Workshop on Nanoscience for Solar Energy Conversion

27 - 29 October 2008

Reduced and Doped TiO2: what is the nature of the defect states?

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Reduced and doped TiO$_2$: what is the nature of the defect states?

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**TiO$_2$ polymorphs**

Anatase, $E_g = 3.2$ eV

![Anatase structure](image)

Ti-Ti $3.79$ Å $3.04$ Å

rutile, $E_g = 3.0$ eV

![Rutile structure](image)

Ti-Ti $3.57$ Å $2.96$ Å

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**TiO$_2$: very important role of defects**

Color change in TiO$_2$ samples induced by increasing level of defects

Defects change electronic properties of the material

Defect engineering of TiO$_2$ for photocatalytic applications

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Main defects: oxygen vacancies, Ti$^{3+}$ ions
OUTLINE

Part I: intrinsic defects
O vacancies and Ti interstitials

Part II: extrinsic defects
N impurities and their interplay with other defects
What is the nature of “reduced titania”? 

Excess of metal compared to oxygen results in formation of “Ti$^{3+}$” ions. But ... 

\[
\begin{align*}
\text{TiO}_{2-x} & \quad \text{Ti}_{1+x}\text{O}_2 \\
\text{O vacancies} & \quad \text{Ti interstitials}
\end{align*}
\]
Experimental proofs of formation of reduced bulk titania:

1. UV-vis
2. UPS
3. XPS
4. EPR

Every theoretical method dealing with reduced TiO$_2$ should be able to reproduce these features...

(1) absorption bands in the visible region responsible for the change in color (assigned to d-d transitions)

(2) occurrence of a new state in the gap at about 0.8 eV below the conduction band attributed to the reduced Ti$^{3+}$ ions

(3) shift in the core level binding energies of the reduced Ti atoms from X-ray photoemission (XPS)

(4) presence of more than one EPR signal associated to various kinds of paramagnetic Ti$^{3+}$ ions in the lattice
DFT calculations

**QUANTUM EXPRESSO** (pure DFT, DFT+U)
- plane-wave-pseudopotential approach
- PBE functional – spin polarized calculations
- 96-atoms supercells

**CRYSTAL06** (hybrid DFT)
- atomic gaussian basis set approach
- Hybrid DFT functionals – spin polarized calculation
- hyperfine coupling constants (EPR)
O vacancy in bulk anatase: standard DFT

No states in the gap, electrons fully delocalized, no major geometrical distortion around the defect

Problem due to self-interaction in DFT
Pragmatic ways to improve the model

**DFT+U methods**

Systems where atomic-like features are persistent in the solid:
explicit description of correlation by an on-site correlation term \( U \)
for a few selected localized orbitals
Add a Hubbard-like \( E_{\text{Hub}} \) term to the standard functional:

\[
E_{\text{LDA+U}}[n(r)] = E_{\text{LDA}}[n(r)] + E_{\text{Hub}}[\{n^{I\sigma}_m\}] - E_{\text{DC}}[\{n^{I\sigma}\}]
\]


**Hybrid functionals**

Use of hybrid functionals where HF-like exchange is mixed in with the DFT exchange: B3LYP (20%), H&H LYP (50%)

\[
E^{\text{B3LYP}}_{xc} = a \ E^{\text{LSDA}}_x + (1 - a) \ E^{\text{HF}}_x + b \ \Delta E^{\text{Becke}}_x + (1 - c) \ E^{\text{LSDA}}_c + c \ E^{\text{LYP}}_c
\]

O vacancy in bulk anatase: B3LYP and DFT+U

Remove an O atom: 2e left on the system.
Quantities of interest:
(1) Energy gap \( (E_g) \)
(2) Distance of impurity levels from bottom of conduction band \( (\Delta E_1, \Delta E_2) \)

B3LYP

\[ \Delta E_1 \, 1.2 \, \text{eV} \]
\[ \Delta E_2 \, 1.3 \, \text{eV} \]

Both electrons are localized on Ti 3d levels ...

DFT+U
(\( U = 3 \, \text{eV} \))

\[ \Delta E_1 \, 0.6 \, \text{eV} \]
\[ \Delta E_2 \, 0.9 \, \text{eV} \]

...but delocalized solution is close in energy

Similar results for rutile (110) surface

B3LYP xc functional, c(4x2) surface cell, AO Gaussian basis sets, spin polarized calculations, CRYSTAL03

O vacancy: two electrons localized on two non-equivalent Ti ions

triplet ground state (magnetic)

Two states in the gap at 1.2 and 0.9 eV below conduction band (as in the experiment)

Polaronic nature of O vacancy

O vacancy in rutile TiO$_2$(110): strong distortion around the defect (similar for hydroxilated surface, where Ti$^{3+}$ forms)

Distortion essential to induce localization but present only using hybrid DFT methods

Geometry: B3LYP
DOS: B3LYP
localization

Geometry: B3LYP
DOS: PBE
localization

Geometry: PBE
DOS: B3LYP
no localization

Geometry: PBE
DOS: PBE
no localization

Reduced titania: a problem for theory

- Pure functionals fail to reproduce the correct band structure
- DFT+U or hybrid functionals improve the description but suffer from the use of “empirical” parameters
- Need to compare different approaches
- Need for clean experimental data (often missing)

Generate defects in controlled way and characterize them by various spectroscopies (central role of EPR)
In summary ...

- F and Nb doping of stoichiometric TiO₂ leads to lattice Ti³⁺ ions in pseudo-octahedral environment
- H doping of stoichiometric TiO₂ leads to the same lattice Ti³⁺ ions
- Reduction of stoichiometric TiO₂ in mild conditions leads mainly to lattice Ti³⁺ ions
- Strong evidence from comparison of measured and computed EPR spectra of localized Ti 3d states at low T
- Only hybrid or DFT+U functionals lead to electron localization
- Localized and delocalized states are very close in energy and can depend on external conditions (T, P, etc.)
Delocalization of trapped electron occurs at RT (but here good agreement for the wrong reason: DFT calculations done at 0 K!)

Barrier for $e^-$ migration from site to site <0.1 eV (see M. Dupuis lecture). At RT $e^-$ is mobile on the time scale of experiment
### Reduced titania: oxygen vacancies versus Ti interstitials

As the annealing temperature increases, the composition and properties of titania (TiO$_2$) changes, leading to the formation of oxygen vacancies and Ti interstitials in different regions (surface, subsurface, bulk).

<table>
<thead>
<tr>
<th>Region</th>
<th>Stoichiometric sample, colorless</th>
<th>O diffusion from bulk to surface</th>
<th>O vacancies form in subsurface regions</th>
<th>Lattice Ti$^{3+}$ (localized states at low T)</th>
<th>Ti diffusion from surface to bulk</th>
<th>Ti interstitials form in subsurface regions</th>
</tr>
</thead>
<tbody>
<tr>
<td>surface</td>
<td>TiO$_2$</td>
<td>TiO$_{2-x}$</td>
<td>TiO$_{2-x}$</td>
<td>TiO$_{2-x}$</td>
<td>Ti$_{1+x}$O$_2$</td>
<td></td>
</tr>
<tr>
<td>subsurface</td>
<td>TiO$_2$</td>
<td>TiO$_{2-x}$</td>
<td>TiO$_{2-x}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>bulk</td>
<td>TiO$_2$</td>
<td>TiO$_2$</td>
<td>TiO$_{2-x}$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
(1) Organic pollutant adsorbes to surface
(2) Adsorbed pollutant breaks down
(3) Final products: CO$_2$ and Water

APPLICATIONS
- Photoelectrolysis of H$_2$O with TiO$_2$ electrode (1970s)
- Photocatalytic production of H$_2$ (1980s)
- Photocatalytic oxidation of organic molecules (1990s)
- Photoinduced hydrophilicity
- Self-cleaning, air and water purification, self-sterilizing

- Band-gap photoexcitation
- Electron-hole recombination
- Migration to surface
- Charge carrier trapping
- Charge transfer

Pure TiO$_2$: band gap does not allow to capture most part of solar light (only a small portion of the solar spectrum is absorbed)

Reduction of band gap obtained by inclusion of dopants: transition metals (V, Cr, Mn, Fe) or main group atoms (N, C, S, F)
Properties of sol-gel prepared anatase N-doped TiO₂

UV-vis absorption spectra of pure and N-doped anatase

Rate of methylene-blue degradation on N-doped (a) and pure (b) anatase

Two paramagnetic species detected (EPR)
- Weakly physisorbed molecular NO
- Stable bulk species (responsible for yellow color)
DOPED TiO$_2$: WHERE ARE THE DOPANTS?

**interstitial (bound to lattice O)** or **substitutional (to O or Ti atoms)**

Distinction possible by XPS? Simple (but often misleading) interpretation:

- Peak at 400-401 eV: interstitial N (N-O, N-H, etc.)
- Peak at 396-397 eV: substitutional N (Ti-N)

**XPS not always conclusive**
Both interstitial and substitutional N (paramagnetic) introduce localized states above the O 2p valence band.
Substitutional versus interstitial N-doping: EPR

EPR: confirms localized nature of N-induced states in the gap

Theory: PBE (Espresso) and B3LYP (Crystal03) calculations show similar level of localization. EPR properties computed at B3LYP level

Hyperfine coupling constants: interstitial $N_{\text{int}}$ more likely than substitutional $N_{\text{sub}}$ (consistent with XPS)

Message from EPR and theory:

- Stable N-species exist in the bulk
- Most likely interestitial N is formed
- N-induced states are localized!

A conclusion of purely theoretical interest?
Interplay between N-doping and oxygen vacancies

DFT predicts: N-doping favors vacancy formation

Energy cost to form $V_o$
- pure TiO$_2$: 4.2 eV
- N-doped TiO$_2$: 0.6 eV

$N_s$-doping stabilized by the presence of oxygen vacancies ($N_{s-o} + V_o$)

- most stable situation under oxygen-poor conditions


Interplay between Ti$^{3+}$ states and N-impurities

DFT predicts: **spontaneous** charge transfer from Ti$^{3+}(3d)^1$ to N$_b^\cdot$
- formation of Ti$^{4+}$ and N$_b^-$ centers (singlet state, lower by 3 eV than triplet state)
- N$_b^-$ centers introduce states above O 2p valence band as neutral N$_b^\cdot$ states

Reduced TiO$_2$ powders exposed to atomic N: decrease of Ti$^{3+}$(3d)$^1$ signal until it is completely quenched

Chiesa, Giamello (2008)

TiO$_2$ single crystal: N implantation reduces peak due to Ti$^{3+}$(3d)$^1$ states in UPS

An interesting experiment on N-doped samples

EPR of N-doped TiO$_2$ under irradiation

Irradiation under O$_2$: O$_2$ captures one electron from TiO$_2$ surface and forms O$_2^-$.
O$_2$ acts as electron scavenger.

Generation of paramagnetic defects under irradiation

N-doped TiO$_2$

$\text{N}_b^-$ $\xrightarrow{\text{vis}-h\nu}$ $\text{N}_b^-$

Process completely reversible by turning light off
Adsorbed O₂ as electron scavanger

N-doped TiO₂

Process irreversible under O₂ exposure; formation of O₂⁻

N-states responsible for photo-activity of N-doped TiO₂
EPR and DFT show unambiguously the localized nature of N-induces states in TiO$_2$.

N dopants favor formation of oxygen vacancies in the material (Ti$^{3+}$ states); vacancies can become hydroxilatated (same behaviour).

Charge transfer occurs from Ti$^{3+}$ states (high in the gap) and singly occupied N-states (low in the gap): Ti$^{3+}$ + N$_b$· → Ti$^{4+}$ + N$_b^-$.

Visible light induces conversion of diamagnetic precursors into paramagnetic centers by excitation of electrons to the conduction band (N$_b^-$ + hv → N$_b$·).

Excited electrons are captured by O$_2$ adsorbed on the surface (formation of paramagnetic O$_2^-$).

N-states responsible for photo-activity of N-doped TiO$_2$. 