Molecular Ordering at the Interface Between Liquid Water and Rutile TiO$_2$ (110)

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Wide range of technological applications

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

Solid/liquid interfaces


http://blog.sciencenet.cn/

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

TiO₂
Rutile phase

TiO₂
Rutile (110) Surface
(lowest surface energy)
RUTILE TiO$_2$ (110) SURFACE – UHV STUDIES…

- **Adsorption of water vapors**


- **Deposition of organic molecules ex-situ**

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

- **Molecular or dissociative water adsorption at the real TiO$_2$/water interface?**

“[…] 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 TiO₂ 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”


“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.”

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


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

Sasahara, A. and Tomitori, M. J.
C4C5-C4C10.
300x300 nm$^2$

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

MONOATOMIC STEPS

previous AFM studies reported a degradation of the surface for UHV prepared samples
RUTILE TiO$_2$ (110) IN HIGH PURITY WATER

- **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

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


Charge density distribution

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

UHV

STM image of TiO$_2$ (110) in water.
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$_2$O molecules adsorbed on alternating Ti atoms

J. Matthiesen…., F. Besenbacher, PRL 102, 226101 (2009)
RUTILE TiO$_2$ (110) IN HIGH PURITY WATER

**H$_2$O molecules adsorption: ordered overlayer**

STM image in water 10x10 nm$^2$

$V_b$= -700mV, $I_t$ = 1nA

2D-FFT

$p(2x1)$ cell

$c(2x2)$ cell

RUTILE TiO$_2$ (110) IN HIGH PURITY WATER

- Theory: DFT MD simulation

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

Molecular Ordering at the Interface between Liquid Water and 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 SEGREGATED - RUTILE TiO$_2$ (110) IN HIGH PURITY WATER

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

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

After 48 hours immersion in water

STM image 18x18nm$^2$; inset 5.3x6.8nm$^2$

STM image: 74x74m$^2$
$V_b= -1V$, $I_t=1nA$
THE TiO$_2$ (110) SURFACE FOR PHOTOVOLTAIC APPLICATIONS: DYE SENSITIZED SOLAR CELLS

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 TiO$_2$(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
  - 3.4 ± 0.2 Å
  - Height (Angstrom) vs. Distance (nm)

- **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, $I_z$=1 nA.
The sample was left overnight in contact with dye solution (10⁻⁶M) and then rinsed with pure ethanol. All the STM measurements are taken in a solution of pure ethanol.

web source:
RUTILE TiO$_2$ (110) IN ETHANOL WITH DYE N-719

STM image about 85x85 nm$^2$, $V_b = +2.69$ V $I_t = 1$nA

isolated spots: 1.6 – 2.0 nm wide

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

• isolated dye molecules

Ti rows
7Å spaced

[1-10]

[001]

17.614 Å

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

• dye molecules
RUTILE \( \text{TiO}_2 \) (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\(^2\), \( V_d = +2.6 \) V, \( I_t = 1 \) nA.
CONCLUSIONS

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

- 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$_2$O overlayer
  - morphology and stability of the calcium-terminated surface

- TiO$_2$ (110) in ethanol with dye molecules
  - step edge modification (ethanol)
  - adsorption of isolated and aggregated dye molecules

- the interface in bulk liquid is different with respect to UHV !!!
SURF Group: *SUface 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)
TIO₂ RUTILE (110) IN ETHANOL WITH DYE Z-907 MOLECULES

- Measurements in dye solution
- Stability at zero potential

Sample
0 Volts vs. Pt.

STM images, sequence:
115.2 x 115.2, nm²
V₀ = -1.1 V, I₁ = 1 nA

POTENTIODYNAMIC IMAGES

potential applied to the sample