First principles simulations of materials and processes in photocatalysis

Annabella Selloni
Department of Chemistry, Princeton University

Work with:
Ulrich Aschauer, Jia Chen, Hongzhi Cheng,
Cristiana Di Valentin, Weiyi Hou, Ye-Fei Li,
Patrick Sit, Federico Zipoli

Expt: U. Diebold & co, TU-Wien
Photocatalysis: the basic mechanism

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

Photocatalyst Materials

Mixture of TiO$_2$ rutile and anatase


Water splitting in PEC cell

\[ \text{H}_2\text{O} \rightarrow \text{H}_2^+ + \frac{1}{2} \text{O}_2 \]

\[ \Delta G = 2.46 \text{ eV/H}_2\text{O} \]

**Oxidation**

\[ \text{H}_2\text{O} + 2\text{h}^+ \rightarrow \frac{1}{2} \text{O}_2 + 2\text{H}^+ \]

**Reduction**

\[ 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \]

N-type semiconductor, e.g. TiO\(_2\)

Pt typically used as cathode

**Issues:** photo-oxidation inefficient

Pt very expensive
Challenges for theory/simulation

- **Materials properties**: electronic structure, excitations (electrons, holes, excitons), transport properties (defects, e-ph, ..)

- **Solid-liquid interface**, surface structure, interface electronic structure (level alignment at the interface)

- **Electron & proton transfer reactions**: chemical reactivity, pathways and barriers
Outline

- **Polaronic states in TiO$_2$:**
  - surface/subsurface defects
  - Electron & holes in photo-excited anatase

- **Interfacial electron transfer at the TiO$_2$-gas & TiO$_2$/water interfaces**
**Approach**

- DFT with GGA-PBE and/or B3LYP/PBE0
- Minimum energy pathways and barriers via NEB
- First principles molecular dynamics (FPMD)
- Free energy barriers via thermodynamic integration
- Quantum ESPRESSO
Polaronic states in TiO$_2$

Color change in rutile samples induced by increasing level of reduction (oxygen vacancies and Ti interstitials)

Anatase: from bulk to nano
The paradigm: surface O-vacancy on rutile 
\( \text{TiO}_2(110) \)

Rutile (110)

Empty state STM image of rutile 
(110) (bright rows \( \equiv \) Ti atoms)
The paradigm: surface O-vacancy on rutile TiO$_2$(110)

O-vacancy $\rightarrow$ two excess electrons: delocalized or localized Ti$^{3+}$ species?

- Experiments suggesting localized Ti$^{3+}$ species:
  - EPR (bulk) shows paramagnetic defects with 3d$^1$ character
  - UPS and EELS show states in the gap $\sim 0.8$ eV below CB

- Expts suggesting partially delocalized Ti$^{3+}$ species
  - defect charge shared by several surface and subsurface Ti sites according to Photoelectron Diffraction (PED) (Krüger et al, PRL 100 (2008)) and occupied state STM (Minato et al, JCP 130 (2009))
Ti$^{3+}$ species in reduced TiO$_2$(110): theory

Delocalized states at energies near the bottom of the CB and no gap state predicted by DFT-LDA and DFT-GGA calculations: in contrast with EPR, UPS & EELS experiments.

Localized triplet state with energy in the band gap predicted by hybrid functional and DFT+U calculations (T= 0K).

Di Valentin et al. PRL 97 (2006)
Polaronic nature of O vacancy states

Polaronic distortion (and spin-polarization) essential for the formation of localized gap states
Polaronic nature of O vacancy and OH groups

How to explain the partial delocalization seen by PED and STM?
Ti$^{3+}$ species in reduced TiO$_2$(110): theory

Distribution of Ti$^{3+}$ sites in reduced rutile TiO$_2$ (110)

DFT+U calculations:
Deskins et al JPCC 115 (2011)

several possible nearly degenerate localization sites at the TiO2 surface

..electrons can hop between different sites
Ti$^{3+}$ species in reduced TiO$_2$(110)

- At $T=0K$, localized states preferred; many possible localization sites, nearly degenerate in energy.

- Electrons easily hop from one site to the other with small ($< 0.1$ eV) activation barrier at finite $T$ → effectively partially delocalized state.

- Hybrid functionals or +U corrections essential to capture polaronic character of excess charges.
TiO$_2$ anatase surface

Natural Anatase crystal

Calculated

(101) surface dominates the anatase morphology

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, $V_s=+1.3V$, $I_t=1.9$ nA

He et al, PRL 2009

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

300 Å x 300 Å, $V_s = +1.3\,\text{V}, \, I_t = 1.9\,\text{nA}$

<table>
<thead>
<tr>
<th>Vac.</th>
<th>$E_{\text{form}}$ [eV]</th>
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<tbody>
<tr>
<td>Vo1</td>
<td>4.15</td>
</tr>
<tr>
<td>Vo2</td>
<td>5.40</td>
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<tr>
<td>Vo3</td>
<td>4.73</td>
</tr>
<tr>
<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
Diffusion of $O_{\text{vac}}$’s into anatase

$\sim 0.75 \text{ eV barrier for O-vacancy surface} \rightarrow \text{sub-surface migration predicted by DFT-GGA}$
Diffusion of $\text{O}_{\text{vac}}$’s into anatase

(STM images @78K)

After irradiation @ 100 K

10 min @ 325 K

Surface & subsurface O vacancy @ anatase (101): DFT + U calculations

Surface $V_{O_1}$, $S=1$

Subsurface $V_{O_4}$, $S=1$

$U = 3.5$ eV (calculated)

Surface & subsurface O vacancy at anatase (101): DFT + U calculations

Polaronic effect over-estimated? Temperature? ???
Surface & subsurface O vacancy @ anatase (101): PBE0 calculations

Surface Vo:
E = 0.

Subsurface Vo:
E = -0.61 eV
Bulk and surface polarons in anatase

Do electrons & holes localize in the absence of structural defects or impurity centers?
Electrons, holes and e-h pairs in photoexcited (defect-free) anatase TiO$_2$

- Role in photocatalysis
- Experimental evidence of trapped holes and self-trapped excitons

Luminescence band from self trapped (triplet) excitons: peak at 2.3 eV & 2-3 μs decay time

Watanabe & Hayashi, J. Lumin. (2005)
Compare electron & hole states in the bulk and at the surface

- Add a single electron or a single hole or excite a *triplet exciton* in a bulk supercell or large anatase (101) slab
- B3LYP functional (CRYSTAL09)

<table>
<thead>
<tr>
<th></th>
<th>HOMO-LUMO</th>
<th>S0→T1 (vertical)</th>
<th>S0→T1 (adiab.)</th>
<th>ΔE_{trap}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>3.9</td>
<td>4.08</td>
<td>3.50</td>
<td>0.58</td>
</tr>
</tbody>
</table>

C. Di Valentin, AS, JPC Lett. 2, 2223 (2011)
### Polaron states in anatase TiO$_2$

#### Bulk Anatase

<table>
<thead>
<tr>
<th>State</th>
<th>$\Delta E_{\text{trap}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e_{\text{tr}}^{-}$, Ti$_{6c}$$^{3+}$</td>
<td>0.23</td>
</tr>
<tr>
<td>$h_{\text{tr}}^{+}$, O$_{3c}^{-}$</td>
<td>0.74</td>
</tr>
<tr>
<td>$e^{-}$, $h^{+}$ pair, Ti$_{5c}$$^{3+}$</td>
<td>0.58</td>
</tr>
</tbody>
</table>

#### (101) surface

<table>
<thead>
<tr>
<th>State</th>
<th>$\Delta E_{\text{trap}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e_{\text{tr}}^{-}$, Ti$_{5c}$$^{3+}$</td>
<td>0.62</td>
</tr>
<tr>
<td>$h_{\text{tr}}^{+}$, O$_{2c}^{-}$</td>
<td>1.45</td>
</tr>
<tr>
<td>$e^{-}$, $h^{+}$ pair, Ti$_{5c}$$^{3+}$</td>
<td>-----</td>
</tr>
</tbody>
</table>
One particle levels

**BULK**

- **a** $e^{-}_{\text{tr}}$, Ti$_{6c}^{3+}$
  - CB
    - $0.82 e^{-}_{\text{tr}}$
    - 4.00
  - VB

- **b** $h^{+}_{\text{tr}}$, O$_{3c}^{3-}$
  - CB
    - $3.90 h^{+}_{\text{tr}}$
    - 1.90
  - VB

- **c** $e^{-}$----$h^{+}$ pair, Ti$_{3c}^{3+}$----O$^{-}$
  - CB
    - $0.73 e^{-}_{\text{tr}}$
    - 3.99
    - $h^{+}_{\text{tr}}$
    - 1.83
  - VB

**SURFACE**

- **a** $e^{-}_{\text{tr}}$, Ti$_{5c}^{3+}$
  - CB
    - $1.28 e^{-}_{\text{tr}}$
    - 4.36
  - VB

- **b** $h^{+}_{\text{tr}}$, O$_{2c}^{3-}$
  - CB
    - $4.25 h^{+}_{\text{tr}}$
    - 2.34
  - VB

- **c** $e^{-}$----$h^{+}$ pair, Ti$_{3c}^{3+}$----O$^{-}$
  - CB
    - $1.03 e^{-}_{\text{tr}}$
    - 4.30
    - $h^{+}_{\text{tr}}$
    - 2.29
  - VB
Some conclusions

- Self-trapped excitons/holes in photo-excited anatase
- Surface polarons energetically more stable than bulk polarons $\rightarrow$ photoexcited carrier tend to migrate to the surface
- Deep hole levels $\rightarrow$ decreased oxidation power
Large polaron, Shallow donor level ~ 10 meV
$O_2$ adsorption on anatase (101)

- $O_2$ used as an electron scanveger in photocatalysis
- $O_2$ does not adsorb on stoichiometric surface
- Adsorption through surface $\rightarrow O_2$ charge transfer
$O_2$ adsorption on reduced anatase (101) & influence of subsurface defects

Selectivity: stronger adsorption close to subsurface defect

Adsorbed $O_2$ is a peroxide $O_2^{2-}$, $d_{O-O} \sim 1.46$ Å

~Same results with GGA, DFT+U, and hybrids
What is the state of adsorbed $O_2$ on reduced titania: peroxide ($O_2^{2-}$) or superoxide ($O_2^-$)??

Evidence of superoxide $O_2^-$ in EPR

Topics in Catalysis 8, 189-198 (1999)
Is the greater stability of the peroxide vs superoxide state an artifact of DFT-GGA?

- U moves states in the gap down
- Charge transfers from surface to \( \text{O}_2 \) more difficult
- Less adsorption strength

Self consistent determination of U
Electron transfer from reduced TiO\textsubscript{2} to O\textsubscript{2}

\[ \overset{\circ}{\text{O}_2} + \text{O}_2(\text{g}) \rightarrow \overset{\circ}{\text{O}_2}^- \]

\[ \overset{\circ}{\text{O}_2} + \text{O}_2(\text{g}) \rightarrow \overset{\circ}{\text{O}_2}^{2-} \]

O\textsubscript{2} approaching a reduced TiO\textsubscript{2} surface

Hybrid functional (PBE0) calculations
The paradigm of Electron Transfer: the Fe$^{2+}$ ↔ Fe$^{3+}$ in water
**Diabatic states:**

(1) $D_e^- A_e$

(2) $D_e^- A_e^-$

**Solvent coordinate**

$$z_e = \int d\mathbf{r} (\rho_2 - \rho_1) \Phi_{\text{in}}(\mathbf{r})$$

**Nonadiabatic ET rate:**

$$k = \frac{2\pi}{\hbar} V_{12}^2 (4\pi\lambda k_B T)^{-1/2} \exp\left[-\Delta G^\dagger/(k_B T)\right]$$

$$\Delta G^\dagger = \left(\Delta G^\circ + \lambda\right)^2/(4\lambda)$$

$V_{12}$: coupling between diabatic states

**Marcus theory**
Qualitatively, a **diabatic** electronic state is one that does not change its physical character as one moves along a reaction coordinate. This is in contrast to the **adiabatic**, or Born-Oppenheimer, electronic states, which change constantly so as to remain eigenstates of the electronic Hamiltonian.

NaCl dissociation in the diabatic and adiabatic representations. The ionic (**green**) and covalent (**blue**) diabatic states maintain the same character across the potential energy surface, whereas the adiabatic states (**black**) change.
A simple ET process: $\text{Ti}_{\text{sub}} \leftrightarrow \text{Ti}_{\text{surf}}$ electron hopping

$\text{TiO}_2$ sites between which electron hops

$$X(a) = a \cdot X(A) + (1 - a) \cdot X(B)$$
* + O_2(g) → *O_2^-

O_2 adsorbs on /desorbs from Ti_{sur}

Adsorption/desorption are reversible

Reaction coordinate: \[ d_{ads} = \frac{[d(Ti_{sur}-O_a) + d(Ti_{sur}-O_b)]}{2} \]
\[ * + O_2(g) \rightarrow *O_2^{2-} \]
Electron transfer between $^*\text{O}_2^-$ and $^*\text{O}_2^{2-}$ states

\[ X(a) = a \cdot X(A) + (1 - a) \cdot X(B) \]

$\text{Ti}^{4+}_{\text{sub}} - \text{O} - \text{Ti}^{4+}_{\text{sur}} < \text{O}_2^{2-}$ (a=0)

$\text{Ti}^{3+}_{\text{sub}} - \text{O} - \text{Ti}^{4+}_{\text{sur}} < \text{O}_2^{-}$ (a=1)
Adiabatic vs non-adiabatic ET

Strong coupling $\rightarrow$ adiabatic $\rightarrow$ Reversible energy profile

Weak coupling $\rightarrow$ non-adiabatic
Some conclusions

- Electron transfer from reduced TiO$_2$ surface to approaching O$_2$ studied by PBE0 calcs.

- Formation of adsorbed superoxide, *O$_2^-$, is barrierless.

- Transfer of second electron to transform superoxo into adsorbed peroxide, i.e. *O$_2^-$ + e$^-$ $\rightarrow$ *O$_2^{2-}$, is nonadiabatic with a barrier of 0.3eV.

- Nonadiabaticity originates from instability of intermediate with second electron localized at superoxo adsorption site.
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