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SMR 1564 - 31

SPRING COLLEGE ON SCIENCE AT THE NANOSCALE
(24 May - 11 June 2004)

Surfaces

Annabella SELLONI
Princeton Univ., Dept. Chemistry, Princeton, USA

These are preliminary lecture notes, intended only for distribution to participants.

Surfaces – Trieste, June 2004

- Basic concepts: surface energy, reconstruction mechanisms
- “Functional” surfaces: reaction pathways and properties

The surface energy

- When a crystal is cleaved, its internal energy is modified:

$$U(S,V,N,A) = TS - pV + \mu N + \gamma A \ ,$$

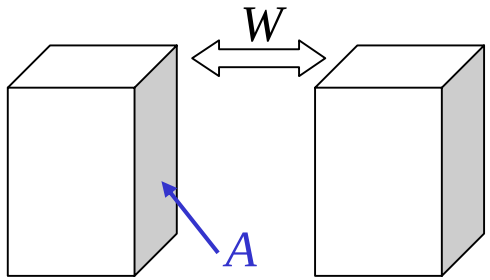
where the surface energy γ is:

$$\gamma = [G(T,p,N) - \mu N] / A$$

A: surface area

μ: chemical potential in the bulk

- γ is related to the work W needed to separate a body in two halves:



$$W = 2\,\gamma \cdot A$$

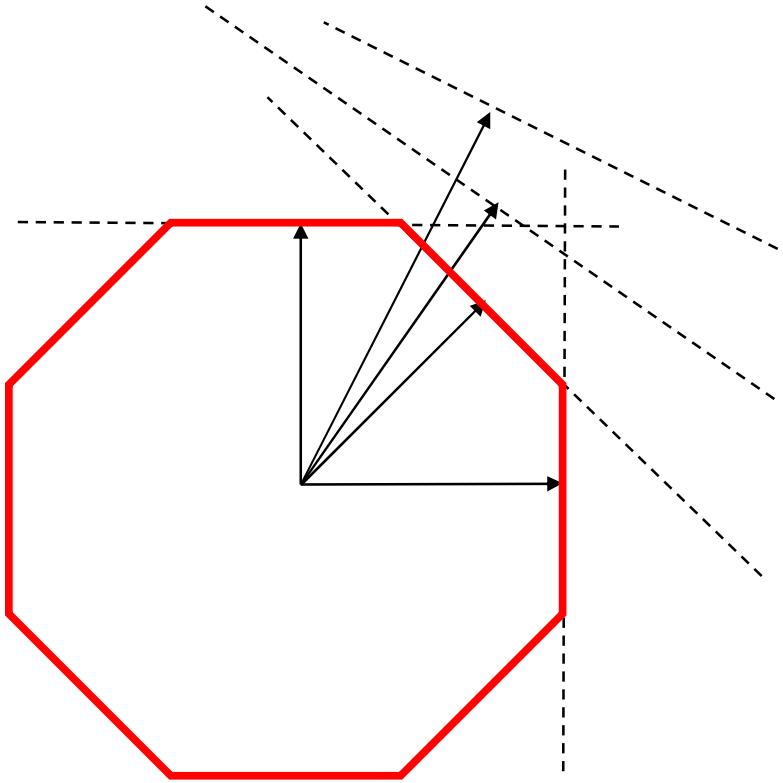
- In practice, we compute γ from the cohesive energies:

$$\gamma = -\,[E^{\,\mathrm{coh}}(\mathrm{surface}) - E^{\,\mathrm{coh}}(\mathrm{bulk})] \,/\, 2A$$

Equilibrium crystal shape: the Wulff construction

Draw the perpendicular plane through the tip of each radius vector in a *polar plot* of $\gamma(\mathbf{n})$.

The complex envelope of these planes describes the crystal shape in equilibrium.



Equivalently:
The distance of a surface plane from the center of mass of the crystal is proportional to the γ of this plane

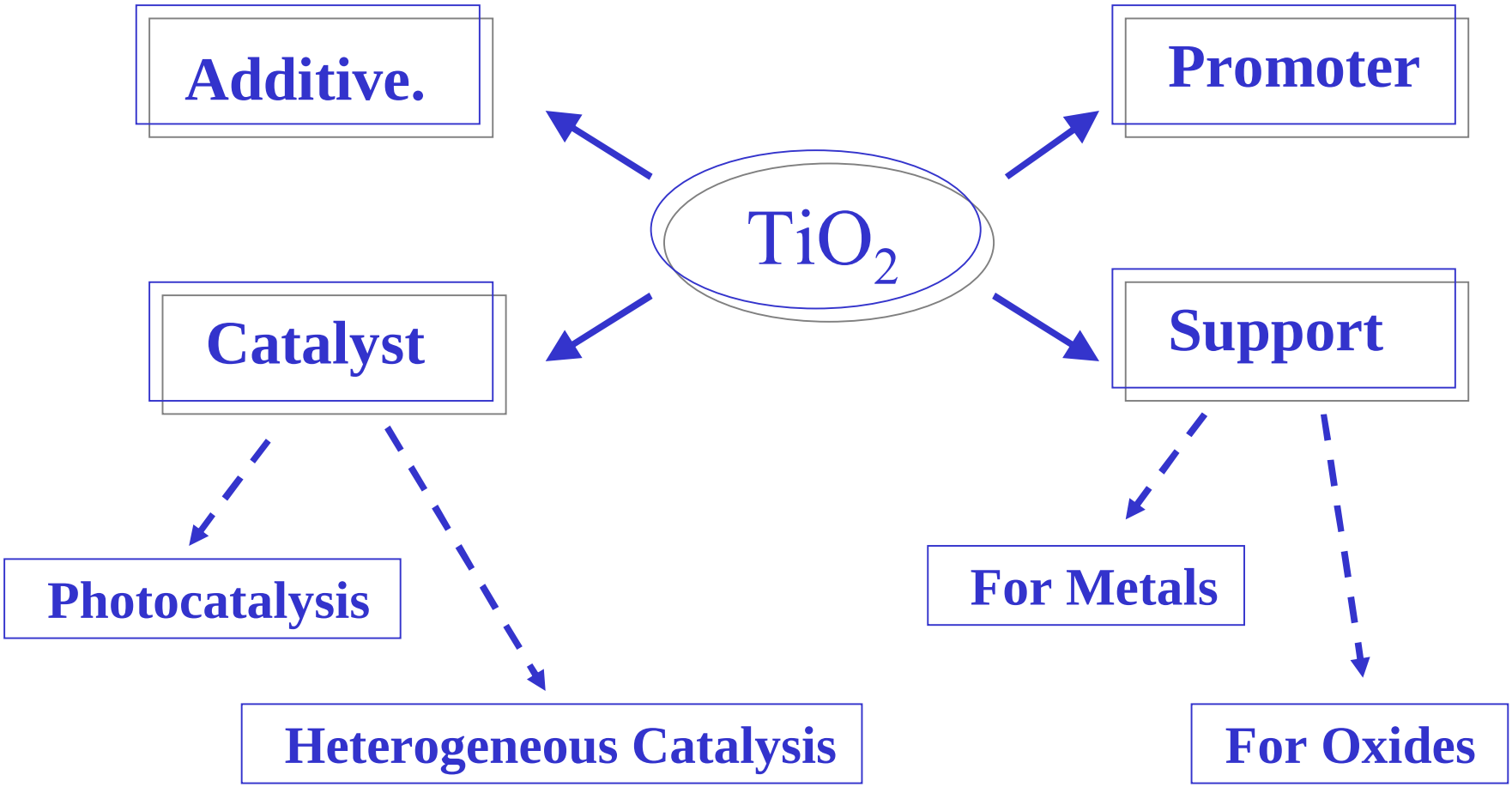
Surface energy and nanoparticle shape: TiO_2, a semiconductor oxide with ionic-covalent character

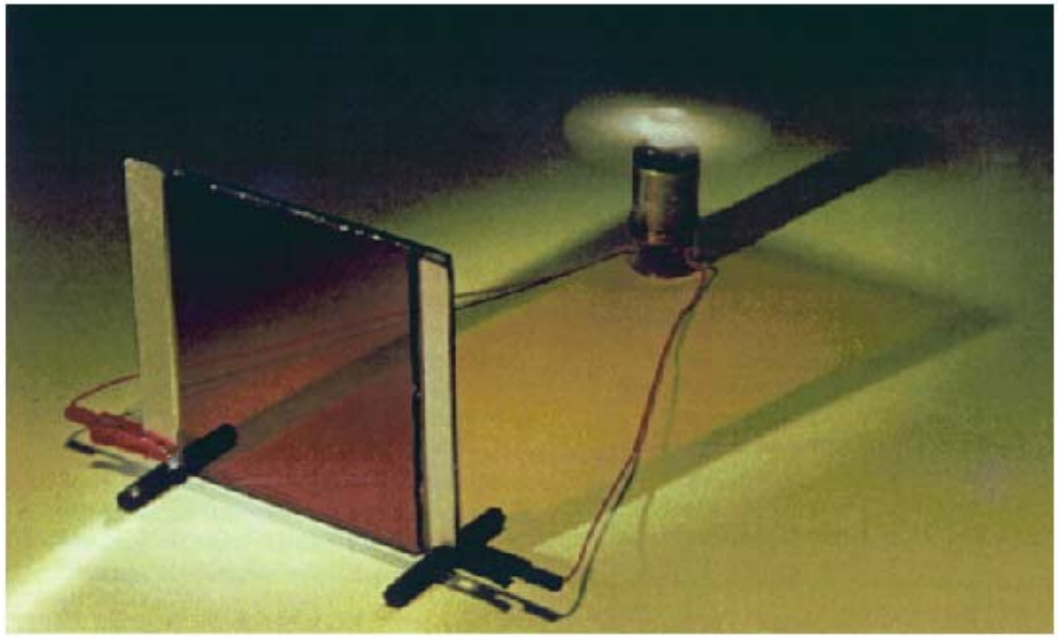
Work with

M. Lazzeri

A. Vittadini

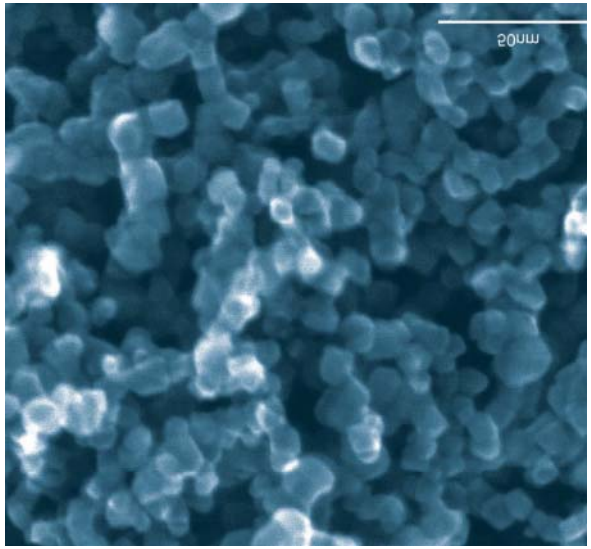
Applications of TiO_2

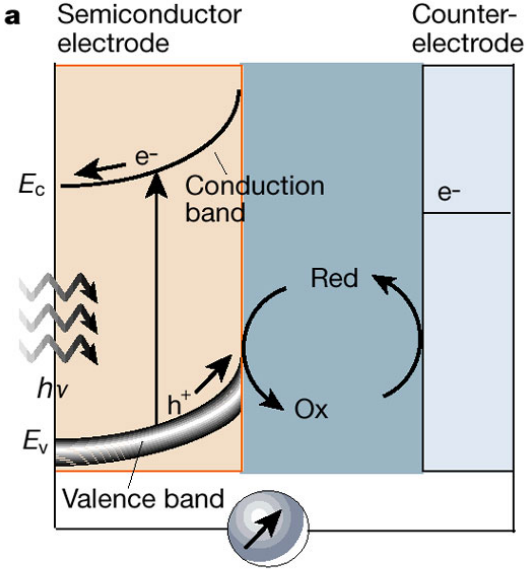


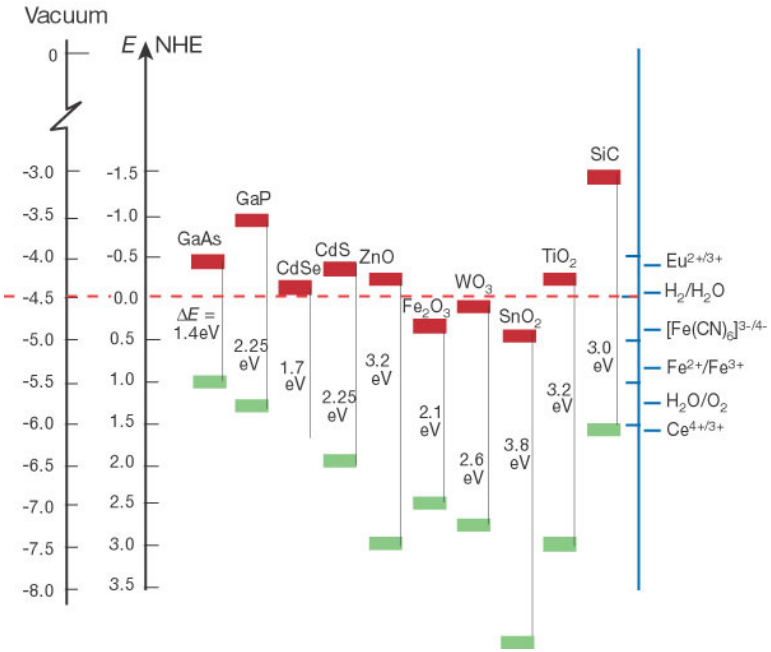


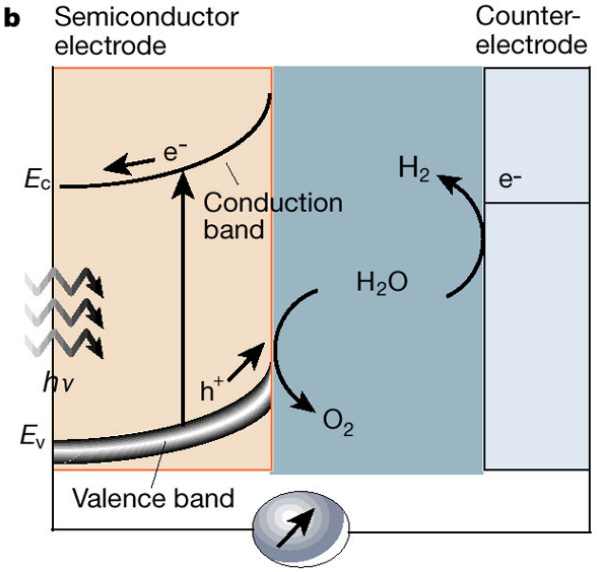
Photoelectrochemical solar cell based on dye-sensitized nanostructured films of **TiO_2 anatase**

From M. Grätzel, EPFL, Lausanne

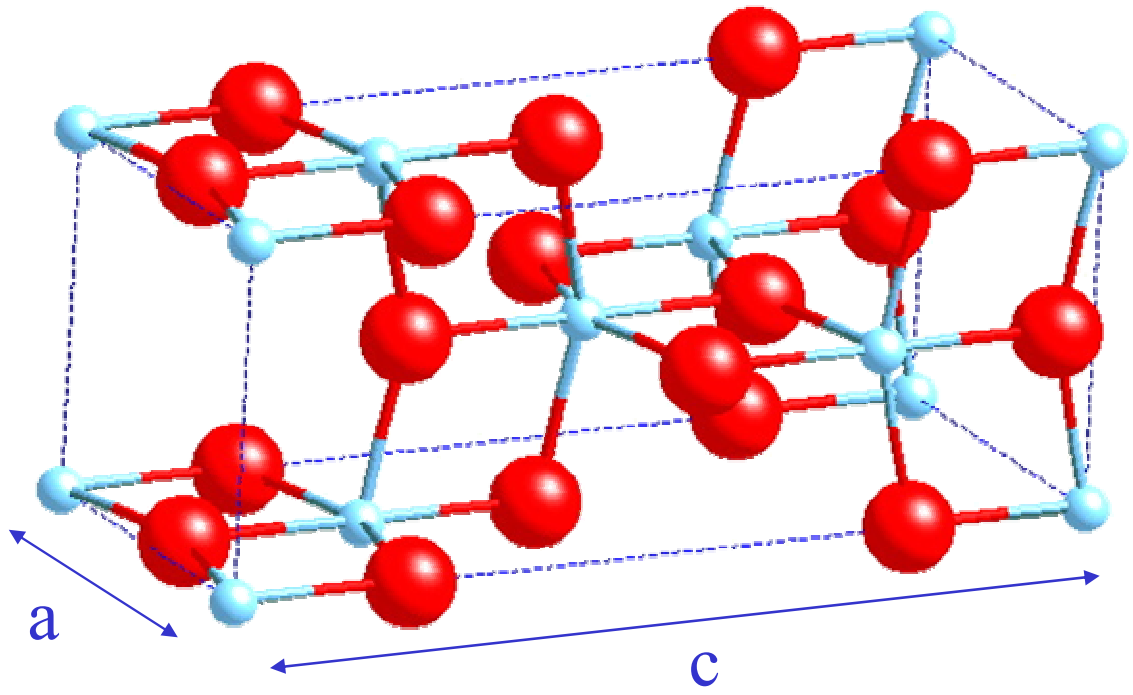

200nm


a
Semiconductor electrode
Counter-electrode
E_c
e⁻
Conduction band
e-
Red
hν
h⁺
Ox
E_v
Valence band

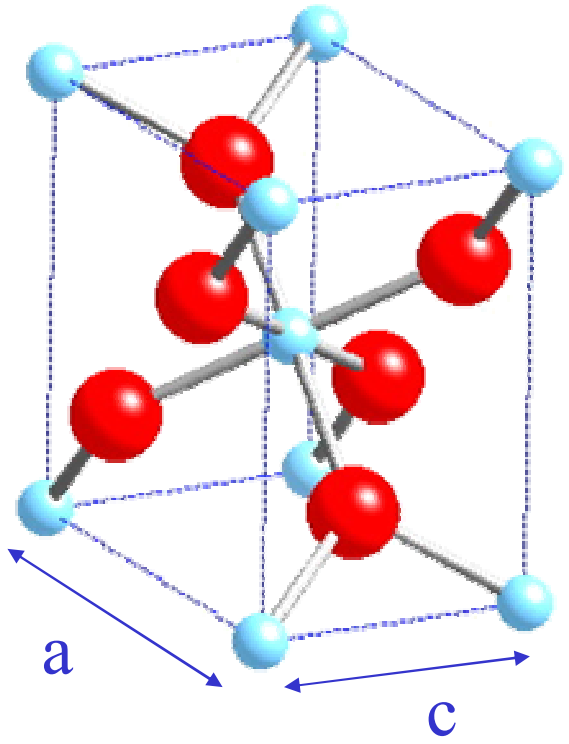

Vacuum
E NHE
0
-3.0
-3.5
-4.0
-4.5
-5.0
-5.5
-6.0
-6.5
-7.0
-7.5
-8.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
GaAs
GaP
CdSe
CdS
ZnO
Fe_2O_3
WO_3
SnO_2
TiO_2
SiC
ΔE = 1.4eV
2.25 eV
1.7 eV
2.25 eV
3.2 eV
2.1 eV
2.6 eV
3.8 eV
3.2 eV
3.0 eV
$Eu^{2+/3+}$
H_2/H_2O
$[Fe(CN)_6]^{3-/4-}$
Fe^{2+}/Fe^{3+}
H_2O/O_2
$Ce^{4+/3+}$


b
Semiconductor electrode
Counter-electrode
E_c
e⁻
Conduction band
H_2
e-
H_2O
hν
h⁺
O_2
E_v
Valence band

Anatase vs. rutile : unit cells



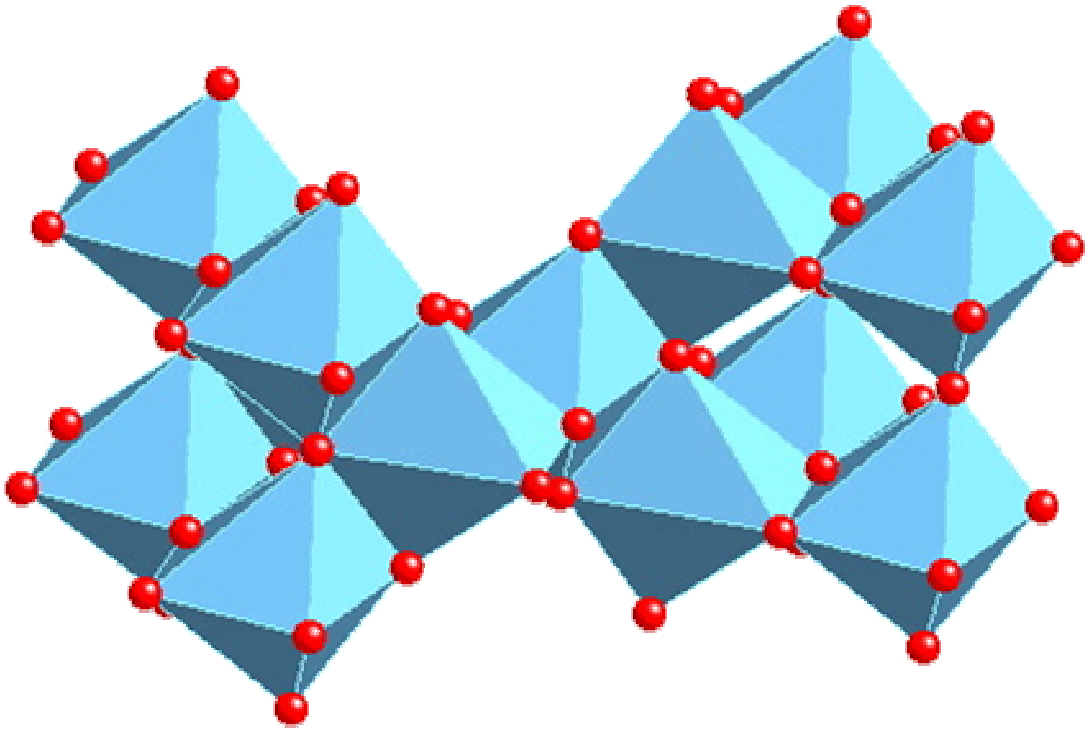
anatase



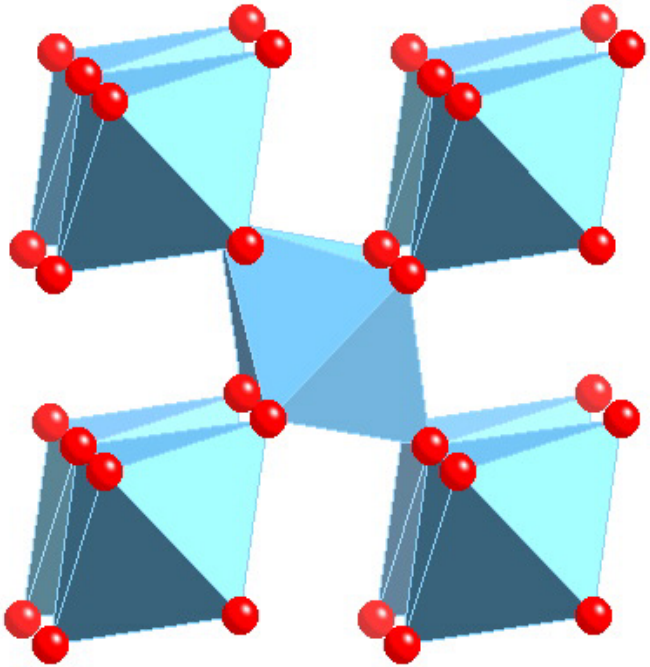
rutile

Formal charge: Ti^{4+} , O^{2-}

Anatase vs. rutile: crystal packing



anatase



rutile

Anatase vs Rutile

- ✓ Both semiconductors, Eg=3.0 eV (Rut.), 3.2 eV (Anat.)
- ✓ Rutile 10% denser
- ✓ Anatase more active for photocatalysis
- ✓ Anatase *unstable* wrt rutile, unless prepared as nanocrystals

Anatase vs. rutile : theory and expt.

$$P = 1.5\, B_0 [(V_0/V)^{7/3} - (V_0/V)^{5/3} \times [1 - 0.75(4 - B'_0) \times (V_0/V)^{2/3} - 1]$$

Ecoh = - (Etot - Eatoms)

		a (Å)	c (Å)	B (GPa)	B'_0	E^{coh} (eV/TiO_2)
Anatase	Expt.	3.782	9.502	179±2	4.5±1.0	
	GGA	3.786	9.737	176	2.99	21.54
	LDA	3.735	9.534	199	1.72	24.46
Rutile	Expt.	4.587	2.954	211±10	6.5±0.7	19.9
	GGA	4.634	2.963	204	4.62	21.44
	LDA	4.546	2.925	249	4.98	24.44

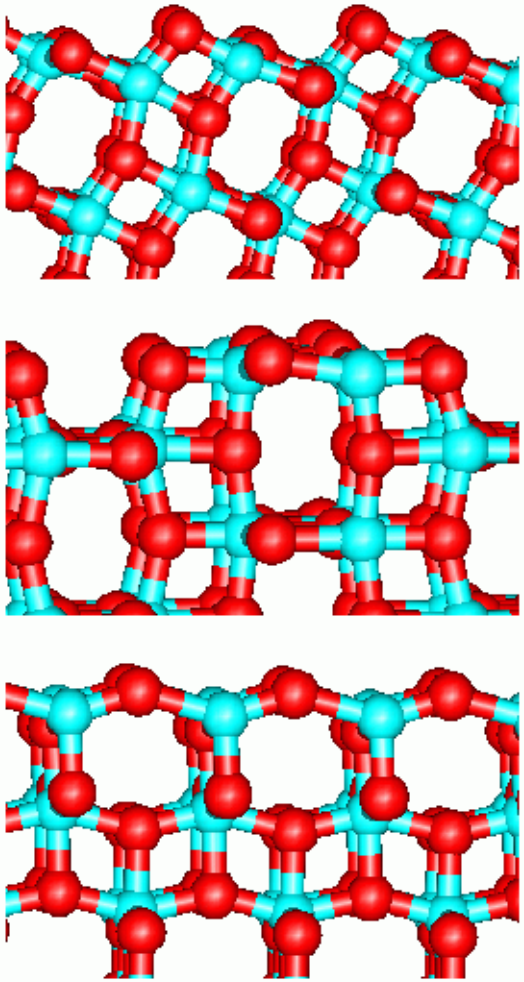
Plane-wave, pseudopotential DFT calcs.

Why anatase nanocrystals are stable?

- *Fact*:
  Anatase nanoparticles are stable up about 14 nm.

- *Suggestion:*
  Anatase crystals have a lower surface energy.
  Therefore, the smaller the crystal, the stabler the anatase phase.
  [Zhang & Banfield, J. Mater. Chem. 8 (2073) 1998]

Anatase stoichiometric 1×1 surfaces



(101)

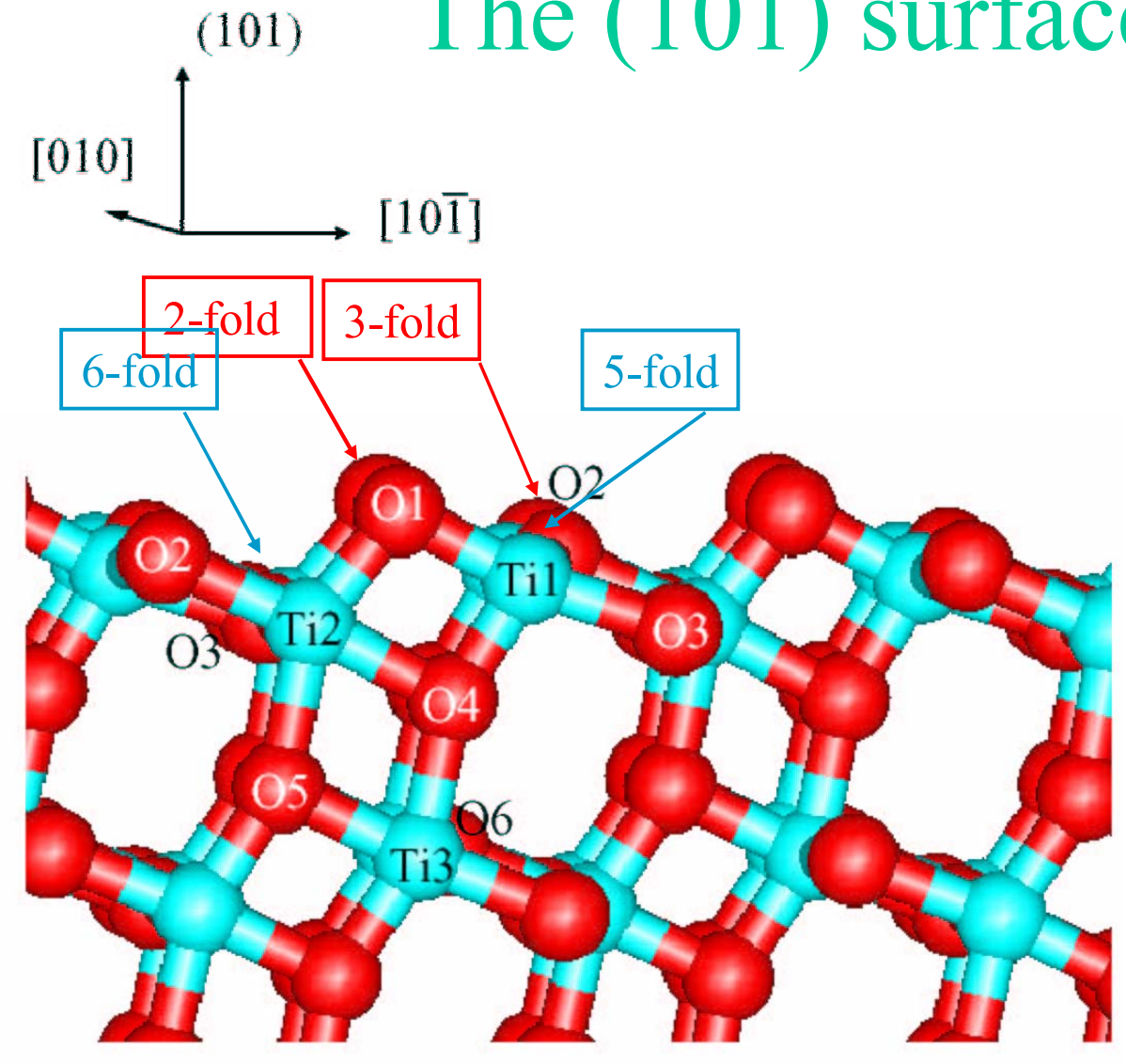
(100)

(001)

Oxygen

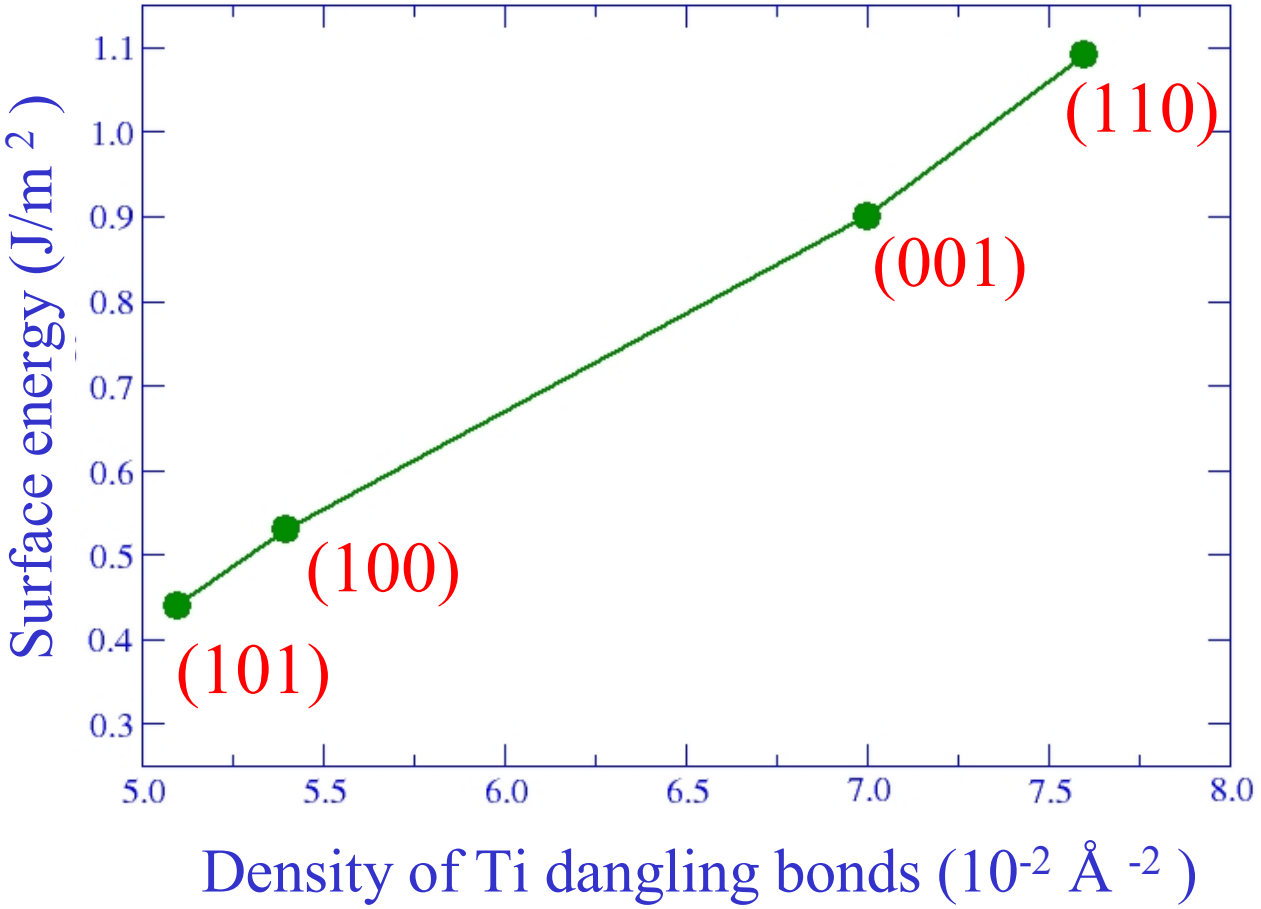
Titanium

The (101) surface

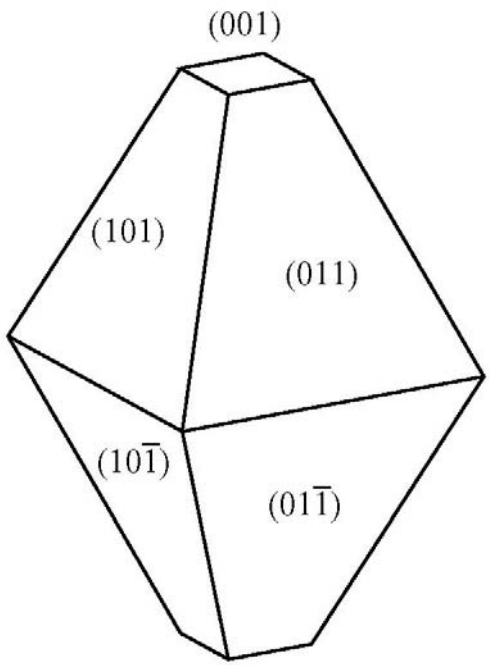


Atomic displacements (Å)			
Atom	[10$\bar{1}$]	[010]	(101)
O1	0.29	0.00	-0.02
O2	0.16	0.00	0.19
O3	0.17	0.00	0.02
O4	-0.15	0.00	0.07
Ti1	0.02	0.00	-0.18
Ti2	0.17	0.00	-0.20

Surface energy depends almost linearly on the density of under-coordinated Ti atoms

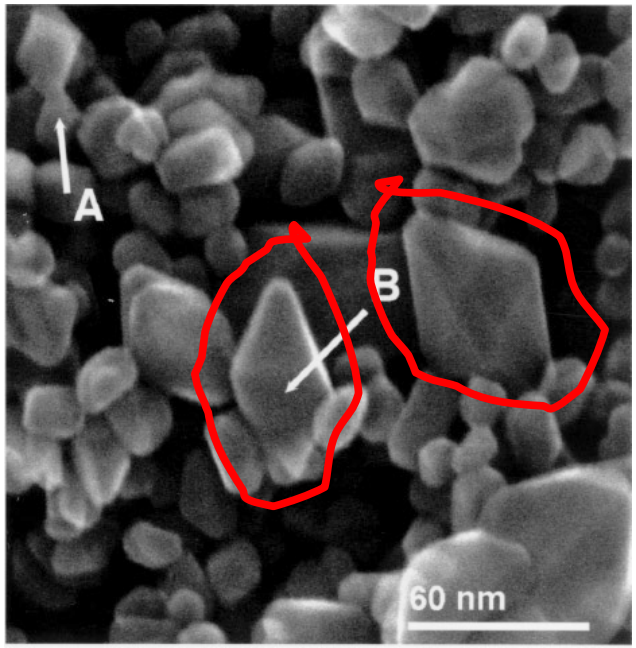


Crystal shape: theory vs. experiment



theory

natural anatase

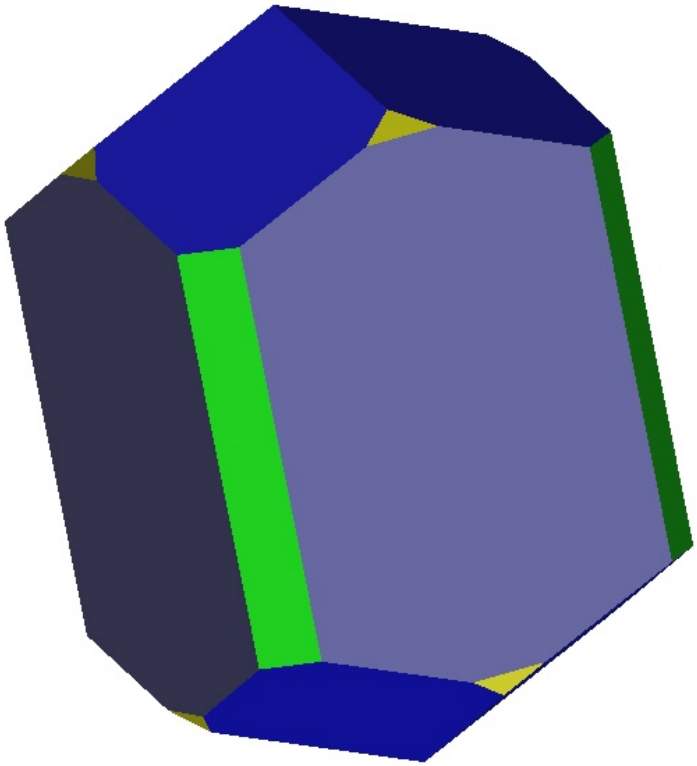


anatase nanocrystals

from: Shklover et al.
J. Solid St. Chem. 132 (1997) 60

Lazzeri, Vittadini, Selloni, PRB 63 (2001) 155409.

Equilibrium crystal shape : rutile



From: M.Buerger *Elementary Crystallography*, 1956

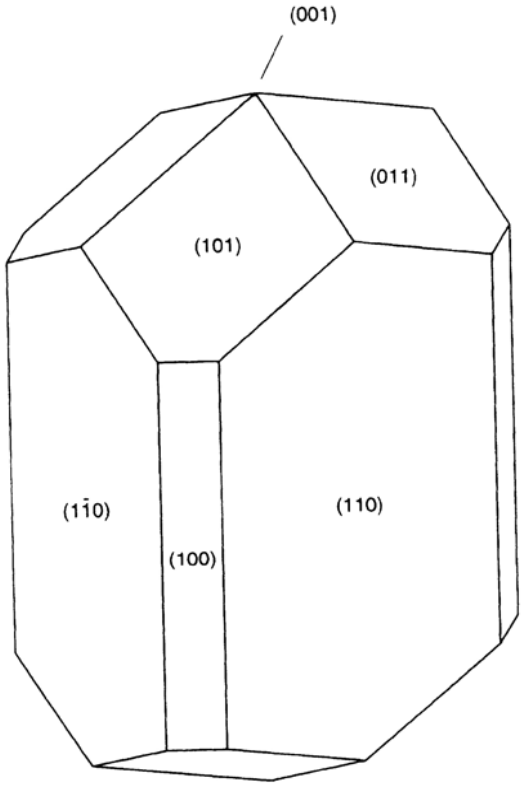


FIG. 6. The equilibrium shape of a macroscopic crystal of TiO_2 using the Wulff construction and the surface energies of Table VI.

Crystal surface energy: anatase vs. rutile

- For anatase, the most stable (101) surface constitutes the 94% of the crystal surface.

- For rutile, the most stable (110) surface constitutes only the 56% of the crystal surface (Ramamoorthy et al., PRB 49 (1994) 16721)

- We computed the total LDA crystal surface energy:

  Rutile = 1.09 J/m^2 (using data by Ramamoorthy et al.)

  Anatase = 0.90 J/m^2

- This confirms the Zhang & Banfield suggestion.

Message

Because of surface energy, nanoparticles (up to a crtain size) may prefer a crystal strucure which is *not* the most stable bulk structure
(TiO_2, ZrO_2, …)

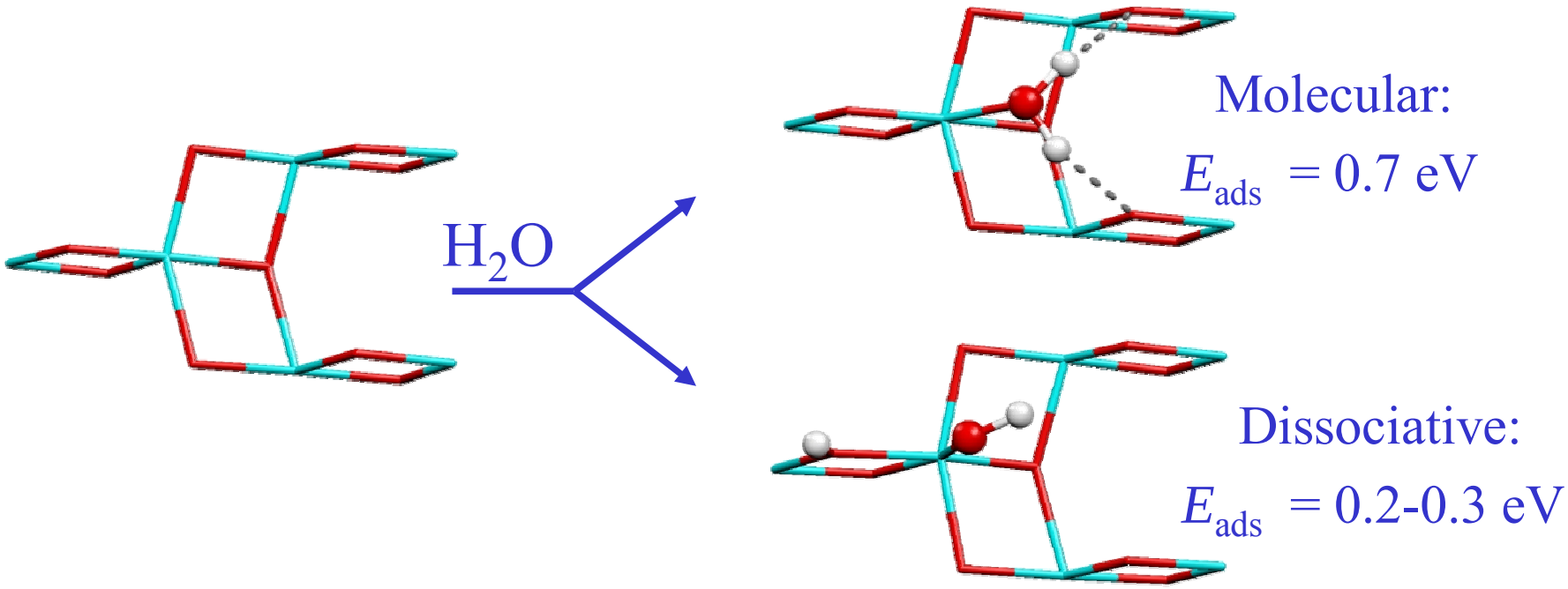
The anatase/water interface

- Importance:

  * Anatase is often grown by wet methods;

  * The anatase/water interface is present in photoelectrocatalytic devices;

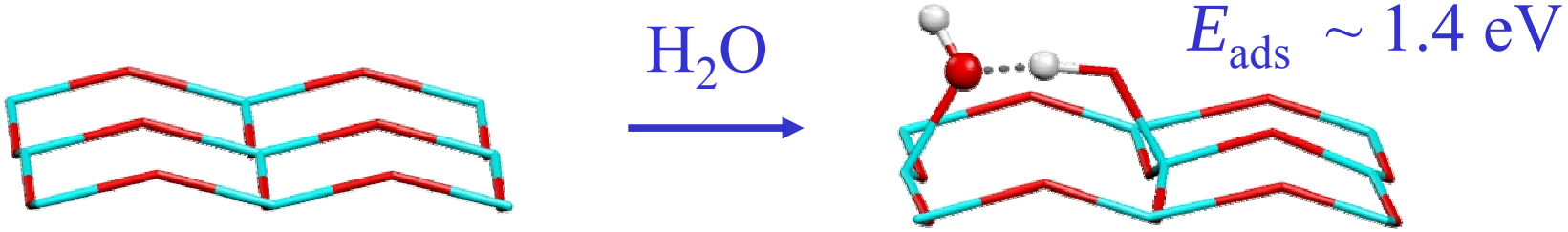
H_2O on (101): coverage < 1



- Dissociation of H_2O on the (101) surface is unfavored, in line with the stability of the surface.
- Adsorption energies are little affected by coverage.

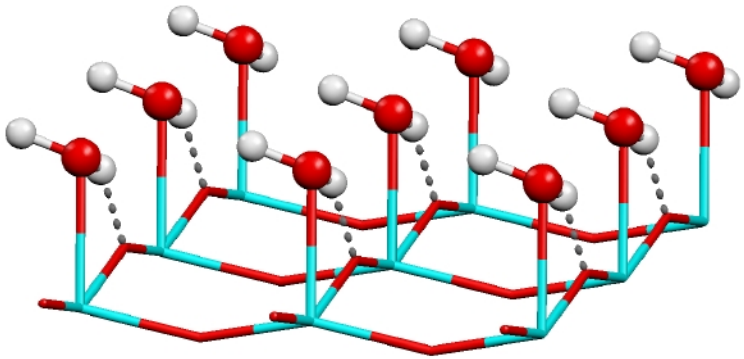
H_2O on (001): coverage < 0.5 ML

- The surface energy of (001)-1x1 is twice that of (101).
- Adsorption is a way to lower surface energy.

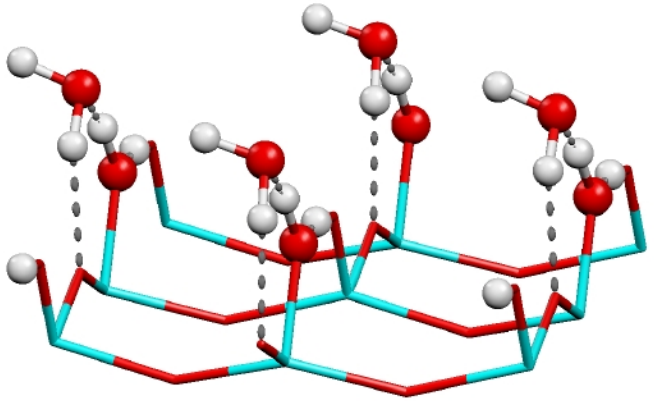


- No local minimum exists for molecularly adsorbed H_2O;
- Instead, immediate dissociation occurs, leading to two H-bonded OH groups.
- The opening of two adjacent O-bridges cannot occur.

H_2O on (001): coverage = 1 ML



Molecular: E_{ads} ~ 0.8 eV



Mixed: E_{ads} ~ 1.0 eV

- Full coverage can be realized by molecular adsorption.
- Most favorable configuration, however, corresponds to 0.5 layers of *molecular* water on 0.5 layers of *dissociated* water.

$\Rightarrow$ hydroxyls are always present at any coverage on the unreconstructed (001) surface.

Water on anatase (100)

molecular adsorption, adsorption energy ~ same as for (101) surface

$\Rightarrow$ equilibrium shape of hydrated nanocrystals not substantially different from dry ones!

Surface reconstruction

- Atomic positions at the surface are generally different wrt a bulk-terminated crystal

- In particular, the periodicity may be different: (m×n) means that the surface unit cell is m times the (1×1) cell of the bulk-terminated crystal along one direction, and n times along the other

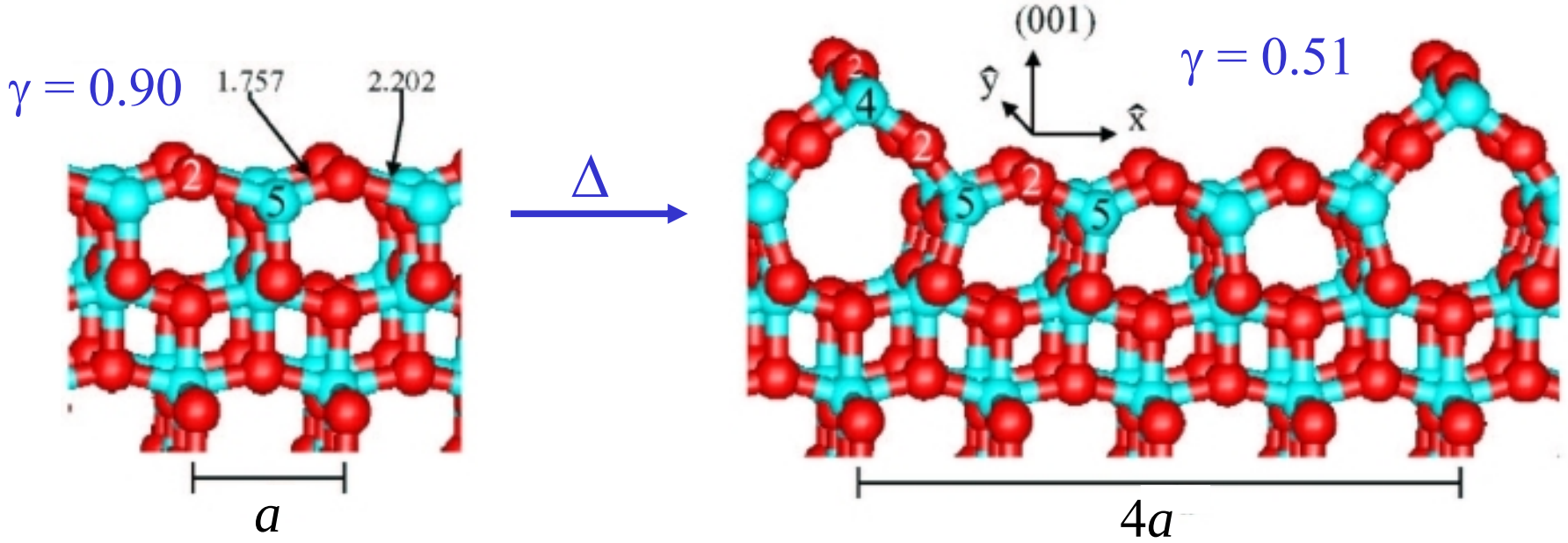
- Most semiconductor surfaces reconstruct, the main driving force being the tendency to reduce the number of (energetically costly) surface dangling bonds: Si(100)-2 ×1, GaAs(100)….

The 1×4 reconstruction of anatase (001)

A reconstruction without reduction of the number of surface dangling bonds!

(1x4) reconstruction of the (001) surface

- Upon heating, the (001) surface reconstructs (1x4).

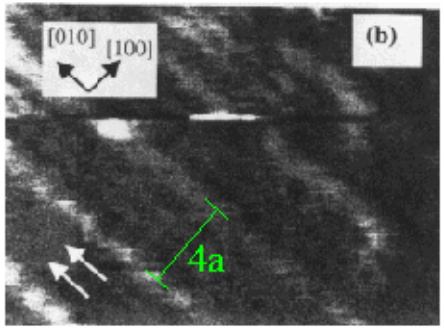


- The most favorable computed model imply the formation of a polymer of TiO_2 units adsorbed on the surface, containing 4-fold Ti atoms!
- This lowers the surface energy from 0.90 to 0.51 J/m^2

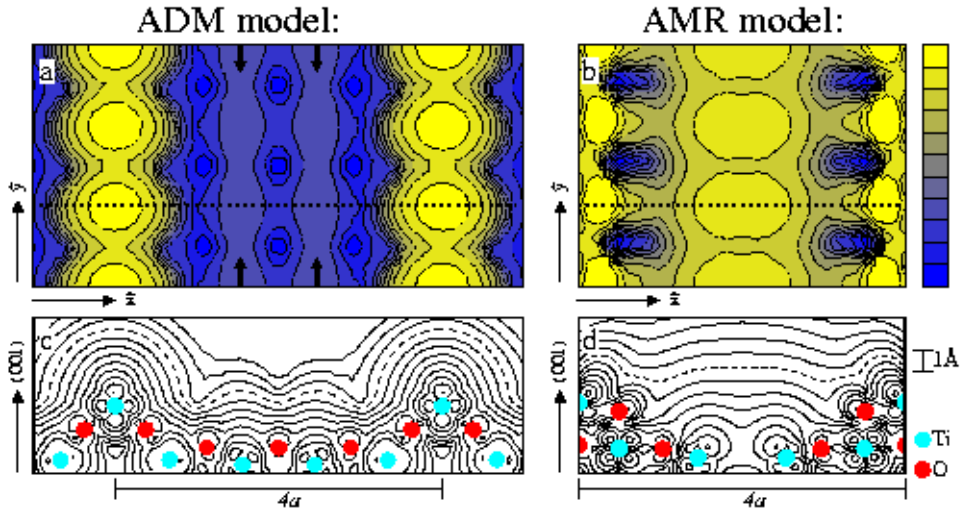
(Lazzeri & Selloni, PRL 87 (2001) 266105)

STM images of the 1x4 reconstruction

Experimental:



Simulation:

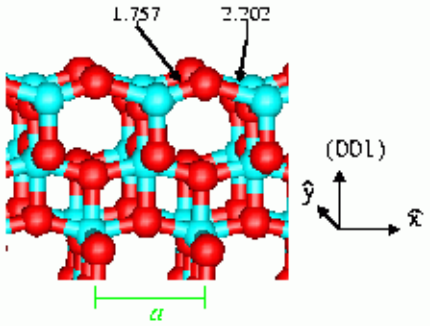


We studied the various peridicities that can be obtained with the ADM model

	1×1	1×6	1×5	1×4	1×3
γ	0.90	0.58	0.53	0.51	0.58
$g_{\hat{x}\hat{x}}$	6.1	4.1	3.1	0.9	-0.9
$g_{\hat{y}\hat{y}}$	-1.2	0.3	0.9	1.1	2.4

γ surface energy (J/m^2)
g surface stress (J/m^2)
$g > 0$ tensile stress

The contraction/expansion of the surface bonds on the 1×1 surface is associated with a large tensile stress



$g_{xx} = 6.1 \quad J/m^2$
$\rightarrow \quad \leftarrow$

There is a relation between the surface stress (g) and the structure of the various reconstructions