The TiO$_2$/water interface: first principles simulations

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Expt: U. Diebold & co, TU-Wien
Under ambient conditions most solid surfaces are covered by a thin film of water.

Water-TiO$_2$ interfaces are relevant to all applications of TiO$_2$, ranging from pigments and coatings to photocatalysis, gas sensors, and biocompatible devices.
Photocatalysis: the basic mechanism

Photocatalyst Materials

Mixture of TiO$_2$ rutile and anatase

- Rutile stable in bulk - Anatase in Nanoparticles
  (Zhang, Banfield, J Mater Chem, 1998, 8, 2073)
- Anatase photocatalytically more active than rutile
  (Kavan, Grätzel, Gilbert, Klenzen, Scheel, J Am Chem Soc, 1996, 118, 671)
Scheme for Photocatalytic Water Splitting

typically n-TiO2
Issues of TiO$_2$

- Low efficiency, mainly due to large band gap
- Rutile $E_g = 3.0$ eV (387 nm)
- Anatase $E_g = 3.2$ eV (413 nm)
- No absorption in the Vis
Dye-sensitized solar cells

Device schematics

Operation principle
Water on rutile TiO$_2$(110)

A paradigm for surface science and theoretical studies of water-metal oxide interactions
Rutile TiO$_2$ (110)
5-10% surface $O$-vacancies on rutile TiO$_2$(110)

Rutile (110)

Empty state STM image of rutile (110) (bright rows $\equiv$ Ti atoms)
Does water adsorb in molecular or dissociated form?

- **Surface science experiments**: intact molecules at regular Ti5c sites, dissociation at surface oxygen vacancies

- **Theoretical studies**: many controversial results!
(A) Dissociated water at low coverage
(B) Mixed molecular dissociated adsorption at monolayer coverage

Lindan et al PRL (1998)
Influence of slab thickness and xc-functional on the character of water adsorption on rutile (110)

Liu et al PRB (2010)
TABLE I. Adsorption energies, $E_{\text{ads}}$ (eV/water), from VASP at 1 and 0.5 ML for four-layer and nine-layer slabs with several xc functionals. $E_{\text{ads}} = E_{\text{TiO}_2(110)} + E_{\text{water}} - E_{\text{water/TiO}_2(110)}$, where $E_{\text{water/TiO}_2(110)}$, $E_{\text{TiO}_2(110)}$, and $E_{\text{water}}$ are the total energies of the adsorption system, the clean TiO$_2$(110) surface, and the appropriate number of isolated gas phase water molecules, respectively. The most stable state is indicated in bold.

<table>
<thead>
<tr>
<th>Layers</th>
<th>Functional</th>
<th>1 ML</th>
<th>0.5 ML</th>
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<tr>
<td></td>
<td></td>
<td>INTACT</td>
<td>PDIS</td>
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<tr>
<td>4</td>
<td>PBE</td>
<td>0.77</td>
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<td>B3LYP</td>
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<td>0.57</td>
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<tr>
<td>9</td>
<td>PBE</td>
<td>0.79</td>
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<tr>
<td></td>
<td>HSE06</td>
<td>0.91</td>
<td>0.85</td>
</tr>
</tbody>
</table>
Water – rutile (110) interface

Liu et al PRB (2010)
Water on anatase(101)
$\text{TiO}_2$ anatase surface

Natural Anatase crystal

Calculated

(101) surface dominates the anatase morphology


Lazzeri et al., *Phys Rev B*, 2001
H$_2$O on anatase (101)

Vittadini et al. PRL 81, 2954 (1998)

• Dissociation of H$_2$O on the (101) surface is unfavored, in line with the stability of the surface.
• Molecular state stabilized by H-bonds with surface O$_{2c}$

Molecular:
$E_{ads} = 0.74$ eV

Dissociative:
$E_{ads} = 0.2-0.3$ eV
Water on anatase TiO$_2$(101)

TPD spectrum

D$_2$O Coverage
(molecules/cm$^2$, x 10$^{14}$)

- 0 (bkgd)
- 1.7
- 3.4
- 5.1
- 6.8
- 8.5
- 10.2
- 11.9
- 13.6
- 15.3

250 K: H$_2$O-Ti$_{5c}$
190 K: H$_2$O-O$_{2c}$
160 K: multilayer H$_2$O

No dissociated H$_2$O

(Herman et al, JPC-B 107, 2788, 2003)
Structure of a water monomer on anatase (101):
two H-bonds with lattice O-2c atoms
STM image of an adsorbed water molecule: calcs vs expt

He et al Nat Mat 2009

V=2.75 eV, constant density image (1e-4 a.u.)

• A single H₂O affects several surface sites!
\[ \Delta \rho = \rho(\text{TiO}_2 + \text{H}_2\text{O}) - \rho(\text{TiO}_2) - \rho(\text{H}_2\text{O}) \]

Blue: \( \Delta \rho > 0 \)

Yellow: \( \Delta \rho < 0 \)
Water clusters & Adsorption energy/H$_2$O
Are the predicted structures in agreement with expt?

4-H$_2$O

Lower H$_2$O coverage

monomer

trimer
dimer

Higher H$_2$O coverage

Local 2x2 structure

1-3 water monolayers

Tilocca & Selloni Langmuir 2004
Short H-bonds between 1\textsuperscript{st} and 2\textsuperscript{nd} layer water molecules
Water multilayer: adsorption energies


\[ E_{\text{ads/mol}} = \left\{ \frac{E(B) - E(A) - n \cdot E(H_2O)}{n} \right\} \]

Trend in estimated desorption T in agreement with TPD experiments
Water on anatase TiO$_2$(101)

TPD spectrum

D$_2$O Coverage
(molecules/cm$^2$, x 10$^{14}$)

- 0 (bkgd)
- 1.7
- 3.4
- 5.1
- 6.8
- 8.5
- 10.2
- 11.9
- 13.6
- 15.3

m/e = 20 Intensity (arb. units)

Temperature (K)

250 K: H$_2$O-Ti$_{5c}$
190 K: H$_2$O-O$_{2c}$
160 K: multilayer H$_2$O

No dissociated H$_2$O

(Herman et al, JPC-B 107, 2788, 2003)
What about O-vacancies on anatase (101)?
STM of cleaved Anatase (101)

300 Å x 300 Å, Vs=+1.3V, It=1.9 nA

Anisotropic step edges
(Gong et al, Nature Mater. 2006)

Adsorbed water
(He et al, Nature Mater. 2009)

Subsurface impurities
No surface oxygen vacancies on cleaved Anatase (101)

300 Å x 300 Å, Vs=+1.3V, It=1.9 nA

Anisotropic step edges (Gong et al, Nature Mater. 2006)

Adsorption of water (He et al, Nature Mater. 2009)

Subsurface impurities

He et al, PRL 2009
Vacancies are subsurface @ anatase

DFT calculations

<table>
<thead>
<tr>
<th>Vac.</th>
<th>$E_{\text{form}}$ [eV]</th>
</tr>
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<tbody>
<tr>
<td>Vo1</td>
<td>4.15</td>
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<td>Vo2</td>
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<td>Vo3</td>
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<td>Vo4</td>
<td>3.69</td>
</tr>
<tr>
<td>Vo5</td>
<td>3.65</td>
</tr>
<tr>
<td>Bulk</td>
<td>3.69</td>
</tr>
</tbody>
</table>

Surface O-vacancies can be created by electron bombardment.
Influence of subsurface O-vacancy on water adsorption on anatase (101)

Selectivity: adsorption is stronger at surface site closest to subsurface defect

Molecular adsorption remains favored above O-vacancy but dissociation barrier is ~ 1/2 wrt stoichiometric surface

Aschauer et al., J. Phys Chem. C 114, 2010
Influence of subsurface interstitial on water adsorption

Dissociation favored at sites near the defect

\[ E_{\text{ads}} = 0.84 \text{ eV} \]

\[ E_{\text{ads}} = 1.10 \text{ eV} \]
Prediction confirmed by experiment?

Q: Why stronger water adsorption on reduced surface?

Water coverage at 300K is larger on defective surfaces.
Influence of subsurface interstitial on the structure & dynamics of a water monolayer

- Increased basicity of $O_{2c}$ sites
- Frequent dissociation/reassociation events near defect

AIMD, $T=160K$
Structure of thin water overlayers on defected vs defect-free anatase surface

Defect-free surface

AIMD, T=160K; GGA

Subsurface interstitial
Structure of thin water overlayers on defected vs defect-free anatase surface

Stoichiometric surface

Subsurface interstitial

Tilocca & AS JPCC 2012
Role of water environment on surface structure

(Stabilization of high energy surfaces)
Rutile TiO$_2$(011)

Rutile crystal structure:

\[ \begin{align*}
  a &= 4.587 \, \text{Å} \\
  c &= 2.953 \, \text{Å}
\end{align*} \]

Equilibrium Crystal Shape for rutile TiO$_2$:

The particle exposes the \{110\} and \{011\} faces.
Motivation

TiO$_2$ rutile particles

The particle exposes the {110} and {011} faces.

**WHY?**

Reductive half-reaction at the {110} face
Oxidative half-reaction at the {011} face

T. Ohno et al., New J. of Chem., (’02) 26, 1167
Rutile TiO$_2$(011)-(2x1)

Sample preparation:
- Ar$^+$ sputtering (1keV)
- Annealing at 550 - 750°C

LEED:
- $\rightarrow$ (2x1) reconstruction

STM:
- wide, flat terraces
- high corrugation, ‘easy’ atomic resolution

STM by Diebold at al. 2004

Sample preparation:
- Ar$^+$ sputtering (1keV)
- Annealing at 550 - 750°C

120 x 90 Å$^2$, +1.57 V, 1.5 nA

STM by Diebold at al. 2004
Structure of Rutile TiO$_2$(011)-(1x2)

Unreconstructed (1x1) surface

“Brookite(001)-like model” from SXRD, STM & DFT


See also Torrelles et al. PRL 101, 185501 (2008)
Water adsorption on rutile TiO$_2$(011)

$E_{\text{ads}} = -0.214 \text{ eV}$, $-0.209 \text{ eV}$, $-0.42 \text{ eV}$

Does the presence of water stabilize the 1x1 structure?

$E_{\text{ads}} = -1.07 \text{ eV}$
FPMD simulations of rutile $\text{TiO}_2(011)$ in water (64 $\text{H}_2\text{O}$ molecules)

- Inversion of the stabilities of the reconstructed and unreconstructed surfaces wrt vacuum!
- Surface structures in vacuo or at low water coverages not representative of those in aqueous environment!

Aschauer & AS PRL 2011
Water on anatase TiO$_2$(001)

Dissociative adsorption $\Rightarrow$ high reactivity, in line with the high surface energy of anatase (001)

$E_a = 1.25$ eV
Anatase (001): (1x4) reconstructed in UHV

Bulk-terminated

Reconstructed

What is the structure anatase (001) in the presence of water??
Water on anatase (001)-1x4

Low coverage

Full coverage

(c)

low coverage

Full coverage

(d)
Water on bulk-terminated anatase (001)

Low coverage

(a)

full coverage

(b)
Anatase (001) in humid environment: free energy diagram

Close competition but reconstructed surface remains more stable in the presence of water

Selcuk & AS  JPCC  2013
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