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in collaboration with
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Outline

• Participants and structure
• PhD students and PostDocs
• Background and leading hypothesis
• Sub tasks and synergy
• Novelty and innovativeness
• Results, mobility, future plans …
• Added value
• Time for reflection - what makes this project different?
Project team and principal investigators (PI):

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Organizational issues: Research environment, PhD students and PostDocs

• Göteborg:
  • PhD students:
    • Raja Sellappan*
    • Rafael Martins
    • Hans Fredriksson
  • Post Doc
  • Jiefang Zhu (UU 3/09)
  • Senior researcher
    • Bengt Kasemo*
    • Michael Zäch

• København:
  • PhD students:
    • Rasmus Nielsen
    • Peter Vesborg*
    • Post Doc
    • Yidong Hou*
    • Senior researcher
      Jens Nørskov*

• Oslo:
  • PhD students:
    • Vishnu Vishukathan*
    • Mareike Trunk*
    • Post Doc
  • Agnieszka Gorzkowska-Sobas
  • Senior researchers
    • Helmer Fjelvåg*,
    • Ola Nilsen,
    • Bengt Svensson*,
    • E.Monakhov,

• Reykjavík:
  • PhD students:
    • Jon Steinar G. Myrdal*
  • Post Doc
    • Andri Arnaldsson

* Funded at least partly from the project
+ Collaboration and consulting
Aim

The aim is to develop new electrode materials and schemes for photocatalytic water splitting for hydrogen production.

Background

Sunlight photons have enough energy to split water to hydrogen and oxygen. The efficiency of energy transfer can be orders of magnitudes higher than the natural photosynthesis.

Leading idea

Nanoscience and Nanotechnology will give key contributions to the future energy systems and solutions of many of the associated environmental issues.
“The aim is to develop new electrode materials and schemes for photocatalytic water splitting for hydrogen production.”

**Background:** "Sunlight photons have enough energy to split water"

- Fujishima and Honda [Nature 238 (1972) 37].
- Production of H₂ and O₂ from water with a photoelectrochemical cell consisting of a Pt and TiO₂ electrodes under a small electric bias.
“The absorption spectrum of the system must overlap the emission spectrum of the sun”.

\[ \text{H}_2\text{O} \]

photodissociation
“The aim is to develop new electrode materials and schemes for photocatalytic water splitting for hydrogen production.”

**Challenges:**

Current methods and devices are inefficient, → → →

The *price* of solar hydrogen is too high for the technology to enter a significant market.

**Several weaknesses of the current systems:**

- Limited absorption in the visible, (where the solar irradiation has the highest power density at the Earth surface);
- Fast electron-hole (*e-h*) recombination and fast back-reaction of *H* and *O* to form *H*$_2$*O* again;
- Difficulties of matching the semiconductor band-edge energies with the *H*$_2$ and *O*$_2$ evolution reactions;
- Corrosion resistivity;
- ..........
"The project focuses on the materials- and nanotechnology related issues in the development of PEC devices for hydrogen production from water."

**Specific hypothesis:**

(i) Manipulation of the semiconductor–electrolyte interface is possible through band gap edge control and engineering;
(ii) Nanostructured electrode materials are superior to unstructured electrodes, due to their high surface-to-volume ratio;
(iii) Functionalized electrodes with noble metal nanoparticles, exhibit enhanced optical absorption as a result of nanoparticle plasmon excitations;
(iv) The combination of metal clusters and/or nanocavities on a waveguiding electrode (support) constitutes a novel approach for optical generation and separation of e-h pairs;
(v) MEMS technology can be used to develop new types of photoreactors;
(vi) State-of-the-art DFT calculations can predict (calculate) new semiconducting electrode material(s) with appropriate structure and properties;
(vii) Band gap calculations can be combined with calculation of the corrosion resistance, that will favor product formation potentials.
“The project focuses on the materials- and nanotechnology related issues in the development of PEC devices for hydrogen production from water.”

**Specific tasks:**

- **Partner 1 - Chalmers University:**
  Experimental studies relevant to plasmon coupled photon energy transfer; Nanofabrication and (optical) characterization of samples.

- **Partner 2 - University of Oslo:**
  Identification and characterization of novel materials- ZnO and other oxide-based materials and band gap engineering based on them.

- **Partner 3 - Technical University of Denmark**
  Materials (clusters) preparation and characterization. Instrument development, new photo reactors with MEMS technology.

- **Partner 4 - University of Iceland**
  Corrected/Extended DFT applied to studies of excitations and charge carriers.
Results

PhD Thesis:

• Hans Fredriksson, AP, CTH, Sweden, Thesis title: Nanostructures of Graphite and amorphous carbon; fabrication and properties, defended on September 4th 2009.

• Peter Vesborg, CINF, DTU, Denmark, Thesis title: Photocatalysis in μ-reactors and related activities, Defended on March 11, 2010.


20. Ib Chorkendorff (invited talk), Design of new catalysts based on molecular level insight, The 4th IDECAT Conference on Catalysis, 12-16 May 2010, Porquerolles, France


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**Results: Publications**

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**Patent application** by DTU team submitted to EPO (2010) "Materials for photoelectrocatalytic hydrogen production".

**Patent application** by CTH team under preparation “Composite semiconductor-carbon films with enhanced optical absorption”.
‘Solar Hydrogen‘ PROJECT MEETINGS:
1st meeting, December 12, 2008, Gothenburg, Sweden
2nd meeting, February 27, 2009, Oslo, Norway
3rd meeting, December 1, 2009, Lyngby, Denmark
4th meeting, June 2, 2010, Gothenburg, Sweden

* Workshop
Project meeting Solar Hydrogen, Copenhagen, 1st December, 2009, CPH, Denmark (oral presentations from ALL participating researchers + invited)

* Workshop
Project meeting Solar Hydrogen, Göteborg, 2nd June, 2010, Göteborg, Sweden (oral presentations from ALL participating researchers + invited)

* Concluding meeting – plan before yearend 2011.
About 40 \((25+15)\) publications and invited talks!
**Milestones: what is achieved**

- The new personnel have been trained and are able to use the relevant techniques (nanofabrication, photoelectrochemical characterization, DFT calculations).

- The model systems have been closely defined and fabrication schemes established.

- The optical properties of these model systems have been investigated.

- Specific systems constructed, tested and results have been published and patent applications submitted.

- Active dissemination of results and activity,
  - new partners and collaborations,
  - ideas for extension towards EU financed activity.
More Dissertations….

The model systems have been evaluated. We expect additional important results from the photoluminescence and electrochemical tests of our systems.

Progress with investigation of the photocatalytic and corrosion properties of the model systems

Prototype devices constructed.

The improved DFT methodology has just recently been developed and several calculations on the materials of interest are now going on.

We expect, based on the obtained results more publications and patent(s).

We have created strong and successful team/network (!!!)
We have ideas and direction, want to explore MORE!
Industry!
“The project will contribute to the fundamental understanding of the energy and charge transfer processes associated with the interaction of light with functional materials.”

**RESULTS: at DTU:**

Fig. 1. Schematic of the tandem "chemical solar cell". To the left, the entire system is shown where pillars are embedded in a proton conducting membrane. The solar light is incident from above and the blue part of the spectrum is absorbed by the anode used for oxidizing water into molecular oxygen and protons. The protons migrate through the membrane and are reduced at the cathode side by Mo$_3$S$_4$ clusters adsorbed on the Si pillars which are excited by the red part of the spectrum. As indicated in the right part of the figure, here we only deal with hydrogen evolution on the Si pillars modified with the adsorbed Mo$_3$S$_4$ clusters and excited by the red part of the solar spectrum.
RESULTS: at UiO

Bandgap engineered samples prepared at MINA lab, Oslo.
Characterization of the electronic defect states

Vacancy states (within the band-gap) can be created by removing an Oxygen atom from the ideal periodic structure of TiO₂

experimentally identified: 0.8eV below conduction band
Optical absorption of TiO$_2$/C composite films of different thicknesses compared to 35nm single TiO$_2$ films and their catalytic performance.

This system is prepared at Chalmers U. to study the charge transport at the semiconductor interface.
Results and Cooperation

Summary:
The project concluding according to its program. It is a very successful project.

The project benefits from:
(i) accumulated experience and track record of the participants and existing good infrastructure,
(ii) Its generic character,
(iii) collaboration with EU and national projects with similar activities.
Thanks for the attention!

Tank you for the "initiative"!
Increased overall optical absorption and red shift of the absorption edge.

Favorable morphological changes at the interface.

Enhanced photocatalytic activity.

The stronger non-radiative recombination is mainly to charge carrier leakage (transfer) at the film/particle interface.