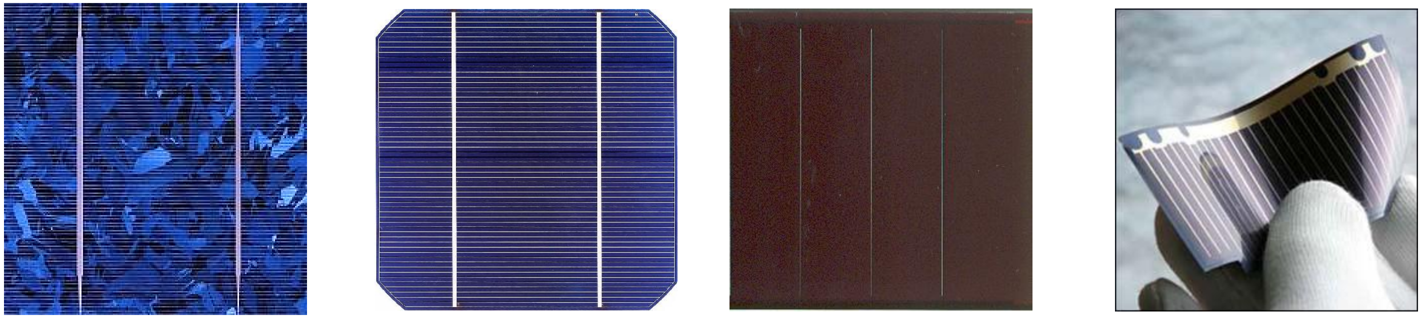
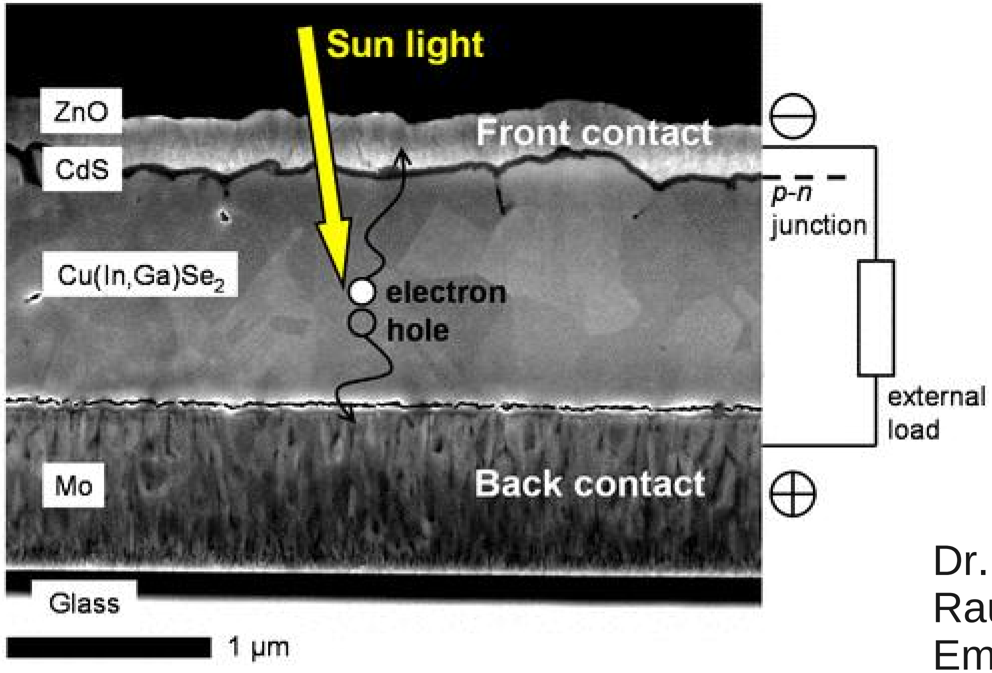
Dye Sensitized Solar Cells (27027-01)

(Dienstag, 8:00-10:00 Departement Physik, Seminarzimmer 3.12)





Dr. Thilo Glatzel
Raum 3.04
Email: thilo.glatzel@unibas.ch

Übersicht der Vorlesung

22.02.2011	allg. Einführung in die Solarenergie
01.03.2011	Physikalische Grundlagen der Photovoltaik I
08.03.2011	Physikalische Grundlagen der Photovoltaik II
15.03.2011	(Fastnachtsferien)
22.03.2011	Photochemische und photoelektrische Methoden der Energiewandlung
29.03.2011	Aufbau der Farbstoffsolarzelle, vgl. org. Solarzelle
→ **05.04.2011**	TiO_2 Nanopartikel als Substrat der Frabstoffsolarzelle
12.04.2011	Geeignete molekulare Farbstoffe zur Sensibilisierung
19.04.2011	Funktionsweise und Alternativen für den Elektrolyten
26.04.2011	(Osterferien)
03.05.2011	(FANAS meeting)
10.05.2011	Experimentelle Methoden zur Solarzellen-Charakterisierung
17.05.2011	Experimentelle Methoden zur Solarzellen-Charakterisierung
24.05.2011	Bau und Charakterisierung eigener Solarzellen
31.05.2011	

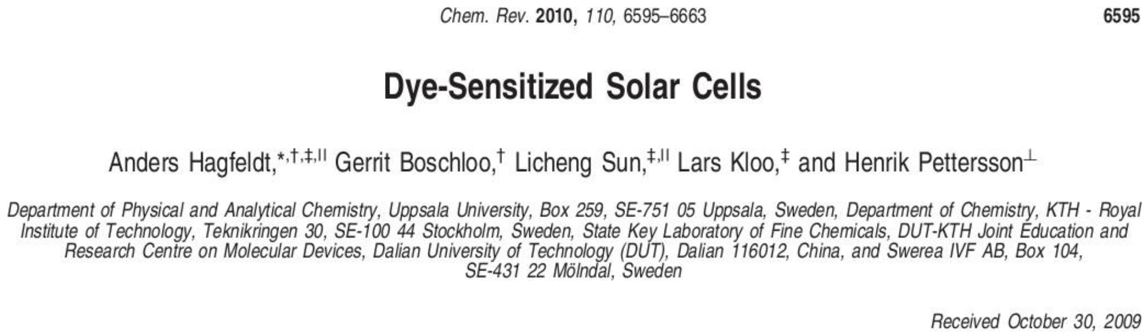
TiO_2 Nanopartikel als Substrat der Frabstoffsolarzelle

- Nanoporous structure of the DSSC
- Sensitization by dye molecules
- Absorption of dye molecules on rutile TiO_2
- Principle of operation

- Organic solar cells
- Setup of a device
- Working principle
- Structural properties / KPFM measurements

Seminars

David Just



Chem. Rev. **2010,** *110,* 6595–6663 **6595**

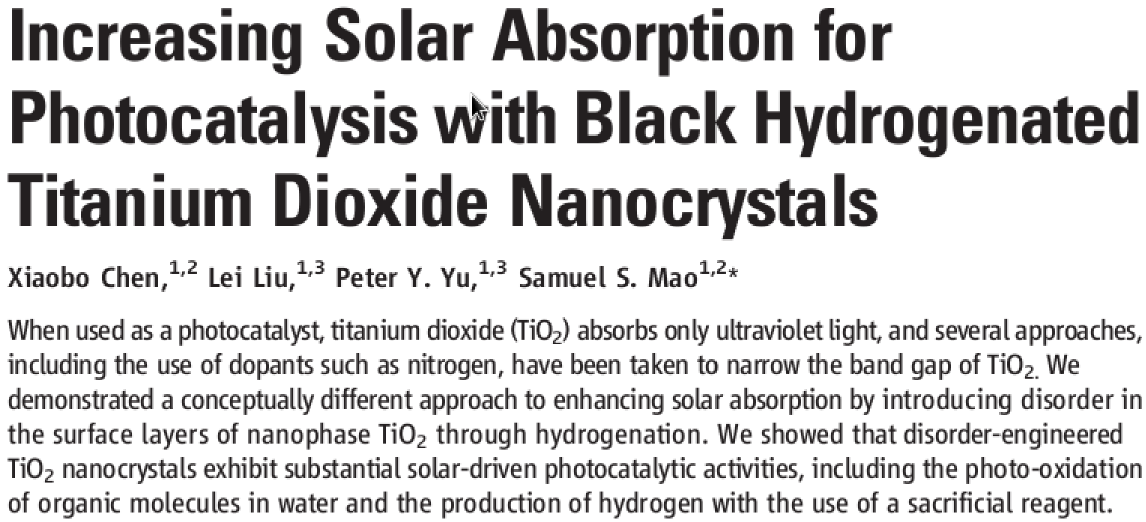
Dye-Sensitized Solar Cells

Anders Hagfeldt,[*,†,‡,∥] Gerrit Boschloo,[†] Licheng Sun,[‡,∥] Lars Kloo,[‡] and Henrik Pettersson[⊥]

Department of Physical and Analytical Chemistry, Uppsala University, Box 259, SE-751 05 Uppsala, Sweden, Department of Chemistry, KTH - Royal Institute of Technology, Teknikringen 30, SE-100 44 Stockholm, Sweden, State Key Laboratory of Fine Chemicals, DUT-KTH Joint Education and Research Centre on Molecular Devices, Dalian University of Technology (DUT), Dalian 116012, China, and Swerea IVF AB, Box 104, SE-431 22 Mölndal, Sweden

Received October 30, 2009

Simon Zihlmann

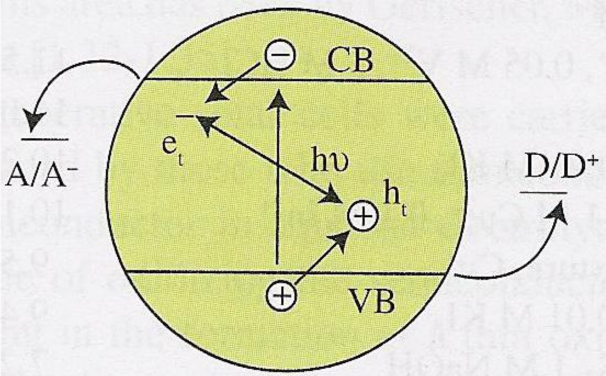


Increasing Solar Absorption for Photocatalysis with Black Hydrogenated Titanium Dioxide Nanocrystals

Xiaobo Chen,[1,2] Lei Liu,[1,3] Peter Y. Yu,[1,3] Samuel S. Mao[1,2*]

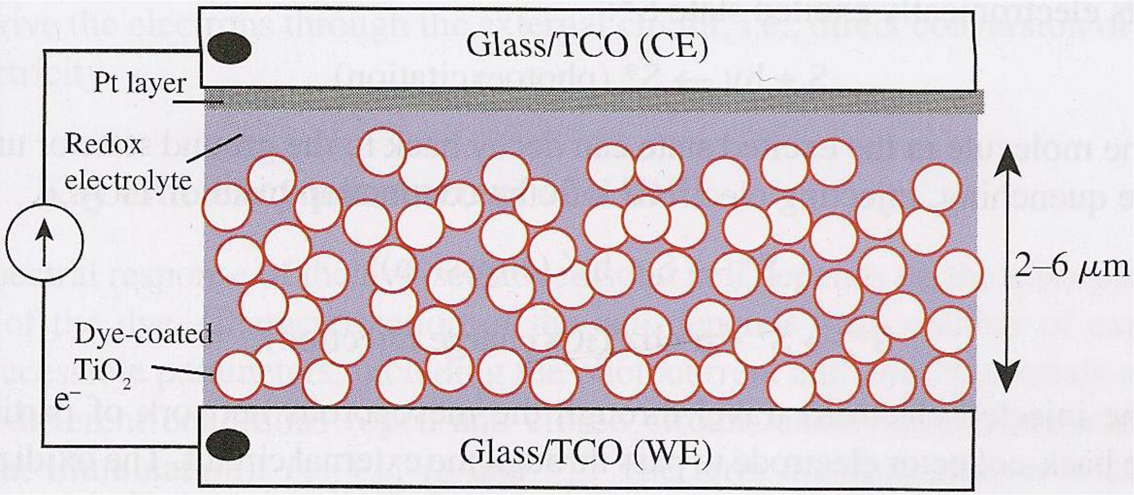
When used as a photocatalyst, titanium dioxide (TiO_2) absorbs only ultraviolet light, and several approaches, including the use of dopants such as nitrogen, have been taken to narrow the band gap of TiO_2. We demonstrated a conceptually different approach to enhancing solar absorption by introducing disorder in the surface layers of nanophase TiO_2 through hydrogenation. We showed that disorder-engineered TiO_2 nanocrystals exhibit substantial solar-driven photocatalytic activities, including the photo-oxidation of organic molecules in water and the production of hydrogen with the use of a sacrificial reagent.

Photoredox reactions of colloidal semiconductors and particulates



Both forms of photo-generated charge carriers reach the surface
Low cost efficient system for degrading toxic waste

Schematic Representation of a DSSC



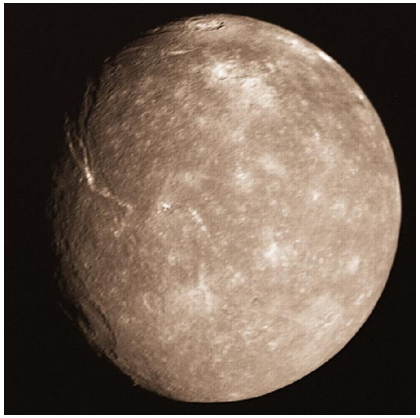
Metal oxide semiconductors nanoparticles:
ZnO, TiO_2, SnO_2, In_2O_3, $SrTiO_3$

Sensitized with: ruthenium polypyridyl complexes, or organic dyes Rhodamine B, rose bengal (xanthenes), fluorescein, and alkalythiacarbocyanines

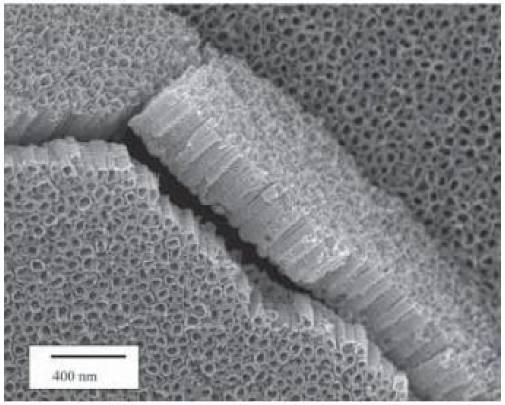
Titania as a substrate for DSSCs

- Titania is the name of a character in William Shakespeare's play
  “A Midsummer Night's Dream”.
  In Shakespeare's play, she is the queen of the fairies.

Picture (wiki): Prince Arthur and the Fairy Queen by Johann Heinrich Füssli, c. 1788.



Titania is the largest moon of Uranus



Titatnia as titanium dioxide TiO_2 for catalysis, additive, food coloring E171

Polymorphs of Titania

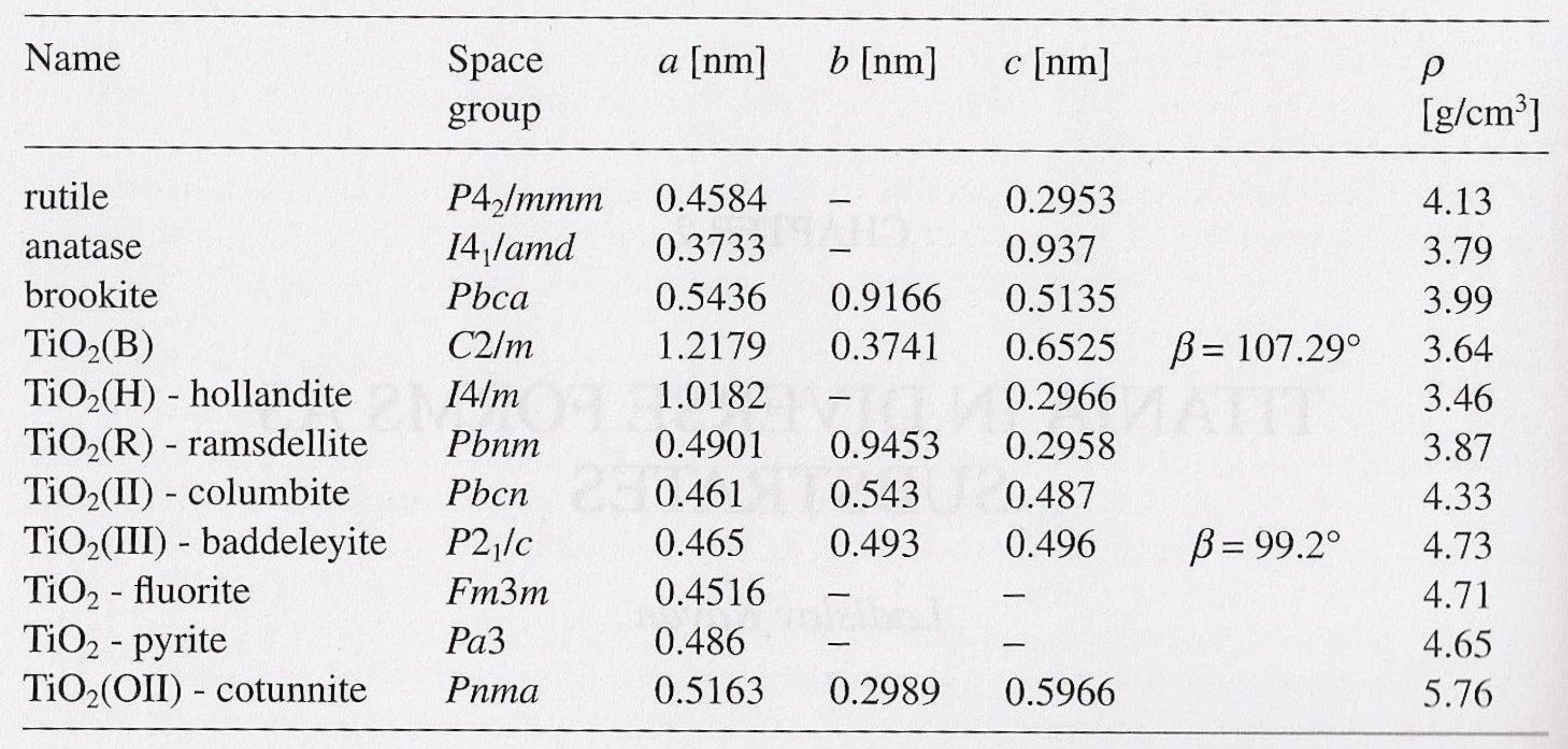
natural

- Tetragonal **rutile**, most stable macroscopic compound
- **Anatase**, most stable for nanocrystals
- Orthorhombic **brookite**
- Monoclinic **TiO_2(B),** found in CH (Binntal, Valais)
- Orthorhombic TiO_2(II) (columbite)
- Monoclinic TiO_2(III) (baddeleyite)

High-presure phases

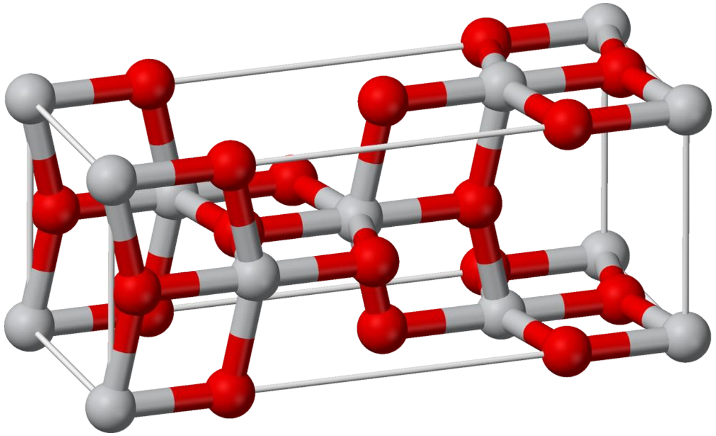
Conversion from anatase to rutile between 700 and 1000°C
Bandgap in the range of 3.0-3.4eV (390-415nm)

Crystalline forms of Titania



Name	Space group	*a* [nm]	*b* [nm]	*c* [nm]		ρ [g/cm^3]
rutile	$P4_2/mmm$	0.4584	–	0.2953		4.13
anatase	$I4_1/amd$	0.3733	–	0.937		3.79
brookite	$Pbca$	0.5436	0.9166	0.5135		3.99
TiO_2(B)	$C2/m$	1.2179	0.3741	0.6525	$\beta = 107.29°$	3.64
TiO_2(H) - hollandite	$I4/m$	1.0182	–	0.2966		3.46
TiO_2(R) - ramsdellite	$Pbnm$	0.4901	0.9453	0.2958		3.87
TiO_2(II) - columbite	$Pbcn$	0.461	0.543	0.487		4.33
TiO_2(III) - baddeleyite	$P2_1/c$	0.465	0.493	0.496	$\beta = 99.2°$	4.73
TiO_2 - fluorite	$Fm3m$	0.4516	–	–		4.71
TiO_2 - pyrite	$Pa3$	0.486	–	–		4.65
TiO_2(OII) - cotunnite	$Pnma$	0.5163	0.2989	0.5966		5.76

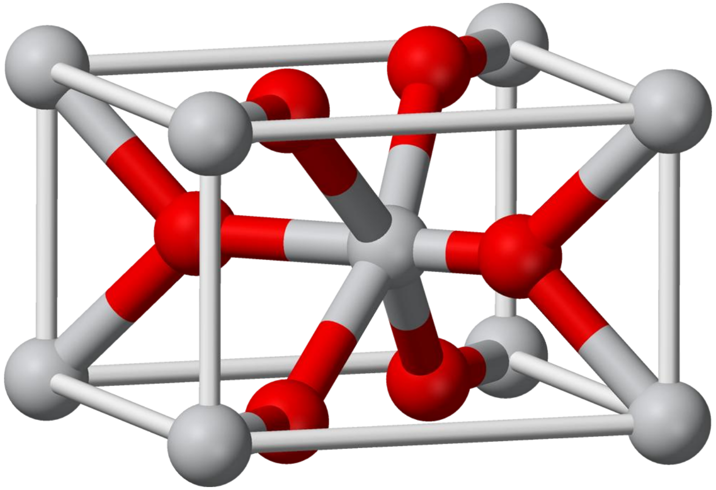
Anatase



● Ti^{4+}
● O 6-fold coordination

E_g=3.2eV, indirect bad gap semiconductor
Homo: O 2p orbitals, LUMO: Ti 3d orbitals
Slightly oxygen-deficient, TiO_{2-x}(x~0.01) -> n-type doping

Rutile



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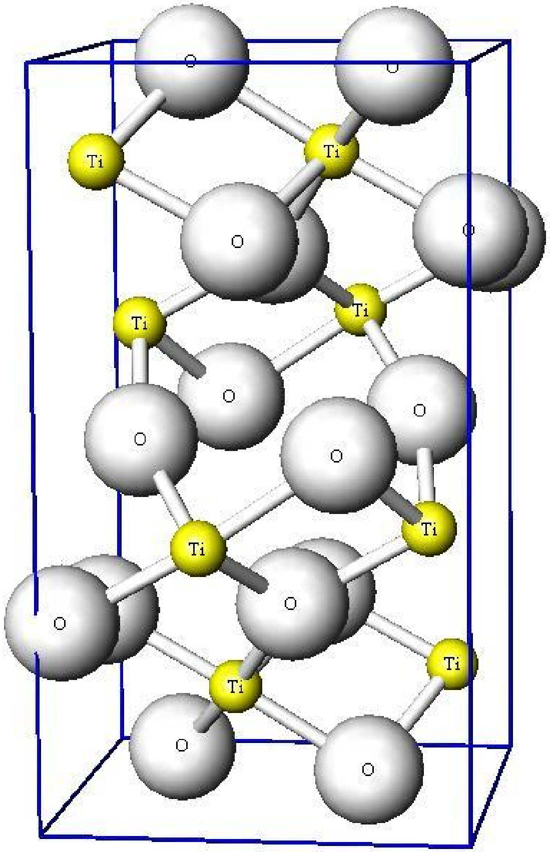
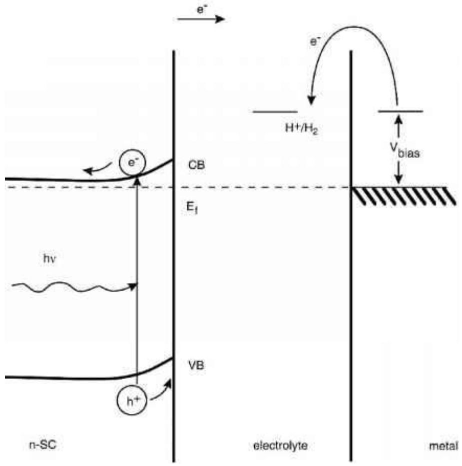
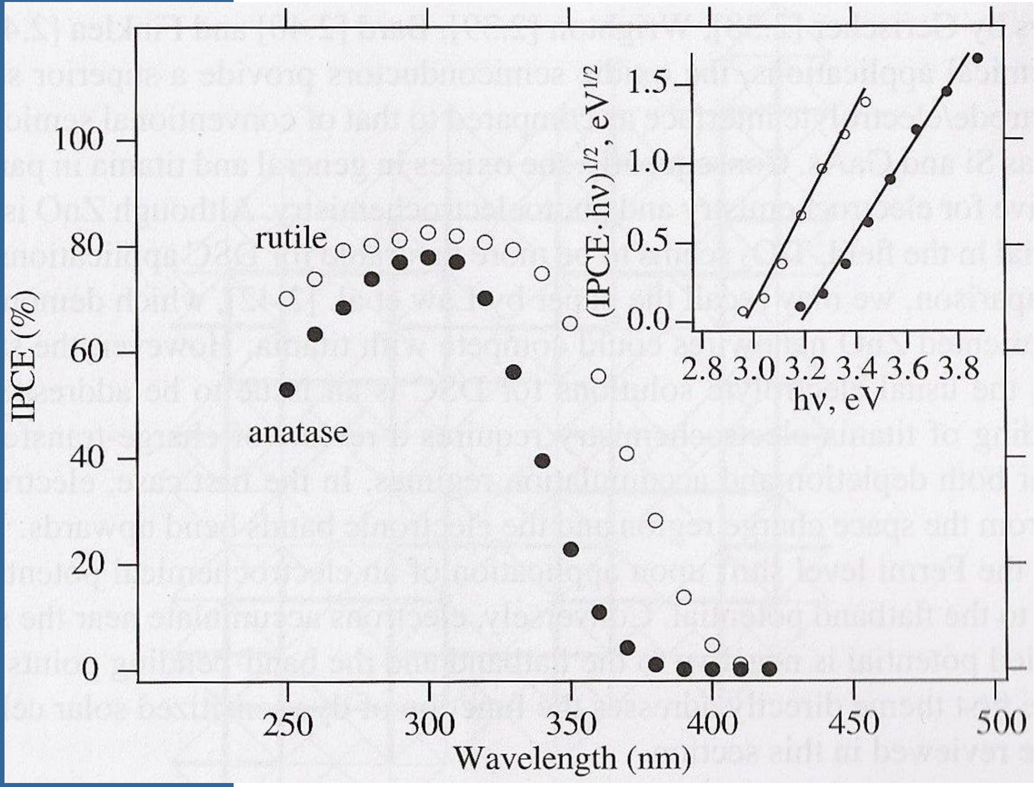
Brookite



E_g=3.1-3.4eV, direct/indirect?

Electrochemistry of Titania Depletion Regime





Incident Photon to Current Conversion Efficiency

$$IPCE = \frac{i_{ph} h\nu}{Pe}$$

i_{ph}: photocurrent density
h: Planck's constant
ν: photon frequency
P: incident light power
e: electron charge

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Electrochemistry of Titania
Depletion Regime

i_{ph} is the limiting factor for the IPCE for positive potentials (large band bending)

In other cases E dependence of i_{ph} has to be considered:

$$i_{ph}^2 = \frac{2e\epsilon_0\epsilon_r P^2\alpha_0^2}{N_D}(E - E_{fb})$$

α_0: optical absorption coefficient
ε_0: permittivity of vacuum
ε_r: dielectric constant
N_D: density of donors
E_{fb}: flatband potential

Electrochemistry of Titania Depletion Regime

Neglecting recombination in the space charge region and that the width of the SCR is much smaller that the penetration depth of the light:

$$IPCE = \frac{A_0 e(L_h + W)(h\nu - E_g)^2}{h\nu}$$

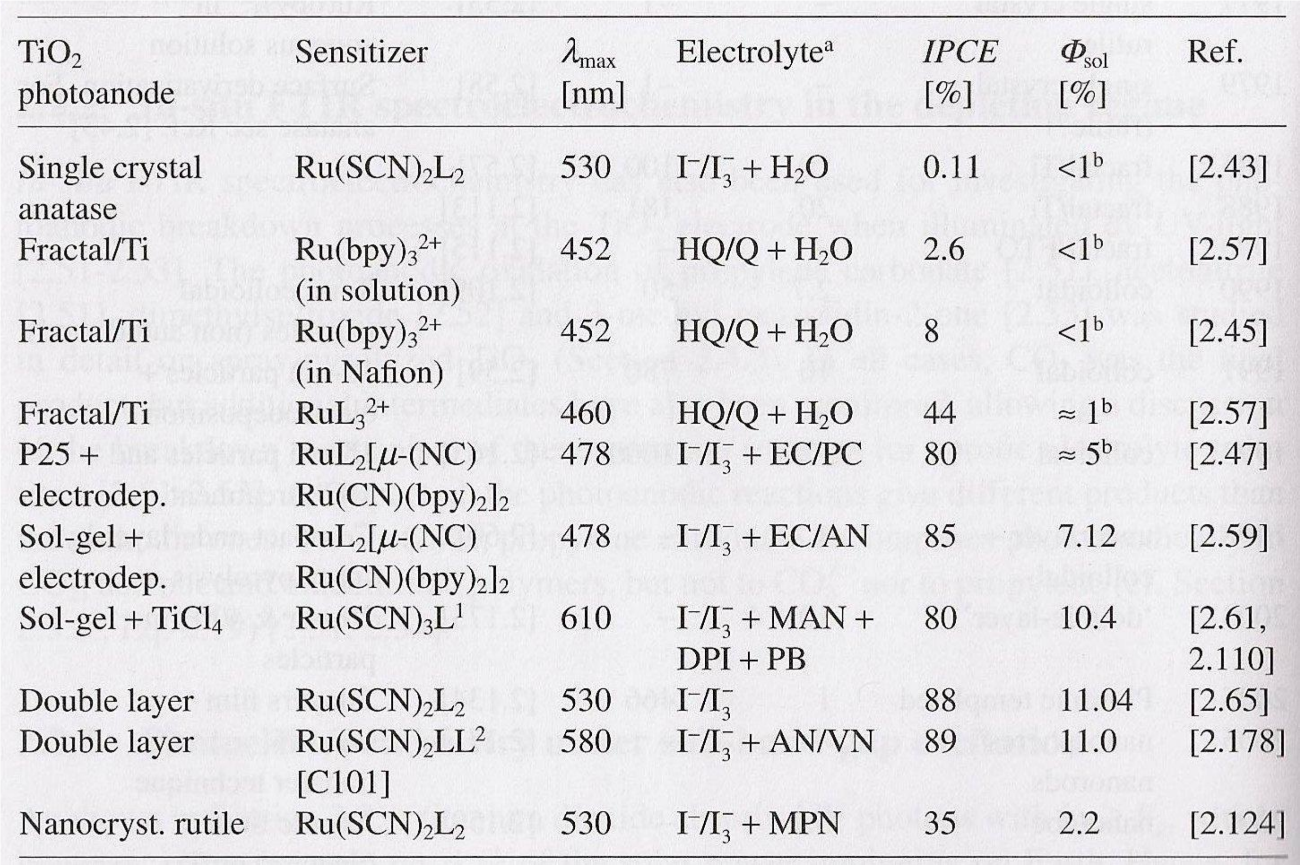
A_0: absorption constant
L_h: hole diffusion length
E_g: bandgap energy

Comparison of flat and nanoporous TiO_2

$IPCE_{max,flat}$= 0.27% (0.11% achieved)
$IPCE_{max, d=100nm}$= 69% (d=100nm)
$IPCE_{max, d=10nm}$= 99% (d=10nm)

the energy range of hν > E_g corresponds to only 4% of solar power
>> sensitization of TiO_2 (1977)

Examples of liquid junction solar cells with a TiO_2 photoanode



TiO_2 photoanode	Sensitizer	λ_{max} [nm]	Electrolyte[a]	*IPCE* [%]	Φ_{sol} [%]	Ref.
Single crystal anatase	$Ru(SCN)_2L_2$	530	$I^-/I_3^- + H_2O$	0.11	$<1^b$	[2.43]
Fractal/Ti	$Ru(bpy)_3^{2+}$ (in solution)	452	$HQ/Q + H_2O$	2.6	$<1^b$	[2.57]
Fractal/Ti	$Ru(bpy)_3^{2+}$ (in Nafion)	452	$HQ/Q + H_2O$	8	$<1^b$	[2.45]
Fractal/Ti	RuL_3^{2+}	460	$HQ/Q + H_2O$	44	$\approx 1^b$	[2.57]
P25 + electrodep.	$RuL_2[\mu\text{-}(NC)Ru(CN)(bpy)_2]_2$	478	$I^-/I_3^- + EC/PC$	80	$\approx 5^b$	[2.47]
Sol-gel + electrodep.	$RuL_2[\mu\text{-}(NC)Ru(CN)(bpy)_2]_2$	478	$I^-/I_3^- + EC/AN$	85	7.12	[2.59]
Sol-gel + $TiCl_4$	$Ru(SCN)_3L^1$	610	$I^-/I_3^- + MAN + DPI + PB$	80	10.4	[2.61, 2.110]
Double layer	$Ru(SCN)_2L_2$	530	I^-/I_3^-	88	11.04	[2.65]
Double layer	$Ru(SCN)_2LL^2$ [C101]	580	$I^-/I_3^- + AN/VN$	89	11.0	[2.178]
Nanocryst. rutile	$Ru(SCN)_2L_2$	530	$I^-/I_3^- + MPN$	35	2.2	[2.124]

Electrochemistry of Titania Accumulation Regime

Electrochemical investigation of accumulation of electrons in the space-charge layer

1. oxidation of $Ti(OH)^{2+}$ leading to an electrodeposition of TiO_2
2. water reduction, applicable to estimate the flatband potential E_{fb}
3. electrochemical n-doping
4. cathodic decomposition of propylene carbonate
5. Li- insertion

Battery materials for ultrafast charging and discharging

Byoungwoo Kang & Gerbrand Ceder

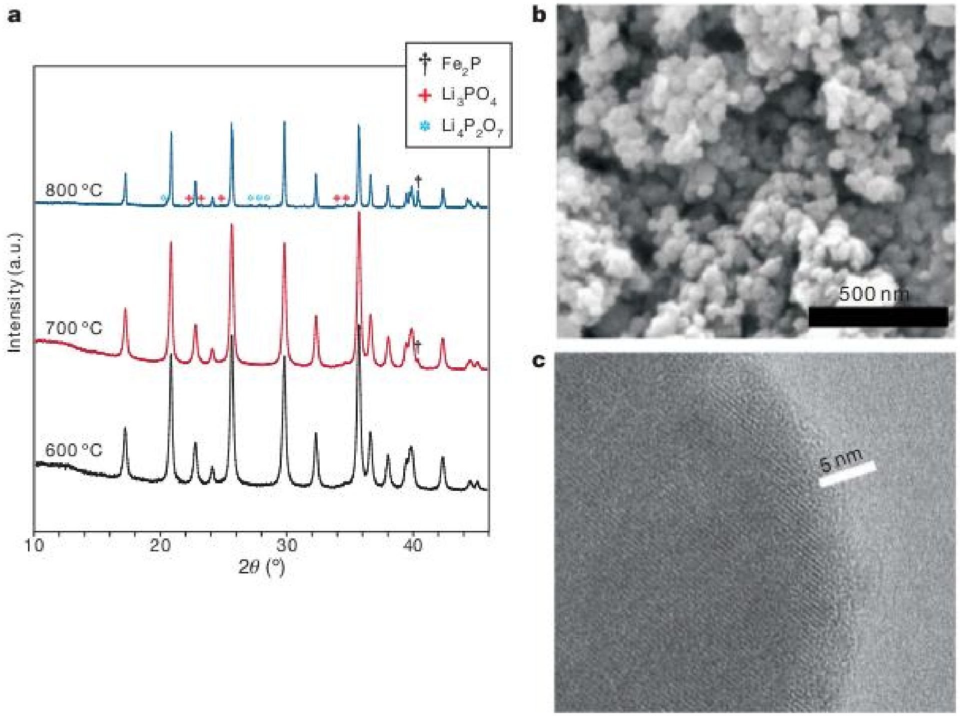


Figure 1 | Characterization of $LiFeP_{0.9}P_{0.95}O_{4-\delta}$ synthesized under argon. **a**, Powder X-ray diffraction patterns (using Cu Kα radiation) for samples synthesized at different temperatures. Fe_2P starts to appear at 700 °C and $Li_4P_2O_7$ starts to crystallize at 800 °C. The lattice parameters for the material synthesized at 600 °C are $a = 10.3134$ Å, $b = 6.002$ Å and $c = 4.691$ Å. θ, diffraction angle; a.u., arbitrary units. **b**, Scanning electron microscopy image showing a particle size of less than 50 nm. **c**, Transmission electron microscopy image of the material showing a poorly crystallized layer less than 5 nm thick on the edge of a particle.

$LiFePO_4$

Nature Letters, Vol 458 | 12 March 2009 | doi:10.1038/nature07853

Titania Photoanodes for DSSCs

Hydrolysis of titanium(IV)alkoxides

$Ti(OR)_4 + 2H_2O \text{ -> } TiO_2 + 4ROH$ (R: alkyl)

Electrochemical deposition of TiO_2

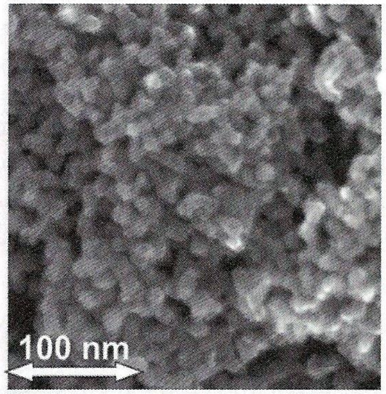
$Ti^{3+} (TiCl_3) + H_2O \text{ -> } TiOh^{2+} + H^+$

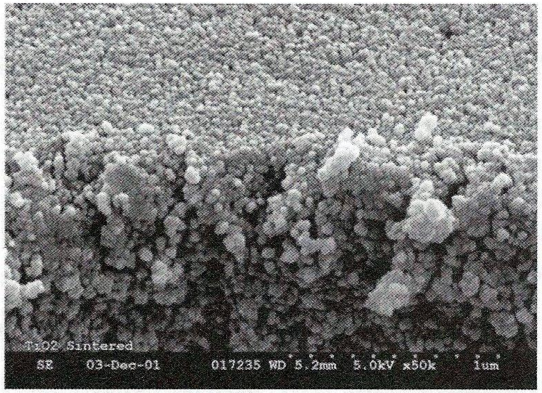
$TiOh^{2+} + H_2O – e^- \text{ -> } TiO_2 + 3H^2$

pH: 2-2.5

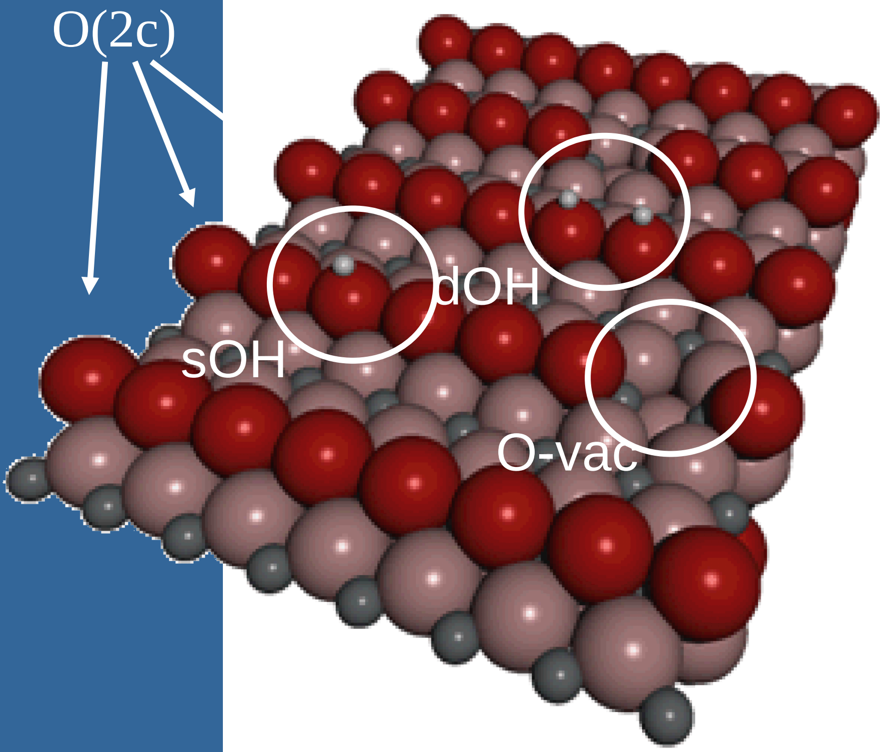
Aerosol pyrolysis

Sol-gel process

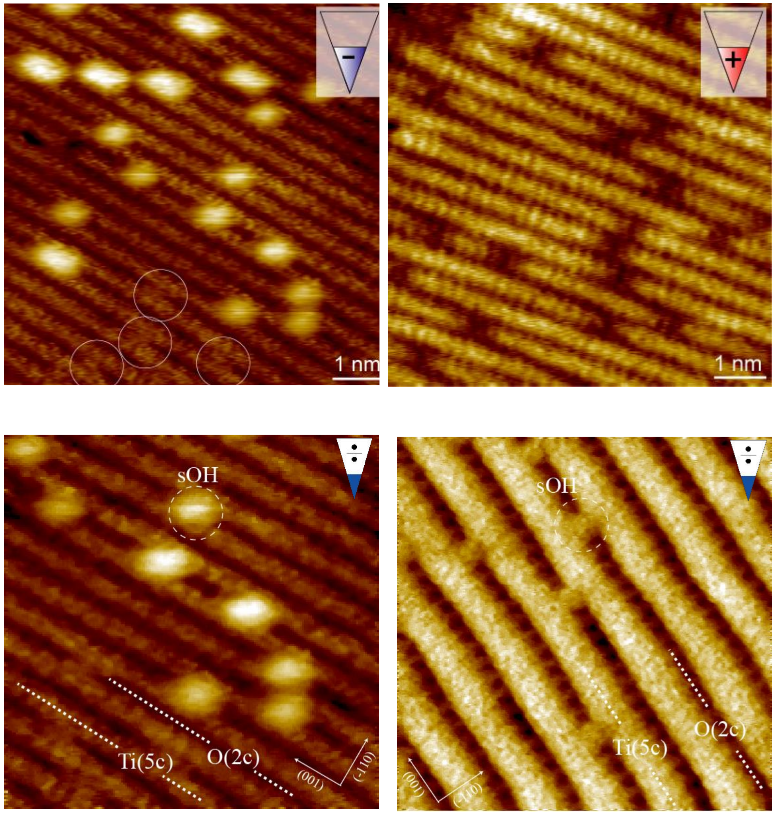




The rutile TiO_2(110)(1x1) surface



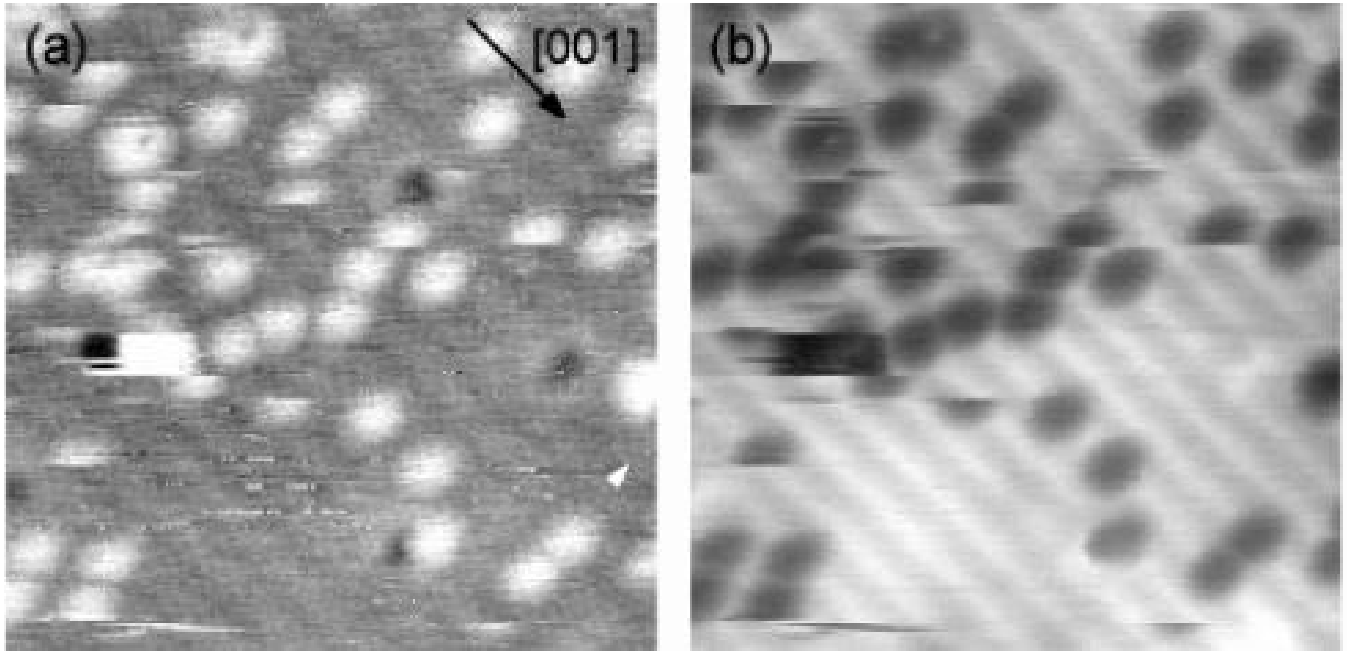
Contrast mechanisms in nc-AFM



J.V. Lauritsen, *et al.* Nanotechnology **17,** 3436 (2006)
G.H. Enevoldsen et al., Phys. Rev. B **76**, 205415 (2007)

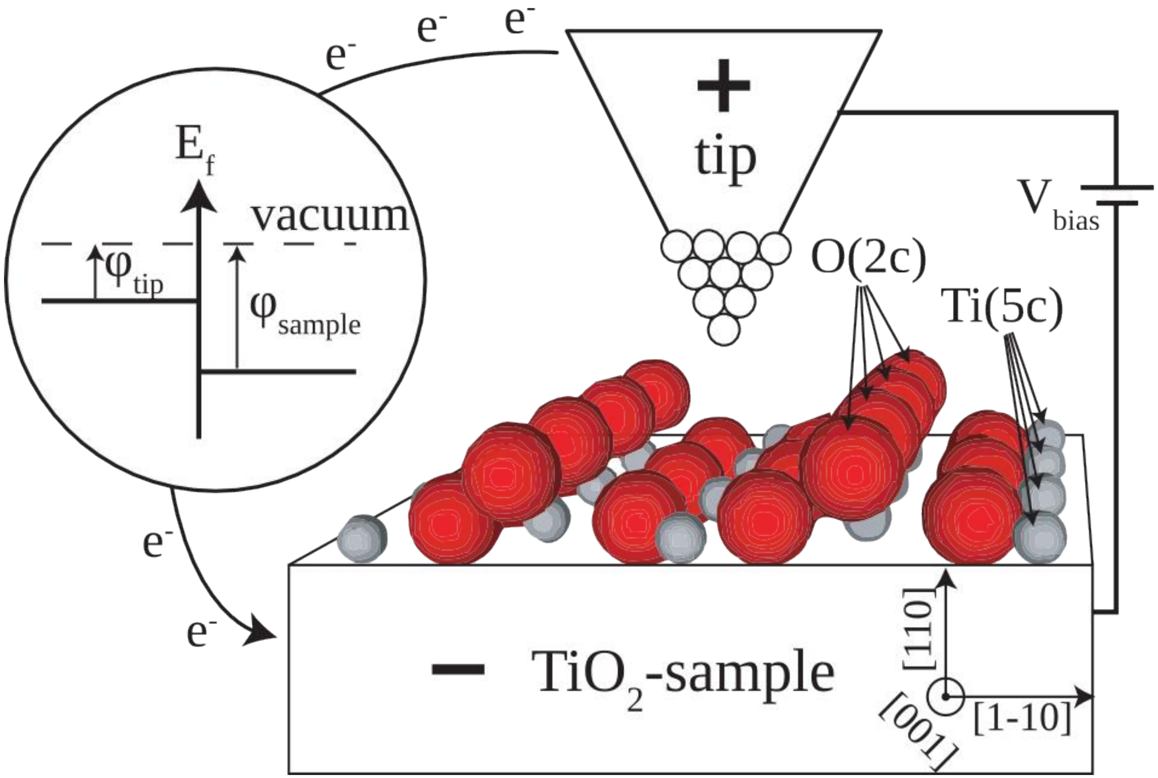
FM-KPFM at the TiO_2(110)(1x1) surface

Pt adsorption on the TiO2(110)(1x1) surface (A. Sasahara)



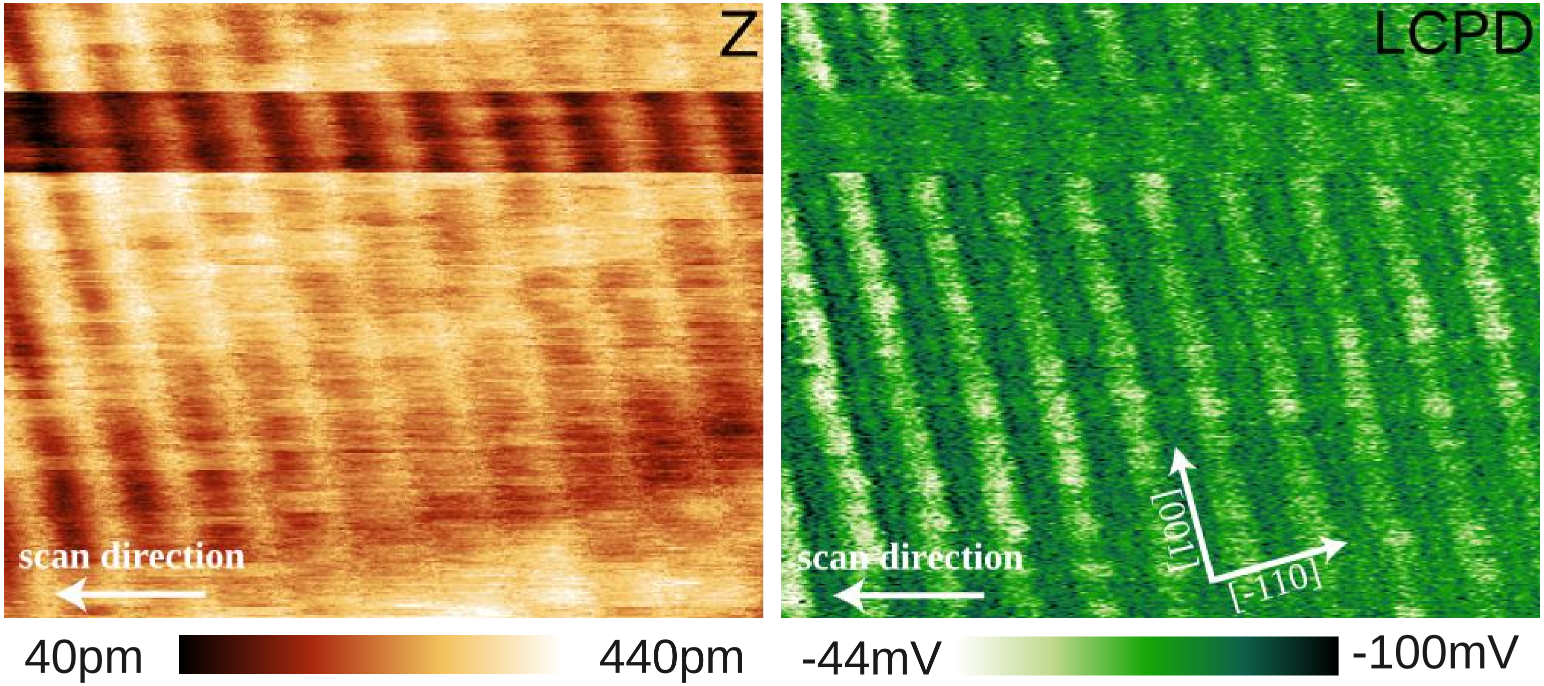
Pt adatoms	>	A. Sasahara, et al., J. Phys. Chem. B 110, 17584 (2006) K. Hiehata et al., Nanotechnology 18, 084007 (2007)
Na adatoms	>	A. Sasahara, et al., Jap. J. Appl. Phys., Vol. 43, 4647 (2004)
adsorbed dye	>	M. Ikeda, et al., J. Phys. Chem. C 112, 6961 (2008)

Schematic Model of AFM tip - TiO_2



G.H. Enevoldsen et al., PRL **100**, 236104 (2008)

AM-KPFM at the $TiO_2(110)(1x1)$ surface



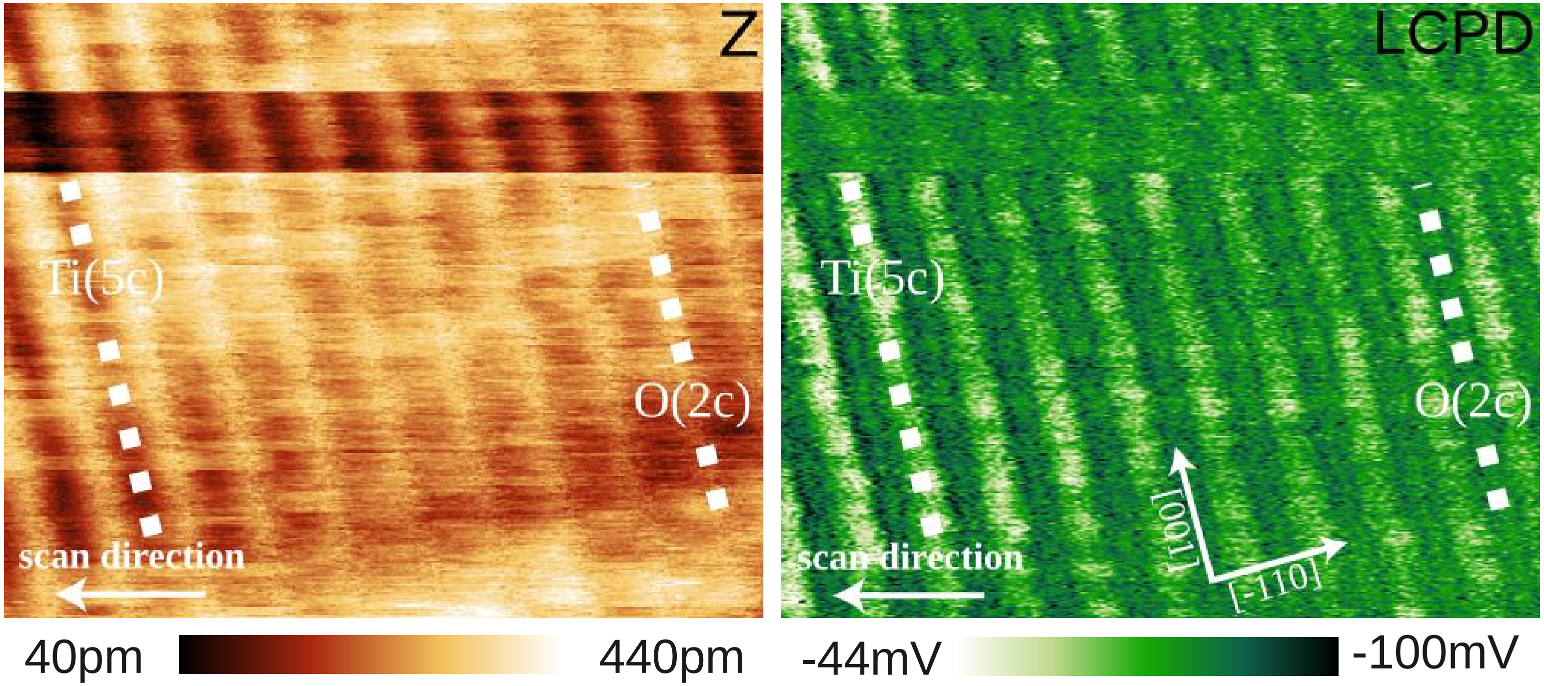
Size: 10x8 nm^2,

$A_{p\text{-}p} \approx 28$ nm, $\Delta f = 121.2$ Hz

$f_0 = 70$ kHz, $f_{mod} = 452$ kHz

$U_{AC} = 300$ mV

AM-KPFM at the $TiO_2(110)(1x1)$ surface



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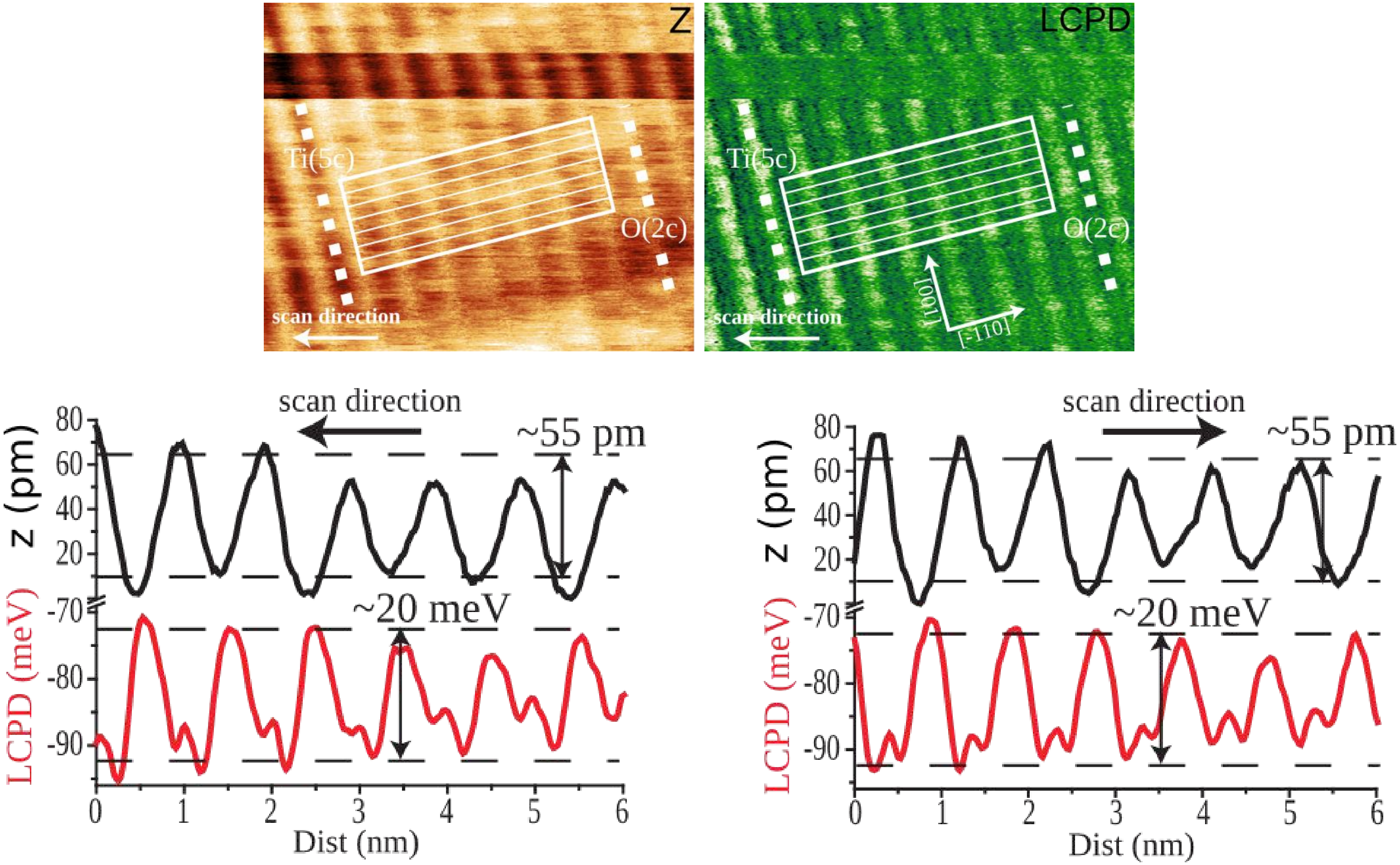
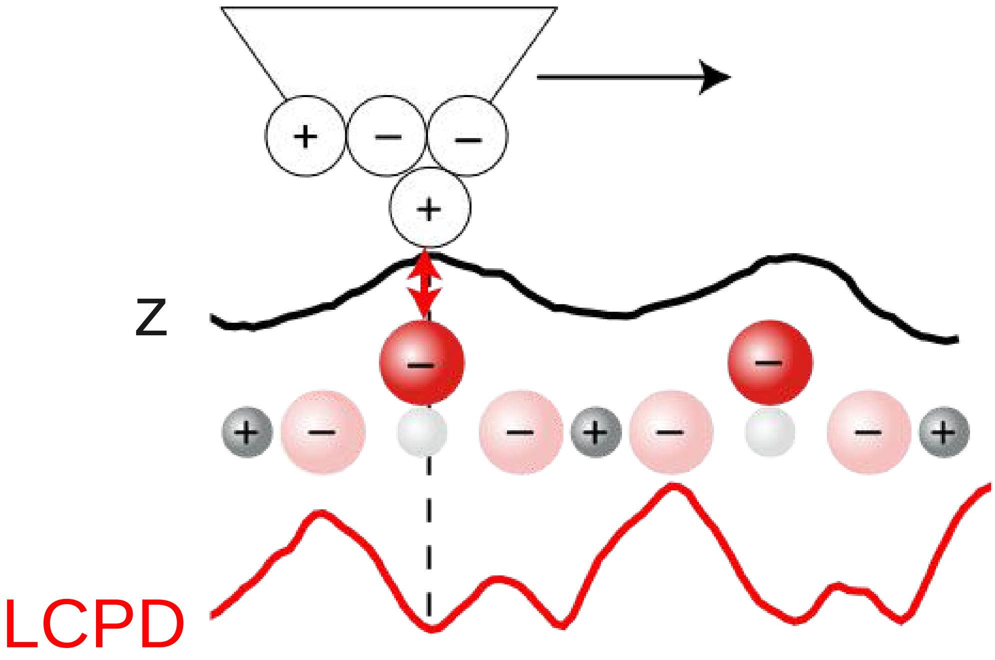
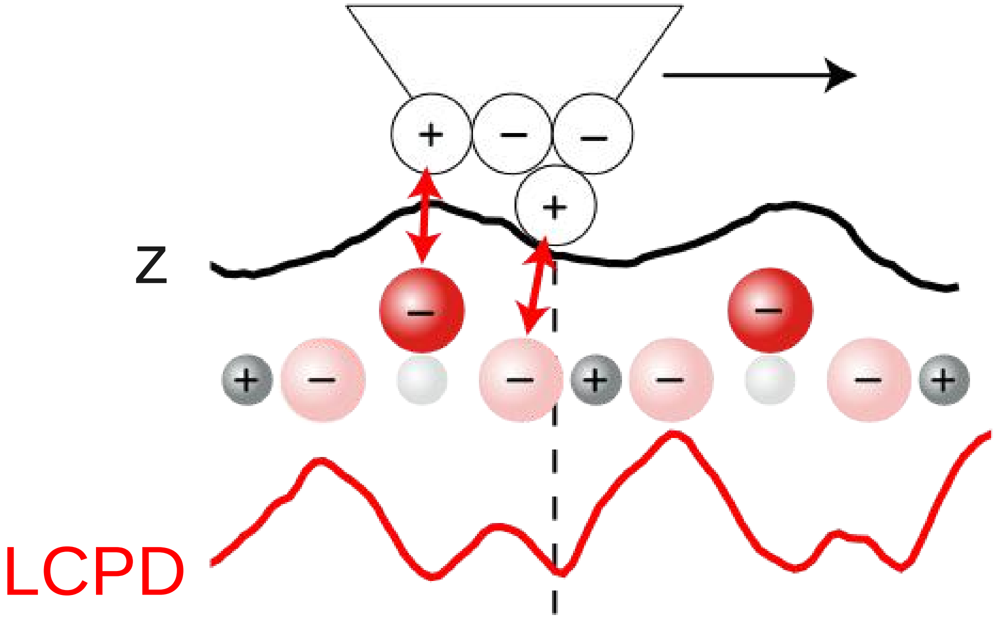


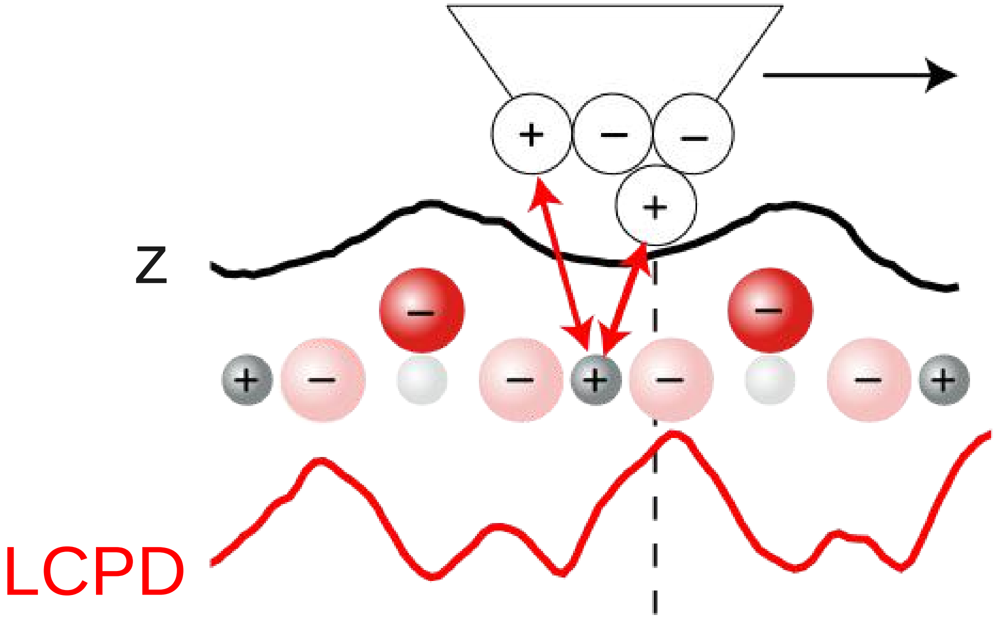
Model of the KPFM signal



Model of the KPFM signal



Model of the KPFM signal



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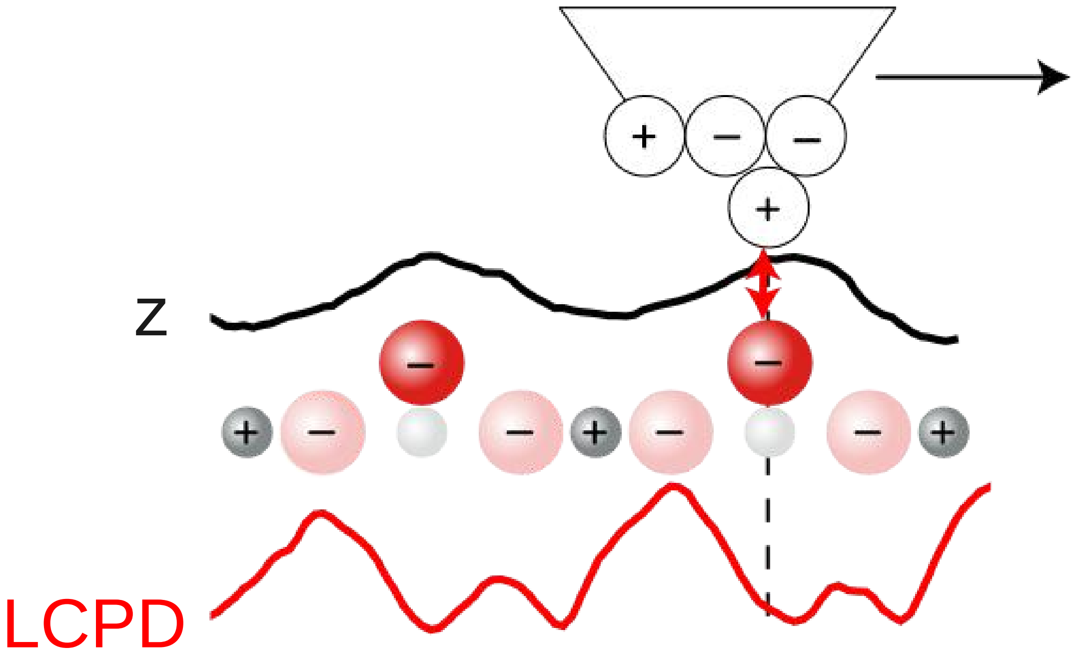

Change of Tip Condition