Supercomputation and realistic models of photocatalysts nanoparticles

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Outline

1. Photocatalysis, TiO$_2$ and H$_2$ production
2. TiO$_2$ bulk and surfaces versus nanoparticles
3. The computational challenge
4. Selected results on realistic models
5. Conclusions
A cartoon description of photocatalysis

TiO$_2$ is the star system
Technological interest is huge and applications go from environment to sustainable energy.

H₂ production from H₂O means unlimited energy supply.

Air cleaning technology.
Photocatalytic concrete already exist!

http://www.mandalaconcrete.com/
At first sight mechanisms of photocatalysis seem fairly simple.
Underlying processes are very complex and, to a large extent, details mostly unknown since excited states of nanoparticles of semiconducting transition metal oxides are involved.

But... how, where and when?
Where is the problem?

TiO$_2$ and related materials adsorb in the UV

Only a part of solar light harvested

MIND THE GAP!
1. Photocatalysis, TiO$_2$ and H$_2$ production

Engineer the GAP!

Need to predict new photocatalytic materials
Modifying, doping and/or co-doping existing ones

Need to understand the electronic structure

Most published work focuses on band gap of bulk TiO$_2$

Not a simple problem, hybrid functionals needed

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<tr>
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<th>Rutile</th>
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<tr>
<td></td>
<td>PBE</td>
<td>PBEx</td>
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<td>$a,b$ (Å)</td>
<td>4.650 (1.3 %)</td>
<td>4.609 (0.4 %)</td>
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<td>$c$ (Å)</td>
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TiO$_2$ extended surfaces may provide better models

BUT

Real systems are made of nanoparticles

Composition?

Size?

Shape?

Doping?
### Electronic structure of realistic TiO$_2$ nanoparticles

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<td>(TiO$<em>2$)$</em>{10}$</td>
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*From Wulff construction*

*Covering subnm to 4-6 nm scale*
Not only huge computational resources needed
Efficient highly parallel code too

FHI-AIMS chosen

An accurate AE electronic structure code package for computational materials science

Numerical basis
Standard GGA and hybrid functionals
Scaling test for \((\text{TiO}_2)_{165}\) with tight tier 2 basis set

- **wall clock time(s)**
- **Solving KS eqs (s)**
- **Density & force components (s)**
✔ Excellent scaling up to 1000 cores

✔ Better scaling expected for larger particles

✔ Memory problems to be solved

✔ Work in progress with developers
PBE optimized nanoparticles

\((\text{TiO}_2)_{10}\)  \((\text{TiO}_2)_{35}\)  \((\text{TiO}_2)_{84}\)  \((\text{TiO}_2)_{165}\)  \((\text{TiO}_2)_{286}\)

Structure of corner atoms as in bulk
PBE optimized nanoparticles

\[
\begin{align*}
(TiO_2)_{10} & \quad (TiO_2)_{35} & \quad (TiO_2)_{84} & \quad (TiO_2)_{165} & \quad (TiO_2)_{286} & \quad (TiO_2)_{455}
\end{align*}
\]

Structure of corner atoms bent
Initial trends on electronic structure

Band Gap vs # atoms

- SP-PBEx-preopt
- PBE opt
- SP-PBE0-preopt
- Experimental
  Anatase Band Gap

Band Gap (eV)
# atoms
4. Selected results on realistic models

Initial trends on stability (energy (eV) /unit)

Energy vs #atoms

Structure of corner atoms as in bulk
Similar results for bent structures
What we learn?

- First principles calculations on realistic particles with nanometer dimensions are possible
- Excellent performance of FHI-AIMS
- Electronic structure seems to converge fast with particle size
- Energy per unit shows asymptotic behavior
What’s next

✓ Shape, composition and solvent effects

✓ Scalable versus non scalable regime about to be accurately defined for the first time

✓ Dynamics of ground and excited states for both nuclei and electrons

✓ Huge amount of data to analyze
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