Workshop on Nanoscience for Solar Energy Conversion

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Materials-related aspects of TiO2-based photocatalysis

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Materials-related aspects in TiO$_2$-based photocatalysis: insights from first principles simulations

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“Surface science” studies of TiO$_2$:

• Structure, energetics & reactivity (mostly anatase)
• Rutile vs Anatase (energies and defects)
• A model dye/TiO$_2$ system: catechol/R-TiO$_2$(110)
TiO$_2$-based Photocatalysis: Applications and Promise

- removal of organic pollutants, purifying of water or air
- self-cleaning/desinfecting coatings (bacteria, viruses, cancer cells)
- photoelectrochemical cells, solar cells
- photocatalytic splitting of water, production of hydrogen

**TiO$_2$: Anatase and Rutile**

- **Rutile** is the most stable bulk phase
- **Anatase** usually more active for photocatalysis
Electronic structure: DOS (GGA-PBE)

anatase

\[
\text{Energy (eV)}
\]

\[
\text{DOS}
\]

\[
\text{eg}
\]

\[
\text{t}_{2g}
\]

rutile

\[
\text{Energy (eV)}
\]

\[
\text{DOS}
\]

\[
\text{eg}
\]

\[
\text{t}_{2g}
\]
Experimental observation: Anatase phase is most stable for nanoparticles up to ~ 14 nm.

- Proposed explanation: the smaller the crystal, the larger is the fraction of surface atoms; surface energy makes the anatase phase more favorable

[ Zhang & Banfield, J. Mater. Chem. 8 (2073) 1998]
Surface energy depends almost linearly on the density of under-coordinated Ti atoms.

**Anatase stoichiometric 1 x 1 surfaces**

- (101)
- (100)
- (001)

**DFT calculations: PBE functional plane-waves, ultrasoft pseudopots**

Quantum ESPRESSO: CP90, PWscf

[http://www.democritos.it](http://www.democritos.it)
Crystal shape: theory vs. experiment

theory  natural anatase  anatase nanocrystals


Crystal surface energy: anatase vs. rutile

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

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

• Average surface energy (LDA):
  Rutile = 1.09 J/m²  Anatase = 0.90 J/m²

[ Zhang & Banfield, J. Mater. Chem. 8 (2073) 1998]
Anatase TiO$_2$

(Lazzeri, Vittadini, Selloni, PRB 63, 155409, 2001)
Adsorption of small probe molecules: majority anatase TiO$_2$(101)

\[ \text{H}_2\text{O} \quad \text{CH}_3\text{OH} \quad \text{HCOOH} \]

\[ E_a = 0.74 \text{ eV} \quad E_a = 0.75 \text{ eV} \quad E_a = 0.92 \text{ eV} \]

Molecular adsorption only (MD, 300K)

(Vittadini et al, PRL 81, 2954, 1998; JPC-B 104, 1300, 2000)
(Tilocca and Selloni, JPC-B 108, 19314, 2004)

Weak molecular adsorption $\Rightarrow$ low reactivity, in line with the low surface energy of anatase (101)
Water on anatase TiO$_2$(101)

TPD spectrum

250 K: H$_2$O-Ti$_5$c
190 K: H$_2$O-O$_2$c
160 K: multilayer H$_2$O

No dissociated H$_2$O

CH$_3$OH: Molecular Adsorption (tiny amount of dissociation)

(Herman et al, JPC-B 107, 2788, 2003)
$\text{H}_2\text{O}$ on anatase (101)


\[
E_{\text{ads}} = 0.69 \text{ eV / molecule}
\]

1 ML

3 ML (TL)

(ice-like structure)
Vertical order: layering
Water multilayer: adsorption energies


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

Trend in estimated desorption T in agreement with TPD experiments
Adsorption of small probe molecules: minority anatase TiO$_2$(001)

Dissociative adsorption $\Rightarrow$ high reactivity, in line with the high surface energy of anatase (001)
SFG spectrum of methanol on thin, nanoparticulate film of TiO$_2$. Peaks at 2844 & 2953 cm$^{-1}$ → symmetric and antisymmetric vibrational modes of molecular methanol. Peaks at 2816 & 2919 cm$^{-1}$ → symmetric and antisymmetric modes of adsorbed methoxy CH$_3$ groups.

~50% of dissociated MeOH & H$_2$O on ~2nm anatase nanoparticles inferred from SFG intensities

SFG: Wang, Groenzin, Shultz JACS 2004, 2005
Anatase TiO2 single crystals with a large percentage of reactive facets


See also: A. Selloni, Nature Materials 7, 613 (2008)
Anatase (001): (1x4) reconstruction

- Clean anatase (001) is actually reconstructed!
  Herman et al. PRL 84, 3354 (2000)

\[ \gamma = 0.90 \quad \rightarrow \quad \gamma = 0.51 \]

- Most favorable model imply the formation of a polymer of TiO$_2$ units adsorbed on the surface. This lowers the surface energy from 0.90 to 0.51 J/m$^2$
  (Lazzeri & Selloni, PRL 87 (2001) 266105)
Water on anatase TiO$_2$(001)-1×4

- **On hill**
  - Side view
  - Two unit cells
  - $E_{ads} = 1.82$ eV

- **On terrace**
  - $E_{ads} = 1.18$ eV (molecular, weaker than on 1x1)

Can the surface be functionalized before reconstructing?

Gong et al., JCPB 110, 2804(2006)
Anatase vs Rutile: point defects
...much of the surface chemistry of metal oxide is defect-driven...


**Step edges:**

- Very common at crystal surfaces.
- Key role in roughening, faceting, growth...
- On nanocrystals, a large fraction of atoms are at steps

**Color change in TiO$_2$ samples induced by increasing level of oxygen vacancies**

Defects change electronic properties of the material
Structure and STM images

Anatase (101)

Empty state STM image of anatase (101)
Diebold & co. (2008)

Rutile (110)

Empty state STM image of rutile (110) (bright rows $\equiv$ Ti atoms)
Much fewer point defects point defects on anatase (101) vs rutile (110) under similar preparation conditions!
Comparing O-vacancy formation energies

Anatase (101)

Anatase (001)- 1x4

Rutile (110)
Anatase (101)

<table>
<thead>
<tr>
<th>Vo1</th>
<th>Vo2</th>
<th>Vo3</th>
<th>Vo4</th>
<th>Vo5</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.15</td>
<td>(5.40)</td>
<td>(4.73)</td>
<td>3.69</td>
<td>3.65</td>
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</table>

Anatase(001)-1x4

<table>
<thead>
<tr>
<th>Vo1</th>
<th>Vo2</th>
<th>Vo3</th>
<th>Vo4</th>
<th>Vo5</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.57</td>
<td>5.17</td>
<td>4.29</td>
<td>4.78</td>
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Rutile(110)

<table>
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<th>Vo1</th>
<th>Vo2</th>
<th>Vo3</th>
<th>Vo4</th>
<th>Vo5</th>
<th>Vo6</th>
<th>Vo7</th>
<th>Vo8</th>
<th>Vo9</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.68</td>
<td>4.50</td>
<td>3.99</td>
<td>5.23</td>
<td>4.73</td>
<td>5.28</td>
<td>4.46</td>
<td>4.67</td>
<td>4.38</td>
</tr>
</tbody>
</table>
Prediction

- **Anatase**: O-vacancies prefer subsurface rather than surface sites.
- **Rutile**: surface O-bridging and sub-bridging sites are favored with respect to subsurface and bulk sites

agrees also with resonant photoemission data (Thomas, Flavell & co, PRB 75, 035105 (2007))
Relaxed atomic structure before (upper row) and after (lower row) creation of an O-vacancy at surface and subsurface sites of the anatase(101) surface: (a,d) Vo1; (b,e) Vo4; (c,f) Vo5. ⇒ Relaxation is more important at subsurface sites, surface is more “rigid”
Facile O-vacancy diffusion from surface to subsurface

Potential energy profile along MEP: barrier = 0.74 eV

Selected configurations along MEP
Surface vs subsurface distribution of O-vacancies in anatase is different from that in rutile.

O-vacancies are most likely to occur on the surface in rutile.

In anatase, a relatively defect-free surface is predicted, i.e. defects are mainly confined in the subsurface region.
Adsorption of catechol on TiO$_2$(110)
(collaboration with U. Diebold, Tulane)

1,2 benzenediol

Motivation:
- Model dye/TiO$_2$ semiconductor system
- Model ‘sticky molecule’ for photocatalytic cleaning of TiO$_2$ coatings (on EUV mirrors)
Step 1 (expt) -
STM measurements show the formation of a well-ordered superstructure with a $4 \times 1$ periodicity at saturation coverage.

STM images (10 x 10 nm$^2$) of a TiO$_2$(110) surface covered with a $4 \times 1$ overlayer of catechol, recorded on the same area with sample bias voltages of (a) +0.9 V and (b) +0.6 V and a tunneling current of ~0.03 nA.
Step 2 (calc) - Adsorption structures of 0.5 ML catechol on TiO$_2$(110) from DFT (2 mol/(4x1) cell)

D1 = mono-dentate

D2 = bi-dentate

Tilted molecules favored b/c of reduced repulsion
H-bonding favors tilted D1 structures
Adsorption structures & simulated STM images of 4x1 ML catechol on TiO$_2$(110) from DFT calcs
Step 3 (expt)

UPS valence band spectra ($h\nu = 40$ eV), from a clean TiO$_2$(110) surface and after exposure to a saturation coverage of catechol at RT. The inset shows the intensity variation of these states with the analyzer take-off angle.
Step 4 (th)

Total DOS of $4 \times 1$ ML catechol/TiO$_2$ (110) + DOS for the clean surface (back curve). Energy zero = theor Fermi energy.

Only bidentate (D2) molecules introduce states in the gap (increased mixing with Ti conduction band states)
**SUMMARY & CONCLUSIONS**

Catechol / TiO$_2$(110) forms two full coverage H-bonded structures, D1-D1 and D1-D2. These two structures can easily convert from one into the other via proton exchange between the surface and the adsorbed catechol.

Strong correlation between electronic structure & adsorption geometry.

Occupied states in the TiO$_2$ band gap are traps for photo-generated holes $\Rightarrow$ D2 catechol more easily photo-oxidized than D1 catechol.
Many thanks to

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Andrea Vittadini
Jianguo Wang

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