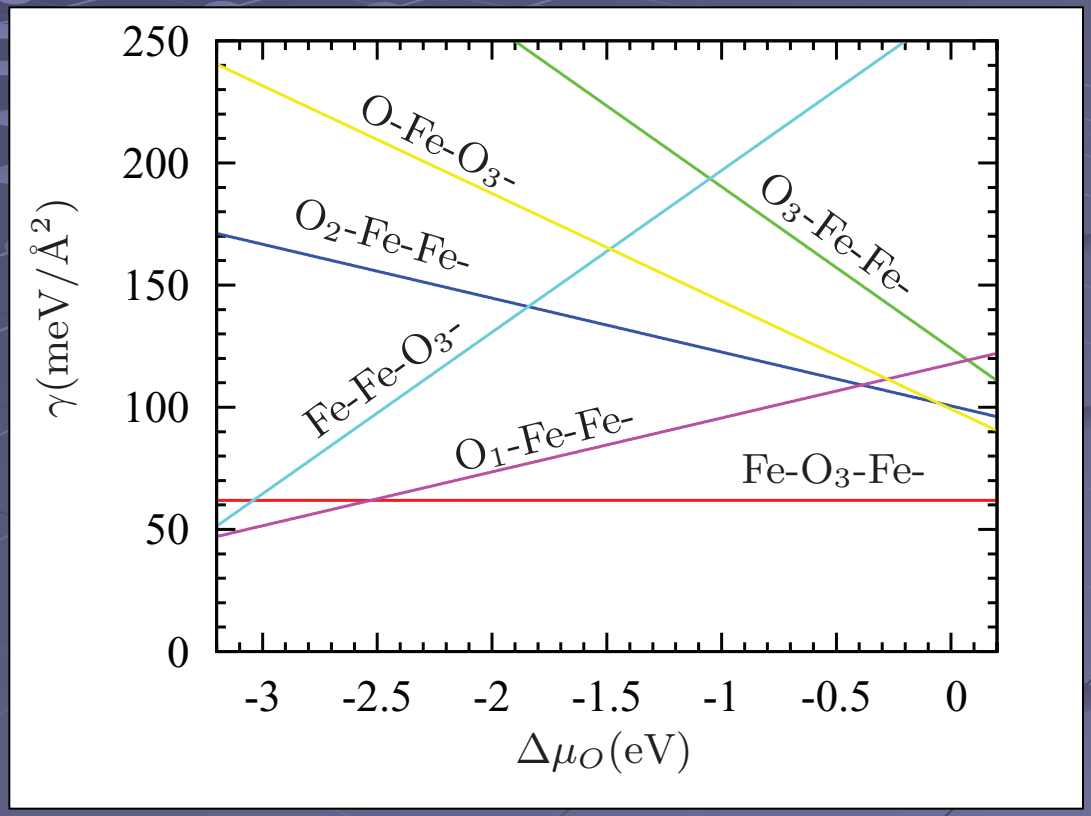
Thermodynamics of the surface process: 1. Surface termination of hematite α-Fe_2O_3 (0001)



Many surface terminations are possible

Nguyen, Seriani, Gebauer, J. Chem. Phys. 138, 194709 (2013)

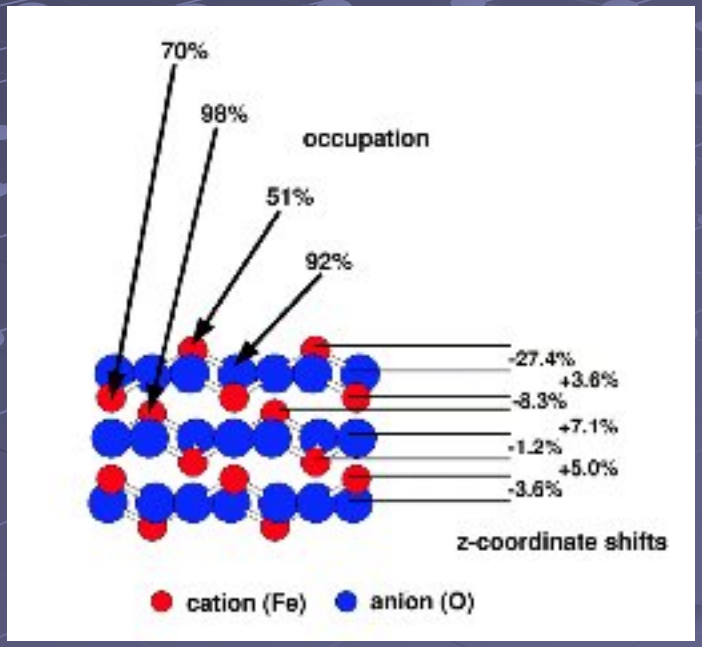
Terminations of hematite α-Fe_2O_3 (0001)



Surface free energies as function of the chemical potential of oxygen

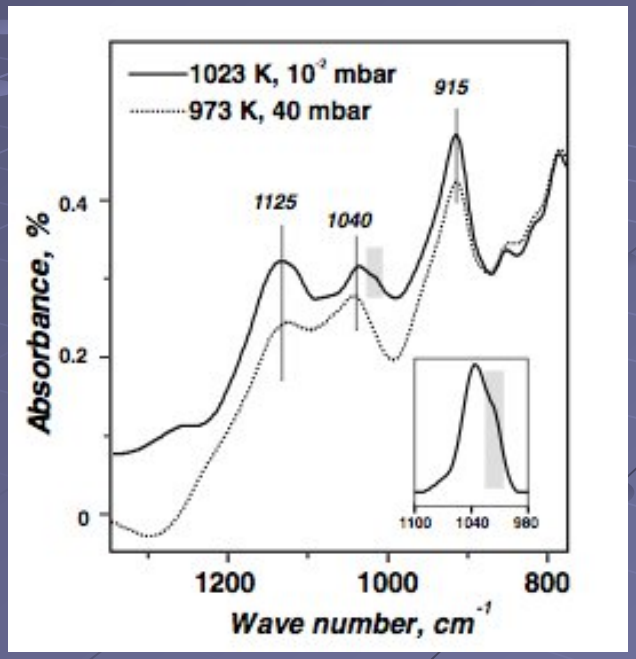
Nguyen, Seriani, Gebauer, J. Chem. Phys. 138, 194709 (2013)

$Fe\text{-}O_3\text{-}Fe\text{-}Fe$ termination



LEED after annealing in $3*10^{-8}$ mbar O_2 at 500° C

Lübbe and Moritz, J. Phys.: Condens. Matter 21, 134010 (2009)



Coexistence with the ferryl termination; 10^{-3} – 1 mbar O_2 at 1050 K

Lemire et al., Phys. Rev. Lett. 94, 166101 (2005)

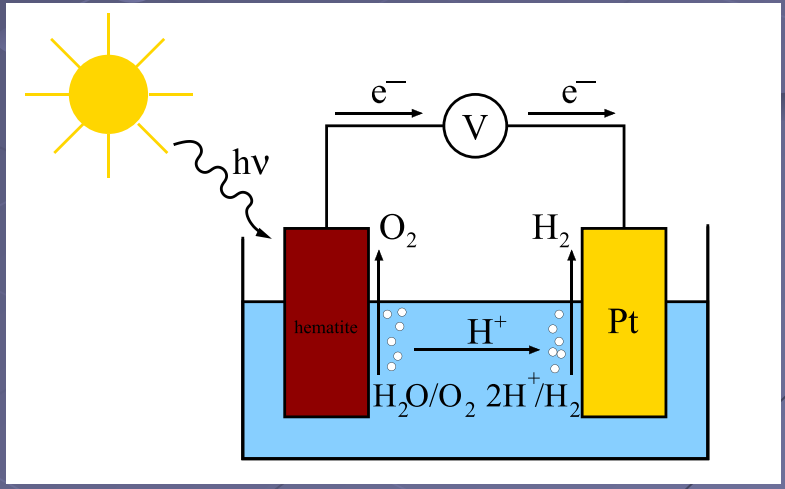
Water oxidation at the photoanode

Overall: $2H_2O \rightarrow O_{2,g} + 2H_{2,g}$

At the anode: $2H_2O \rightarrow O_{2,g} + 4H^+_{aq} + 4e^-$

At the cathode: $4H^+_{aq} + 4e^- \rightarrow 2H_{2,g}$

Acidic conditions...



N. Seriani, J. Phys.: Condens. Mat. 29, 463002 (2017)