Molecular Ordering at the Interface Between Liquid Water and Rutile TiO_2 (110)

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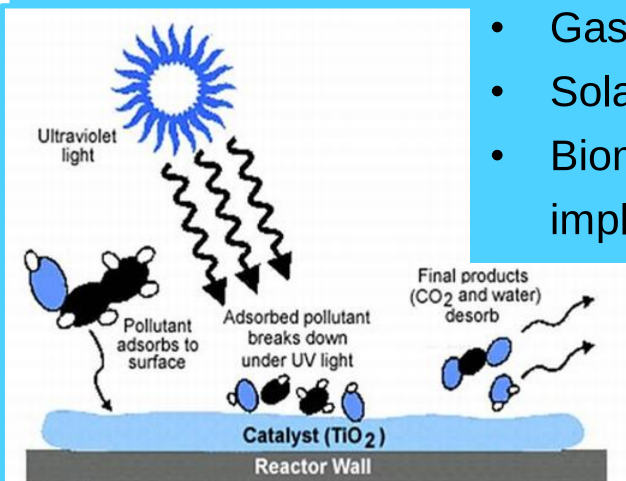
TITANIUM DIOXIDE

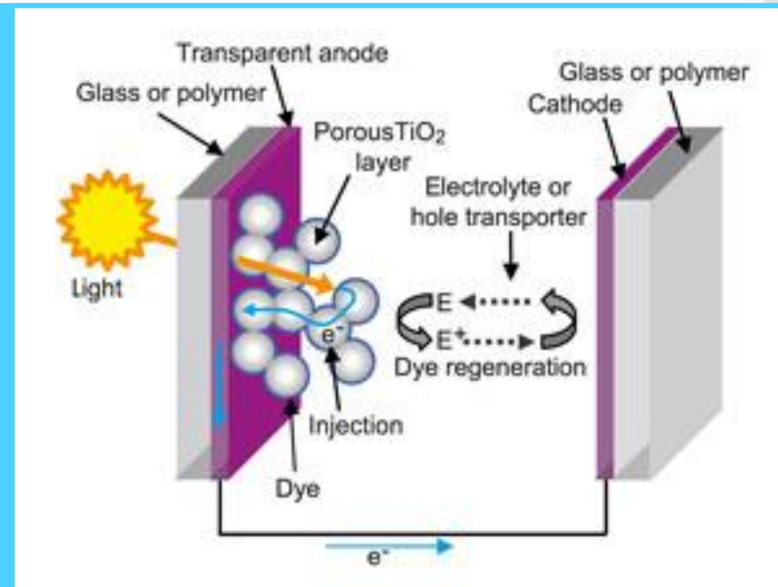
Wide range of technological applications

- Photocatalysis
- Gas sensing/ Biosensing
- Solar cells / Photovoltaics
- Biomaterials / Medical implants

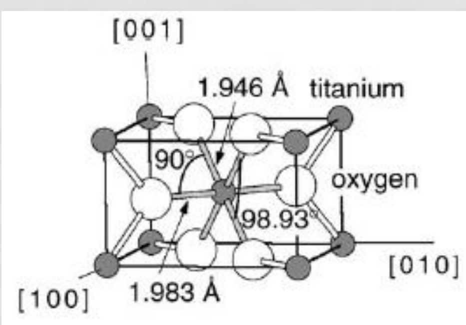


http://www.nanoprotect.co.uk/photocatalyst.html

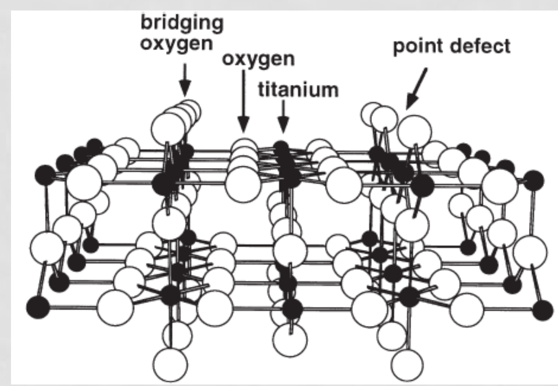
Solid\liquid interfaces



http://blog.sciencenet.cn/



TiO_2
Rutile phase

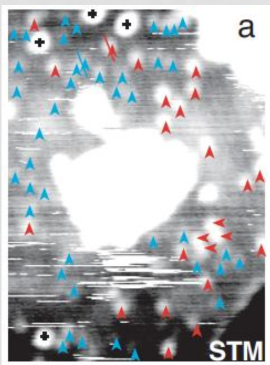


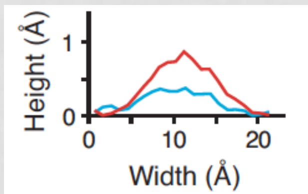
TiO_2
Rutile
(110) Surface
(lowest surface energy)

Diebold, U., et l. (1998). *Surface science*, *411*(1), 137-153.

RUTILE TiO_2 (110) SURFACE – **UHV** STUDIES…

- <u>Adsorption of water **vapors**</u>

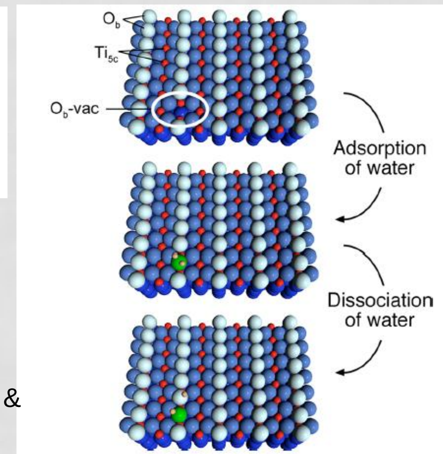




H adatoms

O vacancies

Pang, C. L., Sasahara, A., Onishi, H., Chen, Q., & Thornton, G. (2006). *Physical Review B*, *74*(7), 073411.

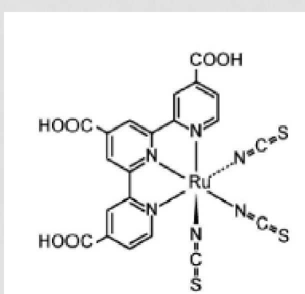


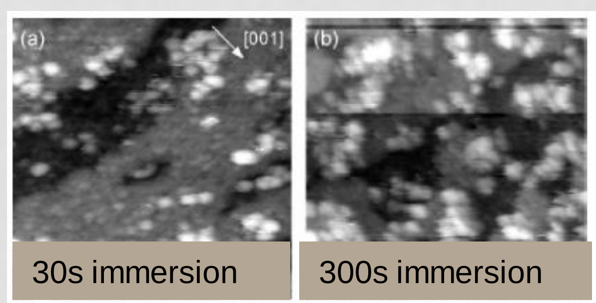
MOLECULAR OR DISSOCIATIVE WATER ADSORPTION AT THE REAL TIO_2 / WATER INTERFACE?

Pang, C. L., Lindsay, R., & Thornton, G. (2013). *Chemical reviews*, 113, 3887-3948.

- <u>Deposition of organic molecules **ex-situ**</u>

Black dye on TiO_2





UHV STM on PIVALATE covered TiO_2 after dye solution immersion

Ikeda, M., Koide, N., Han, L., Sasahara, A., & Onishi, H. (2008). *Langmuir*, *24*(15),8056-8060.

….THE INTEREST INTO IN SITU STUDIES

*“[…] **there is an essentially unexplored range of experiments at ambient pressure and liquid interfaces** that is now technically feasible. The appropriate techniques include surface X-ray diffraction, SPM, ambient pressure photoemission, and X-ray absorption spectroscopy. Measurements of this type will be vital to explore the fundamental physics and chemistry associated with photocatalysis under **more realistic conditions** ...”*

Chi Lun Pang et al. (2013), *Chemical Review.*, 113, 3887−3948.

*“These structures, however, have generally been observed in vacuo, whereas most **applications of TiO_2 involve** instead **an aqueous environment** […]. Therefore, an important question concerns the fate of the surface reconstruction in such an environment […] **surface structures in vacuo and/or at low water coverage can be very different from those present in real photocatalytic applications**”*

Aschauer and Selloni (2011), *Physical Review Letters*, 106, 166102.

*“If one wants to link surface-science studies closer to application, it is also **vital to bring surface science out of UHV**[….]. This would further test the relevance of acquired knowledge **for technical applications**.”*

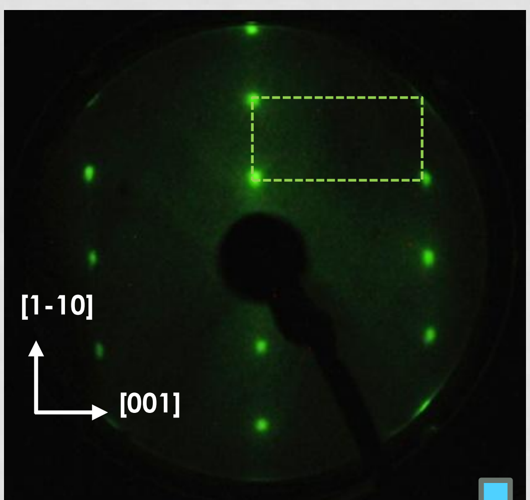
Diebold, U. (2003), *Surface Science Reports*, *48*(5), 53-229.

RUTILE TiO_2 (110) (1x1) – SAMPLE PREPARATION

- bulk reduction in UHV (annealing at T~800K)

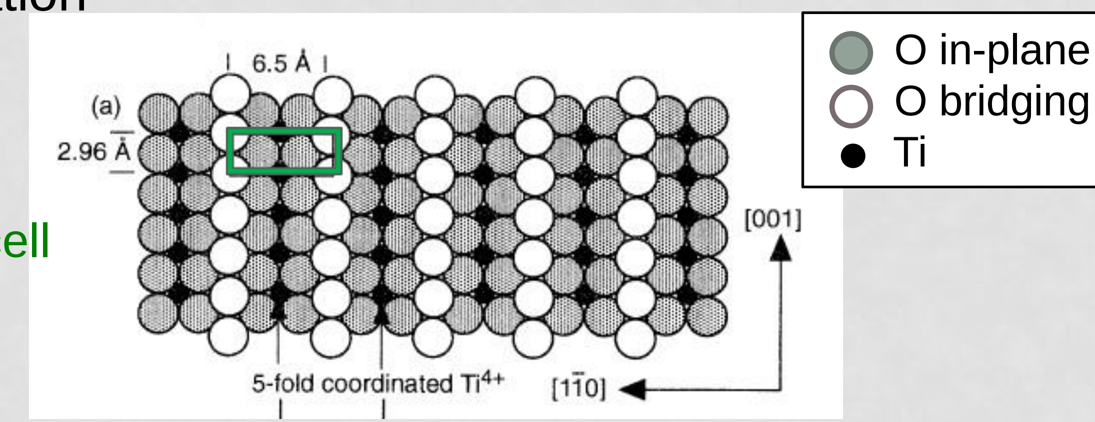
➡ formation of O vacancies and Ti^{3+} interstitials

- surface preparation (Ar^+sputtering and annealing cycles at T~930K)
- LEED and XPS characterization



LEED pattern (56eV)

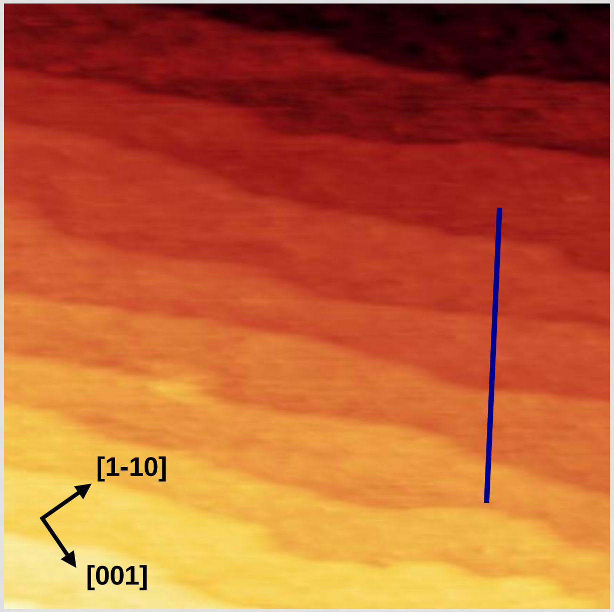
1x1 unit cell



Murray, P. W., Condon, N. G., & Thornton, G. (1995). *Physical Review B*, *51*(16), 10989.

Sample transfer from UHV to STM cell under Ar flux and **immersion in the liquid**

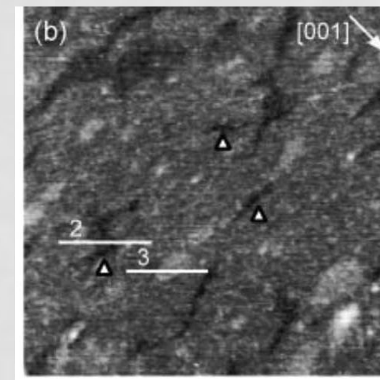
RUTILE TiO_2 (110) IN HIGH PURITY WATER



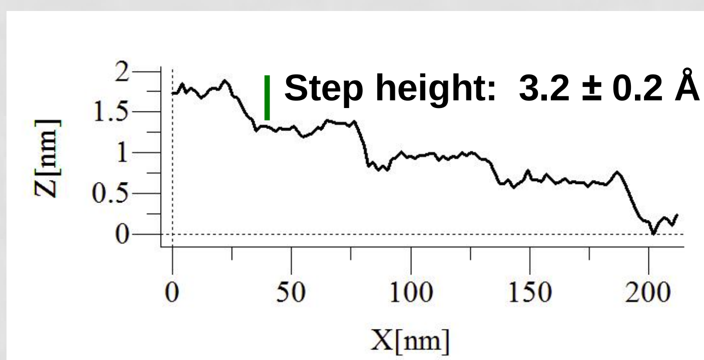
- High purity water: milli-Q water (18.2 MΩ•cm)
- No erosion or dissolution in water
- Structure stability after days of immersion in water

STM image in water 449x449 nm^2
V_b= -700mV, I_t =1nA

Sasahara, A. and Tomitori, M. J. Vac. Sci. Technol. B, 2010, 28, C4C5-C4C10.
300x300 nm^2

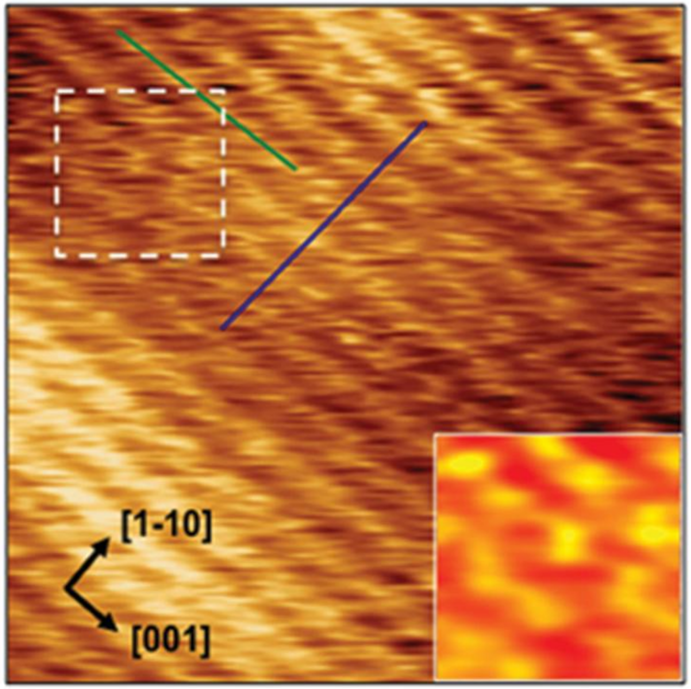


MONOATOMIC STEPS

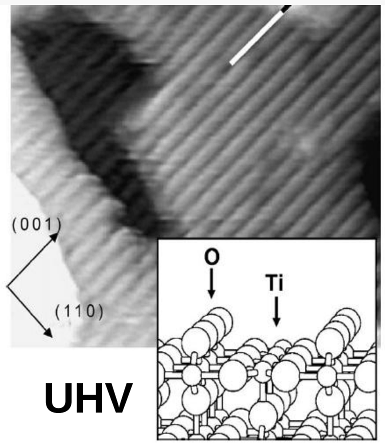


previous AFM studies reported a degradation of the surface for UHV prepared samples

RUTILE TiO_2 (110) **IN HIGH PURITY WATER**

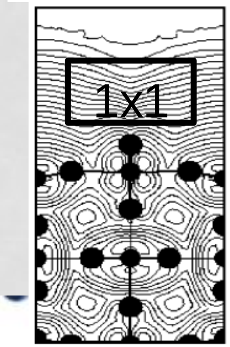


STM in water 10x10 nm^2 V_b= -700mV, I_t = 1nA

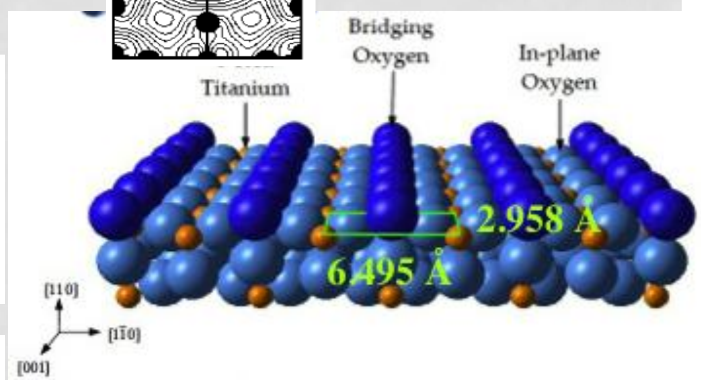


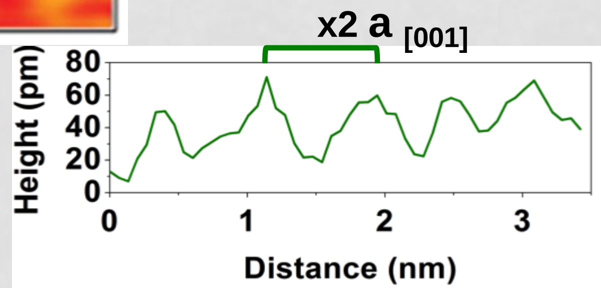
Diebold, U. (2003), *Surface science reports*, *48*(5), 53-229.

Charge density distribution

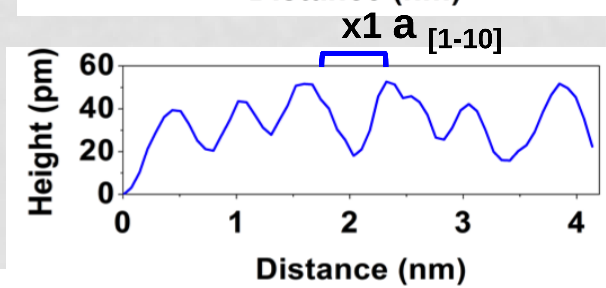


In UHV
- Bright rows: Ti
- Dark rows: O





- **Along the [001]:**
defined spots along the rows spaced 6.8 ± 0.5 Å

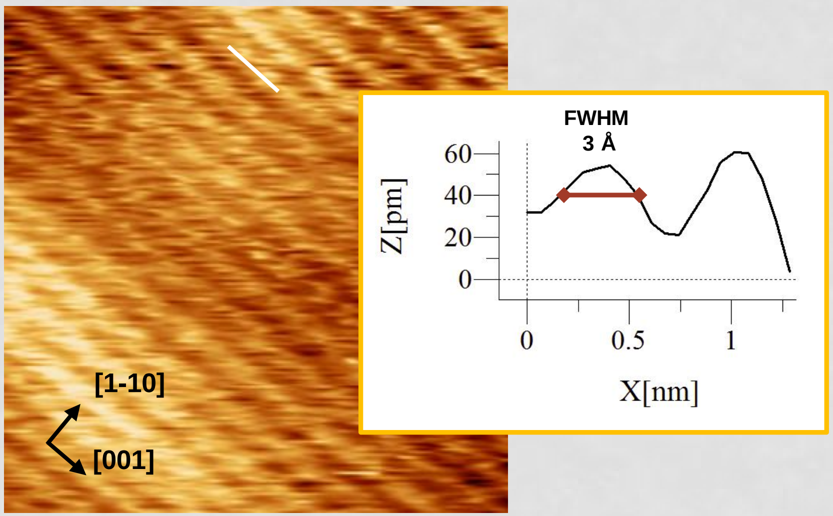


- **Along the [1-10]:**
dark and bright rows spaced 7.0 ± 0.5 Å

RUTILE TiO_2 (110) in HIGH PURITY **WATER *vs.* UHV**

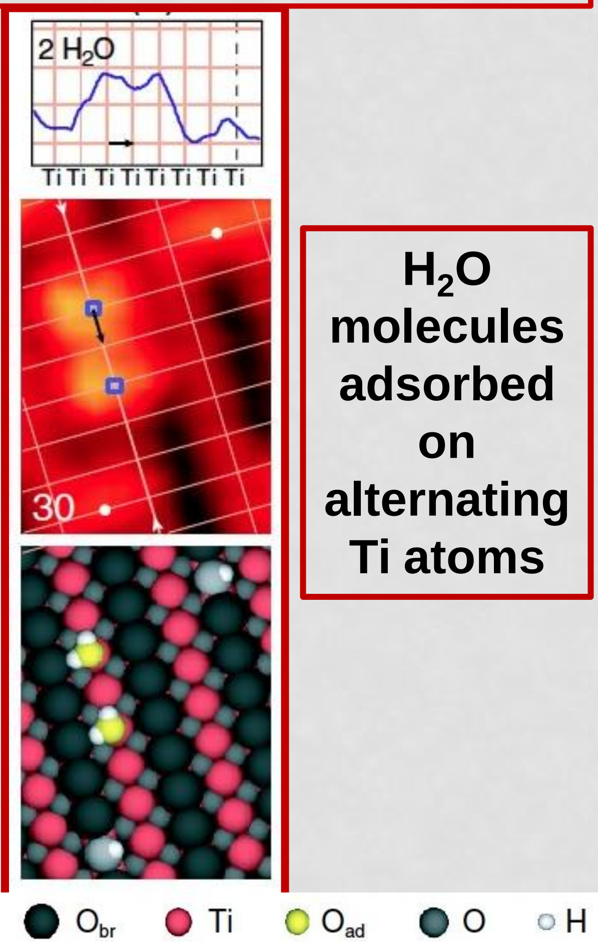
Corrugation values from STM **in water vs UHV**

- along [1-1 0] : about 0.4 Å (as in UHV)
- along [0 0 1] : about 0.3 Å (0.1 in UHV)



- *Which is the origin of the **x2 periodicity along the rows in WATER?***

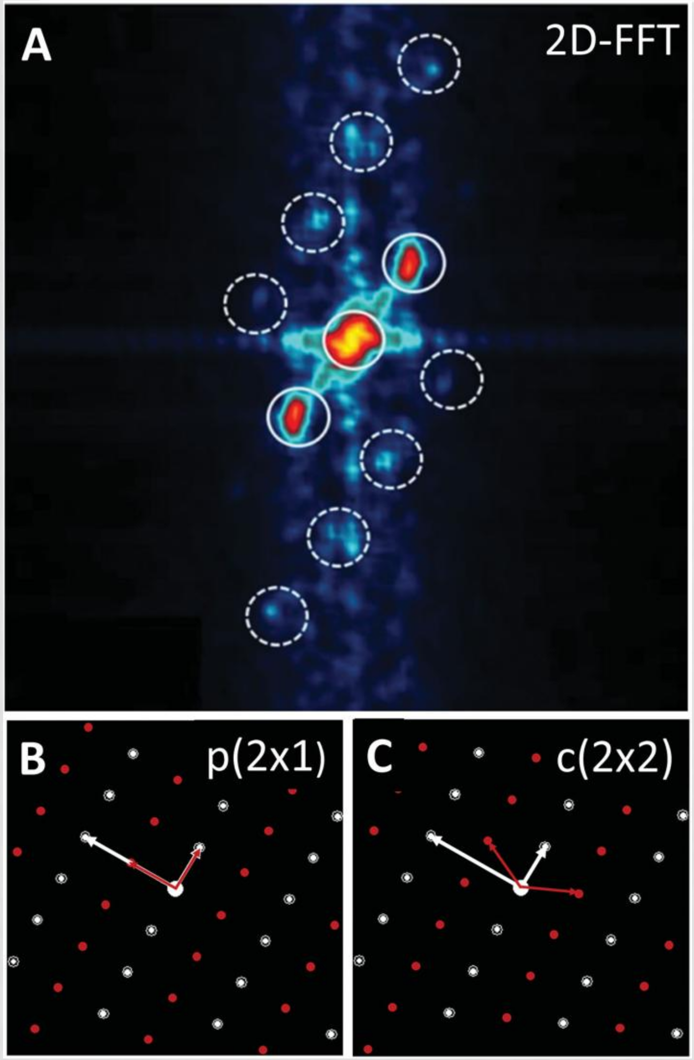
WATER MOLECULES in UHV
(T= 179 K, water coverage of 6% ML)



H_2O molecules adsorbed on alternating Ti atoms

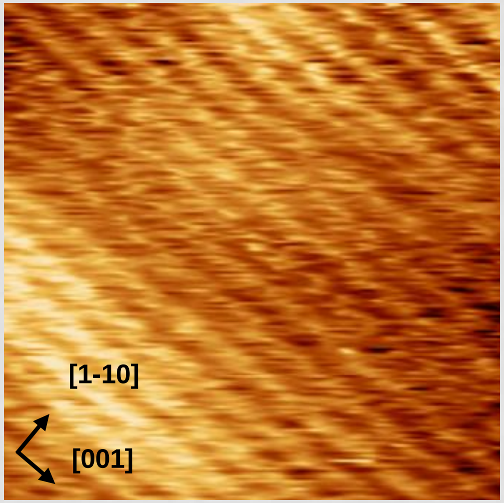
J. Matthiesen…., F. Besenbacher , PRL 102, 226101 (2009)

RUTILE TiO_2 (110) IN HIGH PURITY WATER



Fast Fourier Transform

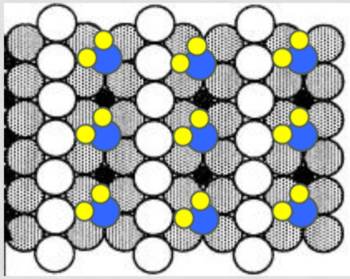
x 2 periodicity along [001]



STM image in water 10x10 nm^2
V_b= -700mV, I_t = 1nA

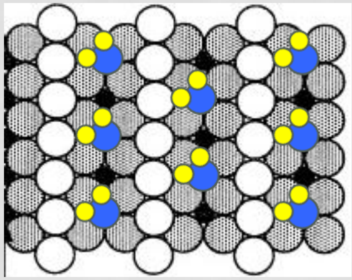
H_2O molecules adsorption: ordered overlayer

p(2x1) cell



OR

c(2x2) cell

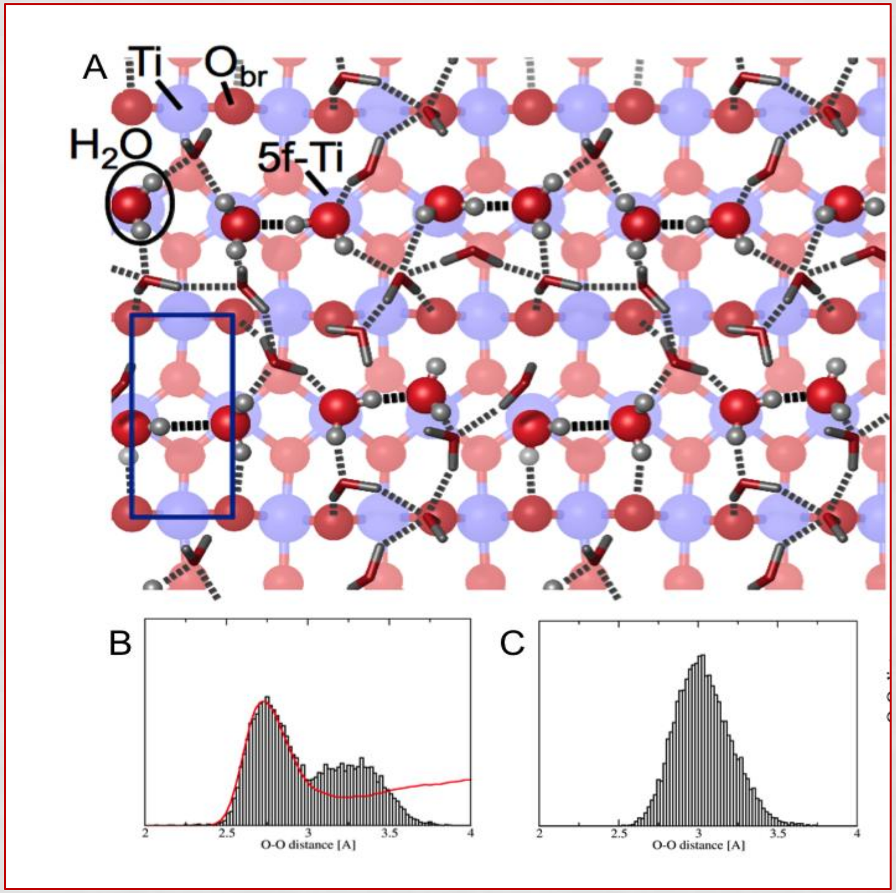


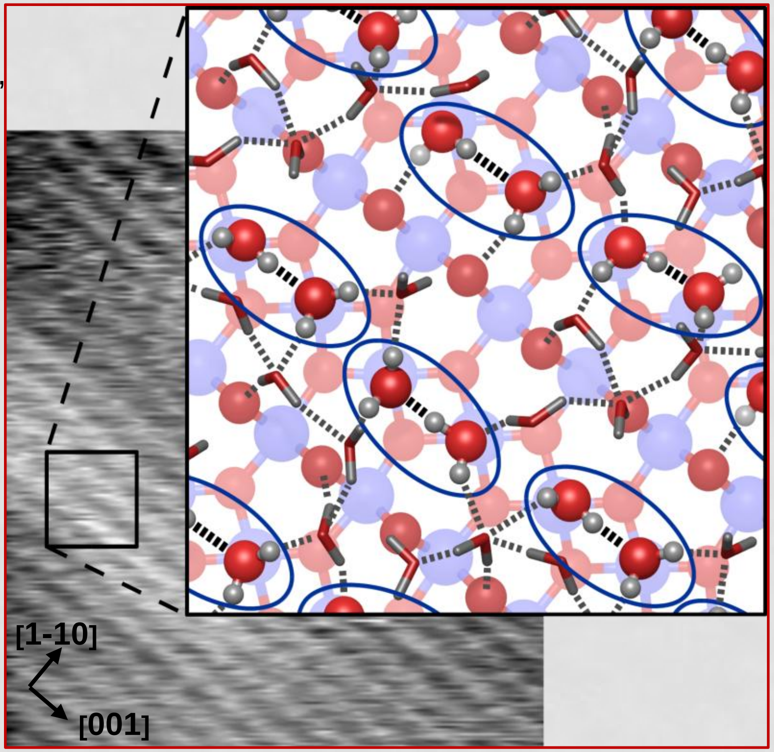
graphic elaboration from: Murray, P. W., Condon, N. G., & Thornton, G. (1995). *Physical Review B*, *51*(16), 10989.

RUTILE TiO_2 (110) IN HIGH PURITY WATER

- Theory: DFT MD simulation

Jun Cheng and Joost VandeVondele Department of Materials, ETH Zürich,





x 2 periodicity along [001]

Molecular Ordering at the Interface between Liquid Water and Rutile TiO_2 (110)

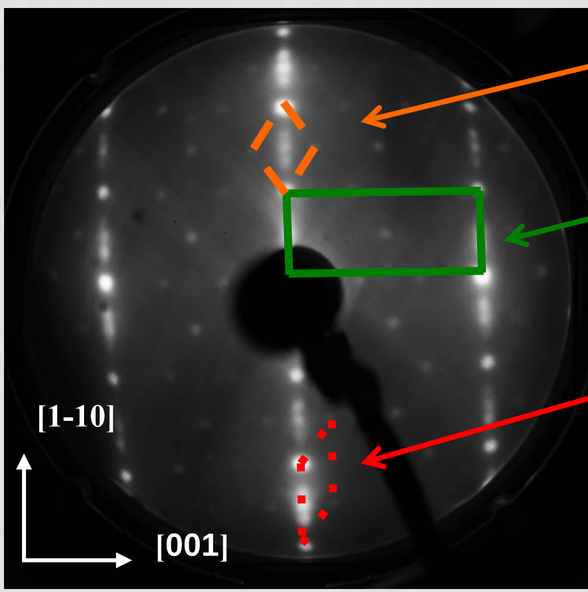
CALCIUM SEGREGATED - RUTILE TiO_2 (110)

The presence of a thin calcium layer onto TiO2 has recently raised the interest of medicine to simulate bone growth in biomedical implants.

Sputtering and annealing cycles
at T ≈ 1000K-1100K

CALCIUM SEGREGATION

c(6x2) superstructure

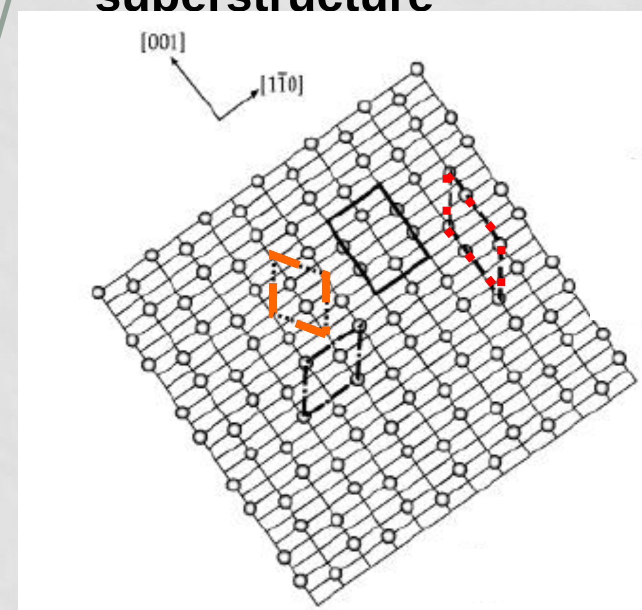


LEED pattern (E=65eV)

$$\begin{bmatrix} 3 & 1 \\ 3 & -1 \end{bmatrix}$$
unit cell

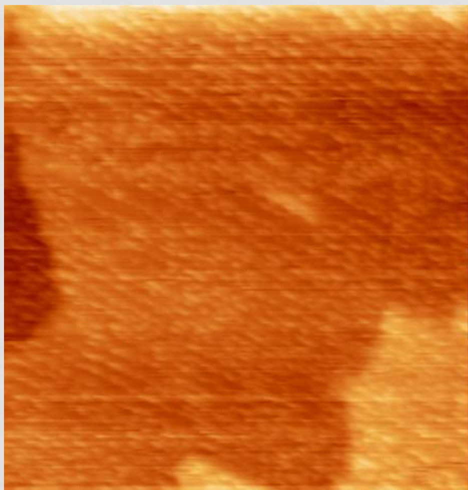
1x1
unit cell

$$\begin{bmatrix} 6 & 0 \\ 3 & 1 \end{bmatrix}$$
unit cell

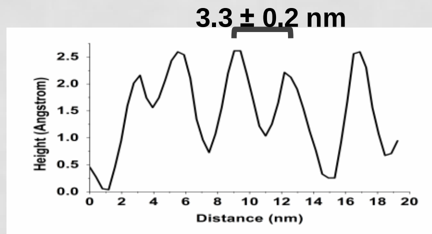


Bikondoa, O. et al. J. Phys. Chem. B, 2004, 108, 16768-16771.

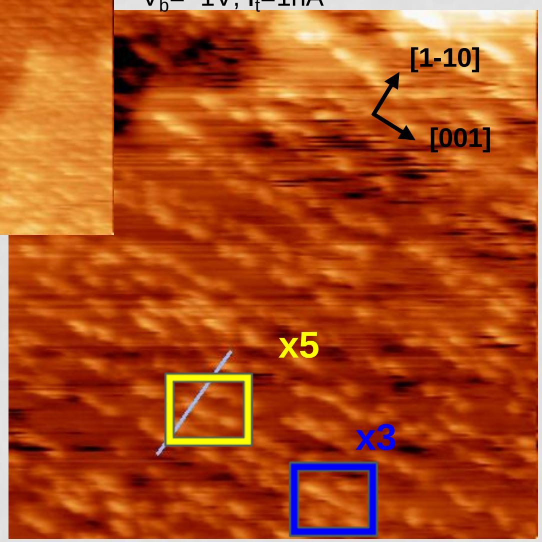
CALCIUM SEGREGATED - RUTILE TiO_2 (110) IN HIGH PURITY WATER



STM image 167x167nm^2
V_b= -1V, I_t=1nA



STM image 82x82nm^2
V_b= -1V, I_t=1nA

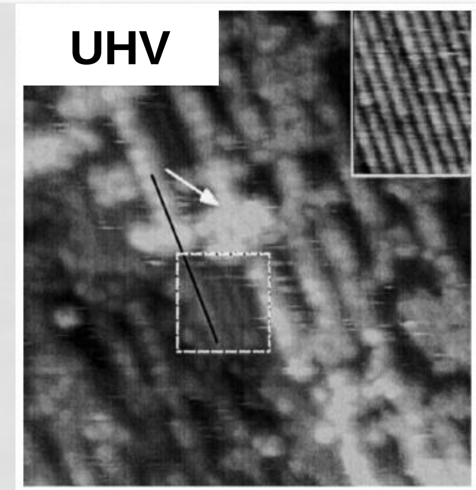


- Monoatomic steps

- Stripes along [001]: Ca structures 1–5nm long

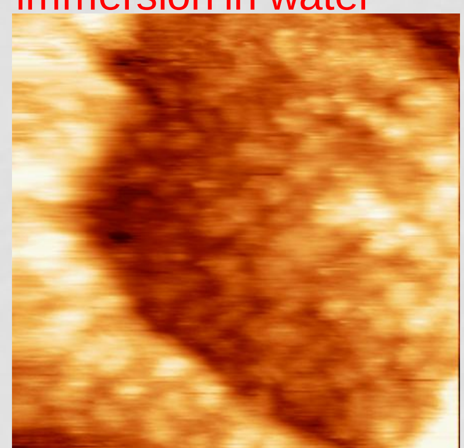
- distances between stripes along the [001]
  x5 ; x4 ; x3 $a_{[1-10]}$, up to x8 $a_{[1-10]}$

- FWHM of 1.2 ± 0.2 nm, height of 2.0 ± 0.5 Å.



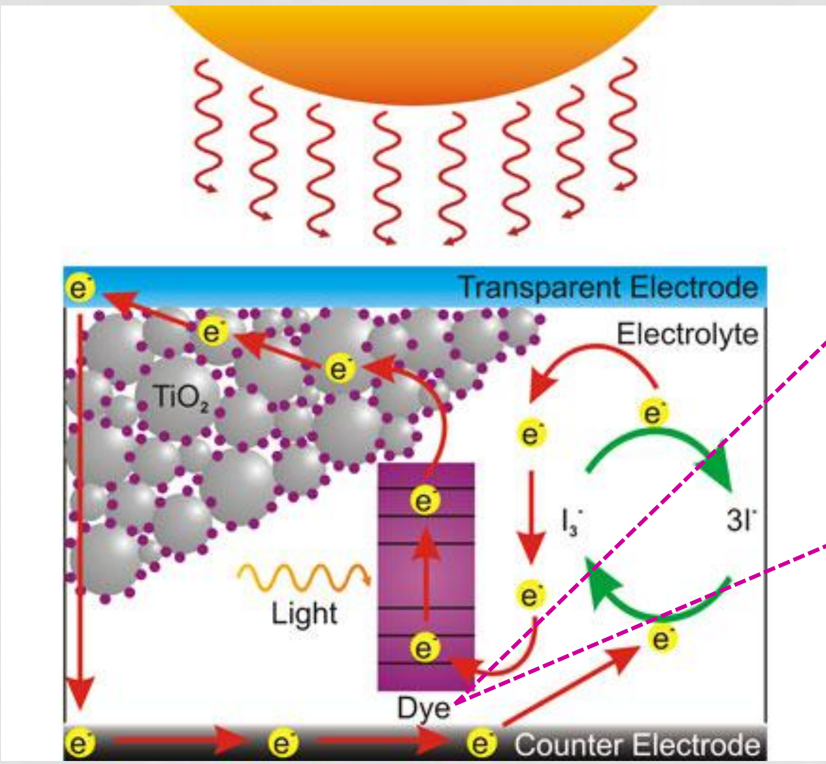
STM image 18x18nm^2; inset 5.3x6.8nm^2
Zhang, et al. Surf.Sci. (1998) *412*, 242.

After 48 hours immersion in water



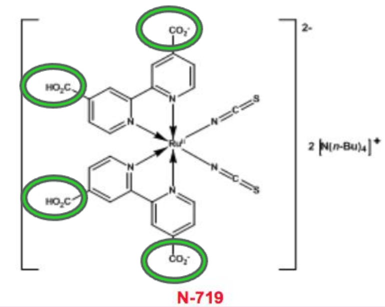
STM image: 74x74m^2
V_b= -1V, I_t=1nA

THE TiO_2 (110) SURFACE FOR PHOTOVOLTAIC APPLICATIONS: DYE SENSITIZED SOLAR CELLS



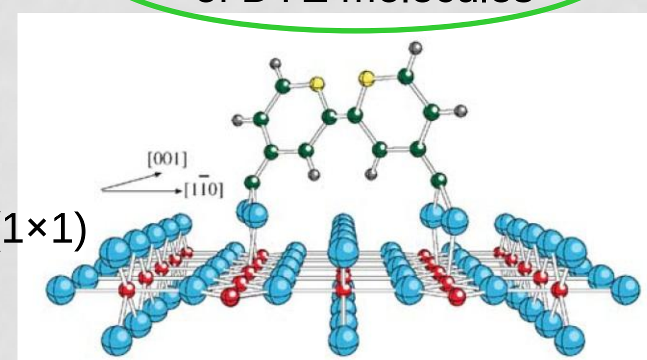
www.merck-performance-materials.html

DYE MOLECULES
N-719



TiO_2 binding groups of DYE molecules

$TiO_2(110)(1×1)$

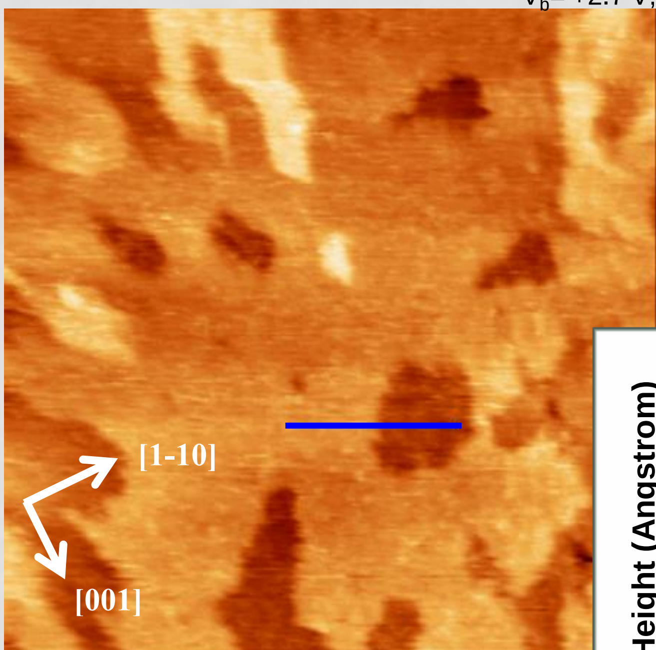


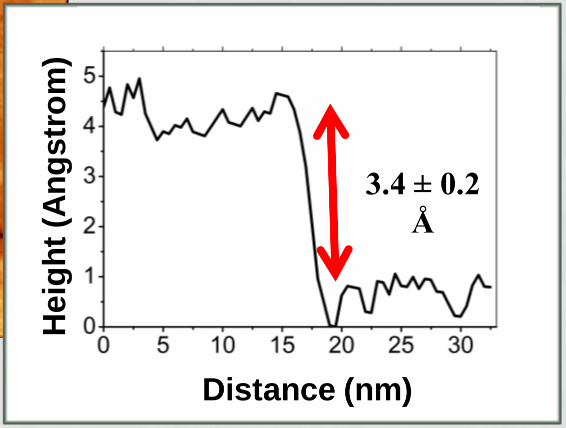
Pang, C. L.; Lindsay, R. and Thornton, G. *Chemical Society Reviews*, 2008, *37,* 2328.
Ball and stick model of the most likely adsorption geometry for bisisonicotinate on TiO2(110)(1×1)

RUTILE TiO_2 (110) IN ETHANOL

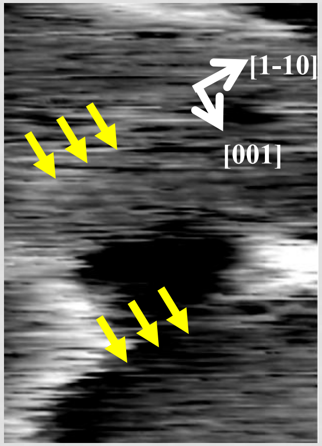
- Preparation of a new sample in UHV: TiO_2 (110) – (1x1) surface
- Immersion in pure ethanol (>99.8%)
- **monoatomic steps**

STM image: 127.9 x 127.9 nm^2, V_b= +2.7 V, I_t=1 nA





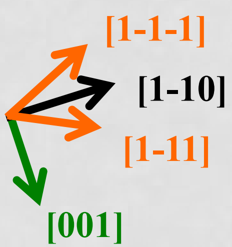
- **structure at low scale**:
- row pattern

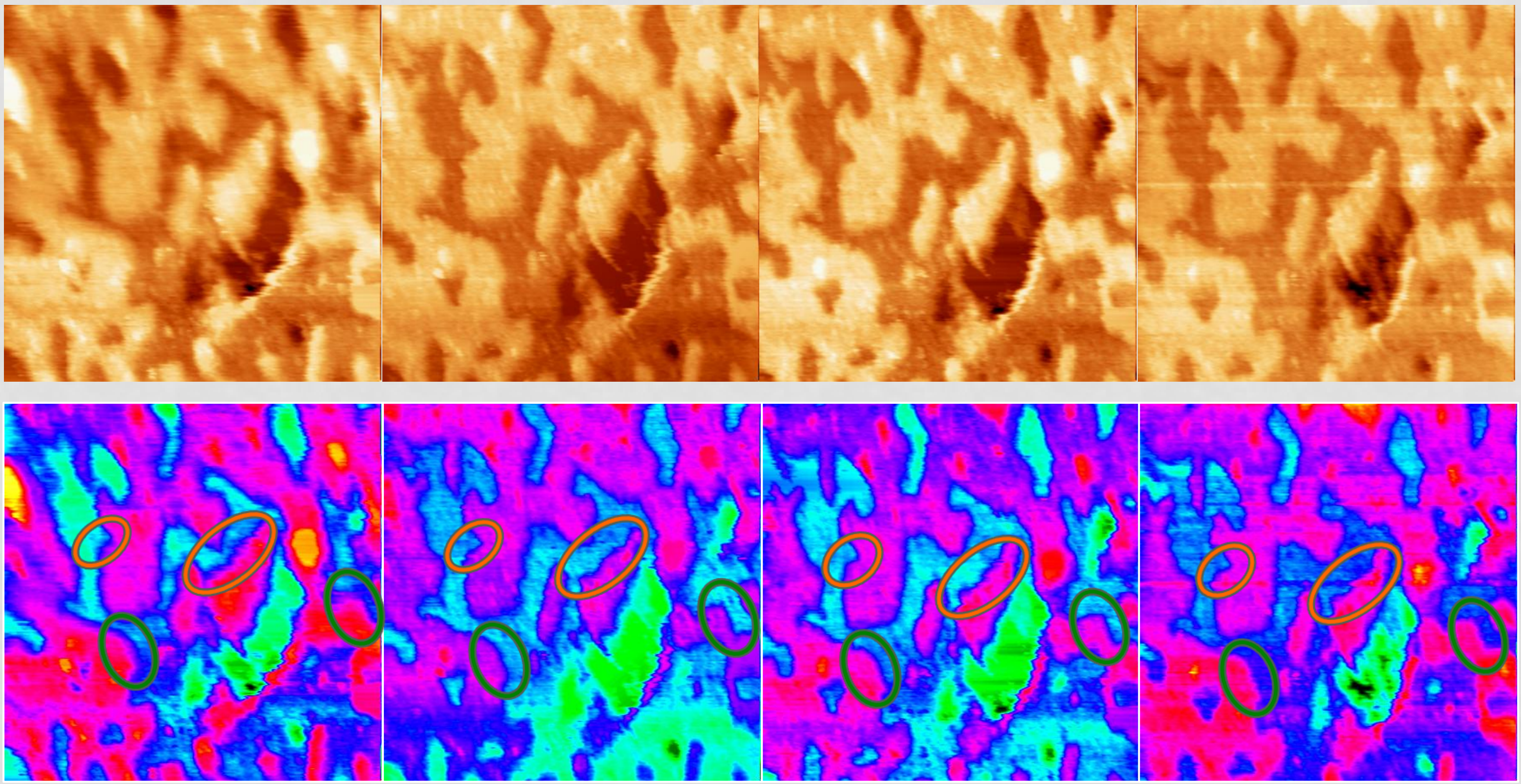


STM image 14.2 x 14.2 nm^2, V_b= +2.6 V, I_t=1 nA.

RUTILE TiO_2 (110) IN ETHANOL

- step edge modification, mainly along the <1-11>

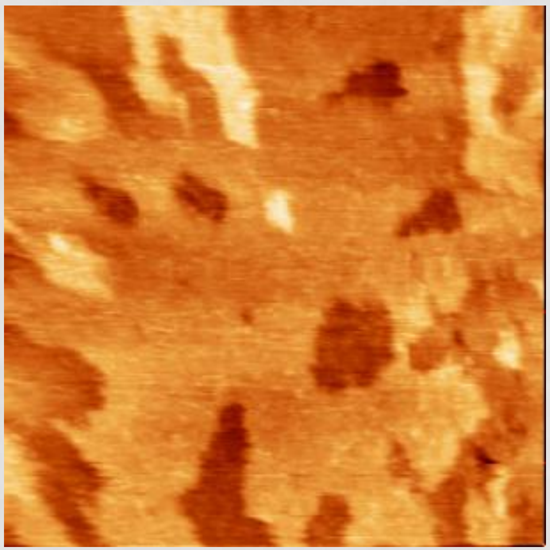




STM images: sequence 71.1 x 71.1 nm^2, V_b= +2.7 V, I_t=1 nA.

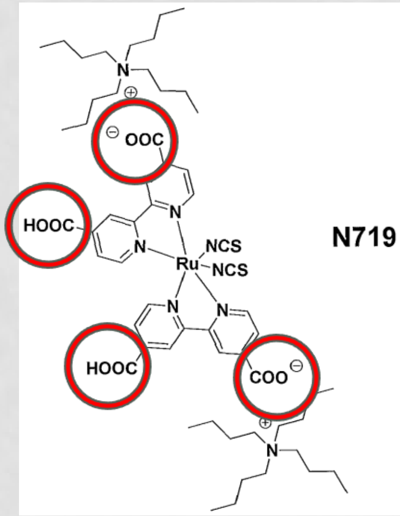
RUTILE TiO_2 (110) IN ETHANOL WITH DYE N-719

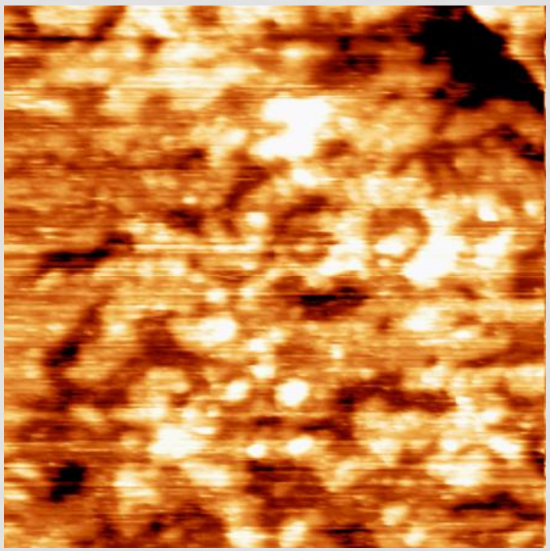
TiO_2 rutile (110) in pure ethanol → **ethanol + dye N719 (10^{-6}M)**



STM image 129x129 nm^2, V_b = +2,7 V I_t = 1nA

The sample was left left overnight in contact with dye solution (10^{-6}M) and then rinsed with pure ethanol. All the STM measurements are taken in a solution of pure ethanol.

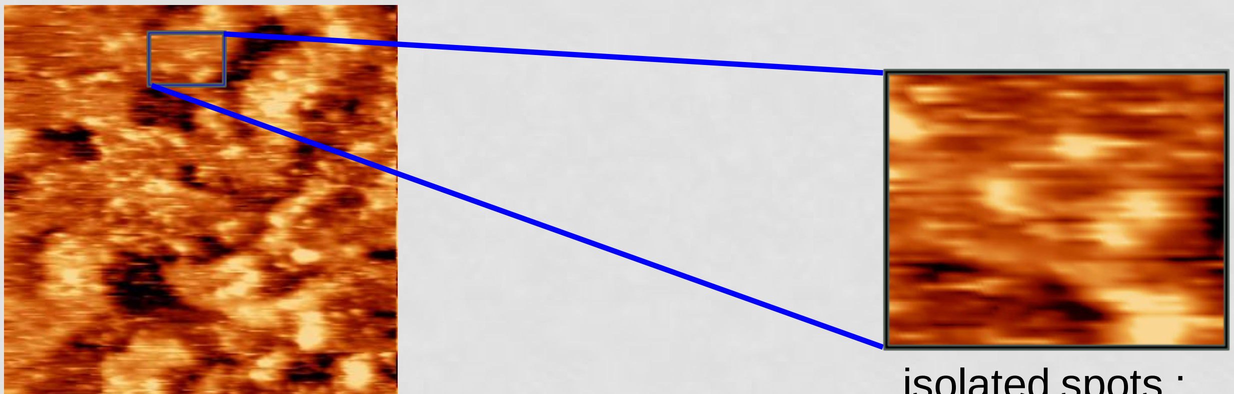




STM image 174x174nm^{2,},V_b = +2.6 V I_t = 1nA

web source: http://www.google.com/patents/EP2455955A2?cl=en

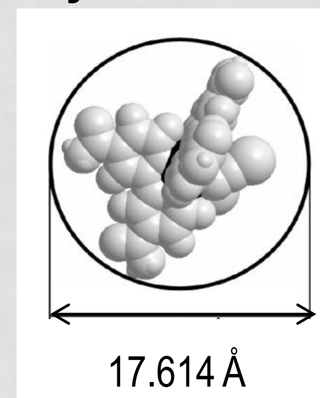
RUTILE TiO_2 (110) IN ETHANOL WITH DYE N-719

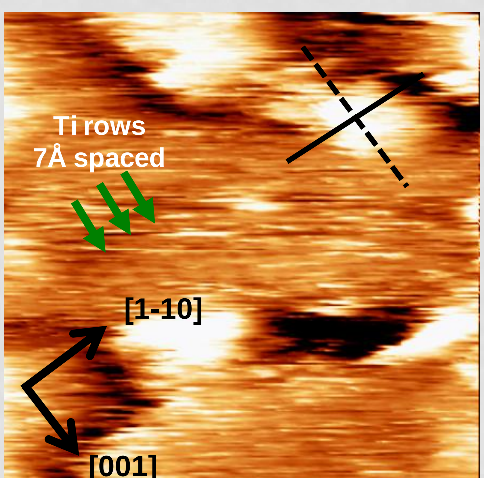


STM image about 85x85 nm^2,
V_b = +2,69 V I_t = 1nA

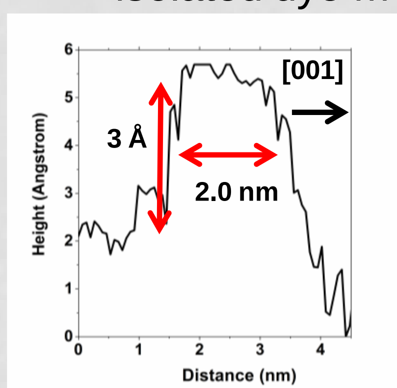
isolated spots :
1.6 – 2.0 nm wide

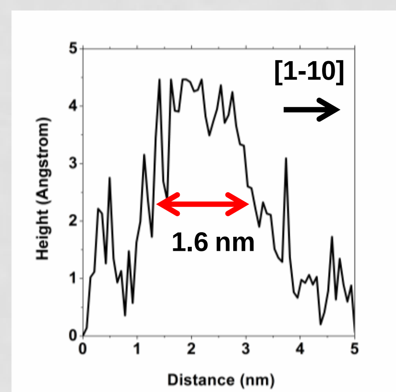
dye molecules





- isolated dye molecules

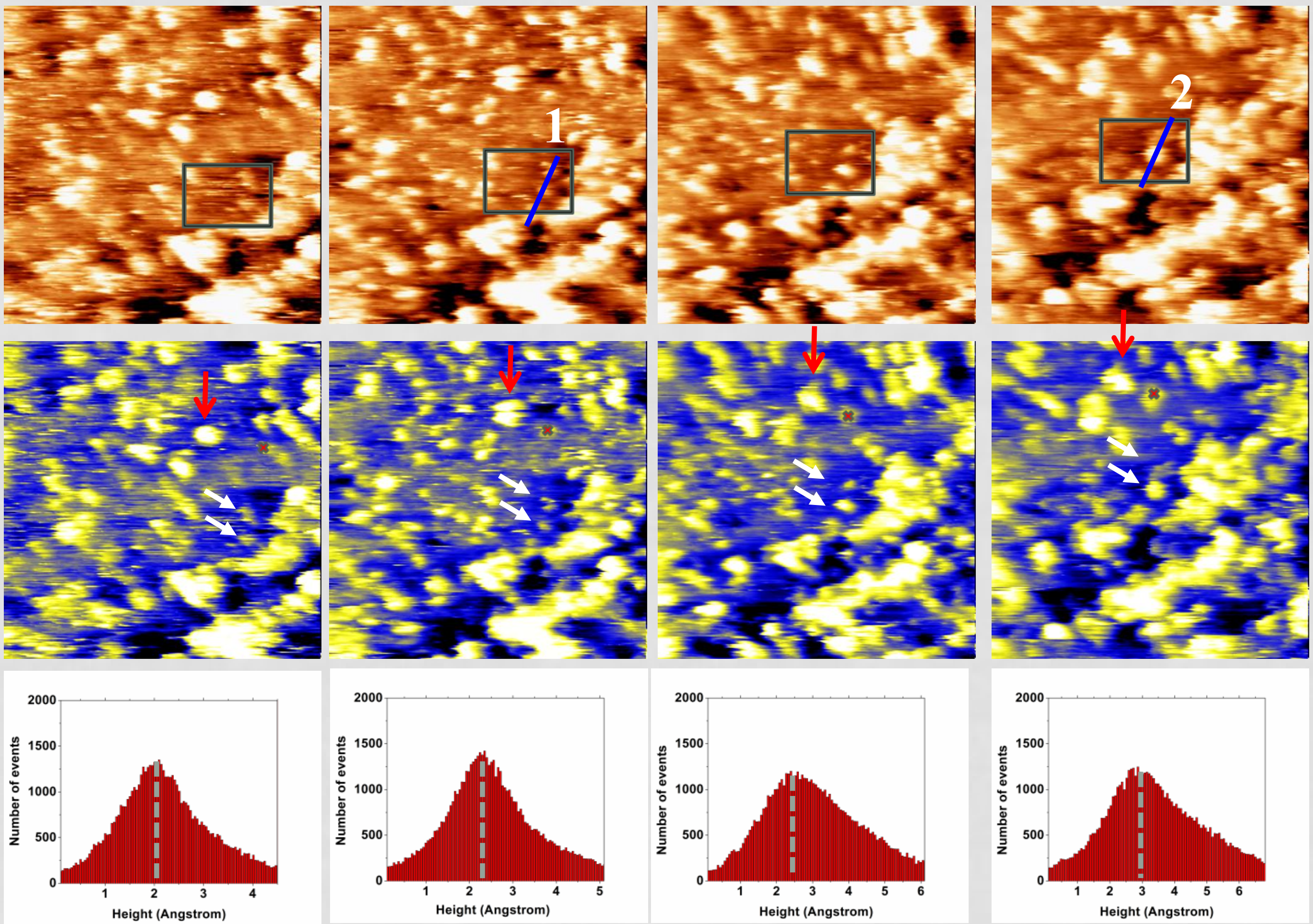


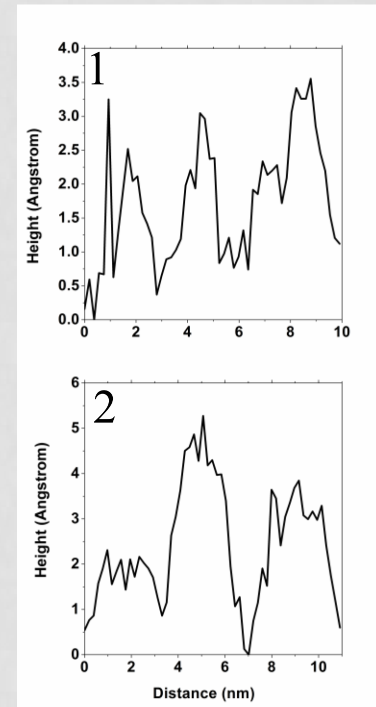


STM image 14.2 x 14.2 nm^2,
V_b = + 2.6 V, I_t = 1 nA

RUTILE TiO_2 (110) IN ETHANOL WITH DYE N-719

- mobility and aggregation of dye molecules on the surface





……

STM images, sequence: 42.6 x 42.6 nm^2, V_b = + 2.6 V, I_t = 1 nA.

CONCLUSIONS

- **Study of metal oxide surfaces in realistic and technologically important environment**


BEILSTEIN JOURNAL OF NANOTECHNOLOGY

In situ scanning tunneling microscopy study of Ca-modified rutile $TiO_2(110)$ in bulk water

Full Research Paper

Abstract

DOI: 10.1002/admi.201500246

Materials Views

ADVANCED MATERIALS INTERFACES

FULL PAPER

Molecular Ordering at the Interface Between Liquid Water and Rutile $TiO_2(110)$

Giulia Serrano, Beatrice Bonanni, Marco Di Giovannantonio, Tomasz Kosmala, Michael Schmid, Ulrike Diebold, Aldo Di Carlo, Jun Cheng, Joost VandeVondele, Klaus Wandelt, and Claudio Goletti*

1. Introduction

In-situ investigation of the rutile TiO_2/liquid interface

TiO_2 (110) in **high purity water**

first atom-resolved images

stability of the surface

ordering of the adsorbed H_2O overlayer

morphology and stability of the calcium-terminated surface

TiO_2 (110) **in ethanol** with **dye molecules**

step edge modification (<u>ethanol</u>)

adsorption of isolated and aggregated <u>dye molecules</u>

- **<u>the interface in bulk liquid is different with respect to UHV !!!</u>**

SURF GROUP @ UNITORV

SURF Group: ***SUrface and inteRFace in liquid and UHV***
Physics Dept., University of Rome "Tor Vergata"

MEMBERS Prof. C. Goletti, Dr. **B. Bonanni**

Post-doc researchers T. Kosmala, S. Breuer

Ph.D. Students **G. Serrano,** M. Di Giovannantonio, L. Fazi

TECHNIQUES: RAS, SDR, **EC-STM, XPS chamber with EC pre-chamber, variable temperature UHV-STM (Prof. K. Wandelt , Bonn Universitat, donation, September 2011)**

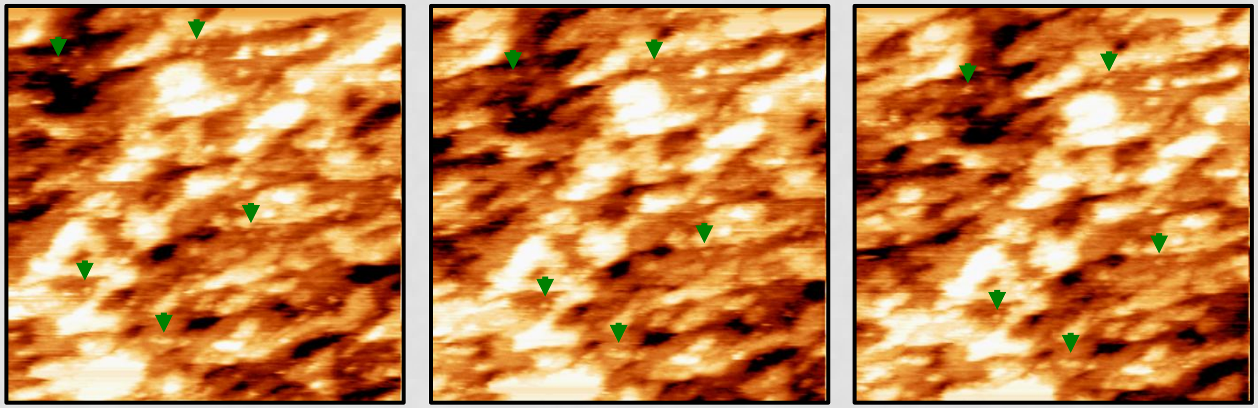
COLLABORATIONS: Prof. K. Wandelt , Bonn Universitat

Prof. Aldo Di Carlo (Electronic Engineering Dept. University of Rome "Tor Vergata", CHOSE Polo Solare Organico Regione Lazio, Rome)

Prof. Ulrike Diebold (Institute of Applied Physics - University of Technology, Wien)

Prof. Joost VandeVondele (Department of Materials, ETH Zürich, Switzerland)

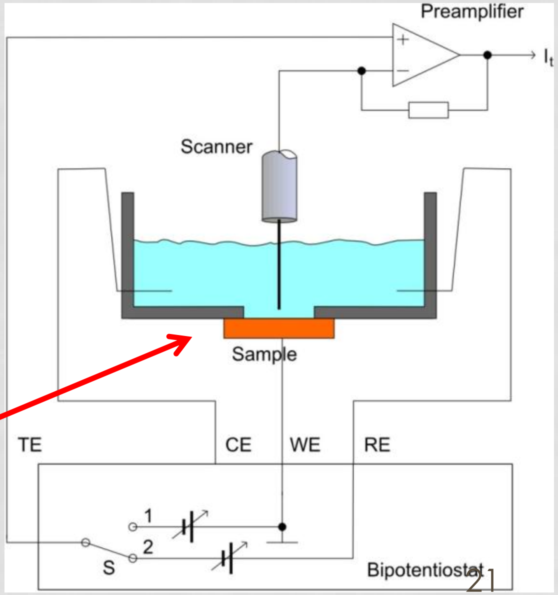
TIO$_2$ RUTILE (110) IN ETHANOL WITH DYE Z-907 MOLECULES



Sample
0 Volts vs.
Pt.

STM images, sequence:
115.2 x 115.2, nm^2
V_b = - 1.1 V, I_t = 1 nA

- Measurements in dye solution
- Stability at zero potential



POTENTIODYNAMIC IMAGES

potential applied to the sample