INNER ERA-NET
Innovative Energy Research

***SusEn** seminar **2011***
**in collaboration with**
**N-INNER seminar**
*Espoo, 22 September 2011*

# SOLAR HYDROGEN

**Dinko Chakarov** Chalmers
**Ib Chorkendorff** DTU
**Andrej Kuznetsov** UiO
**Hannes Jonsson** SIUI

# 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?

SOLAR HYDROGEN

# PARTNERS and STRUCTURE

## *Project team and principal investigators (PI):*

• Göteborg:

***Chalmers University of Technology (CTH),***
***Department of Applied Physics,Göteborg, Sweden***
***PI: Prof. Dinko Chakarov (PROJECT COORDINATOR)***
*Telephone: +46317723375*
*E-mail: dinko.chakarov@chalmers.se*

• Oslo:

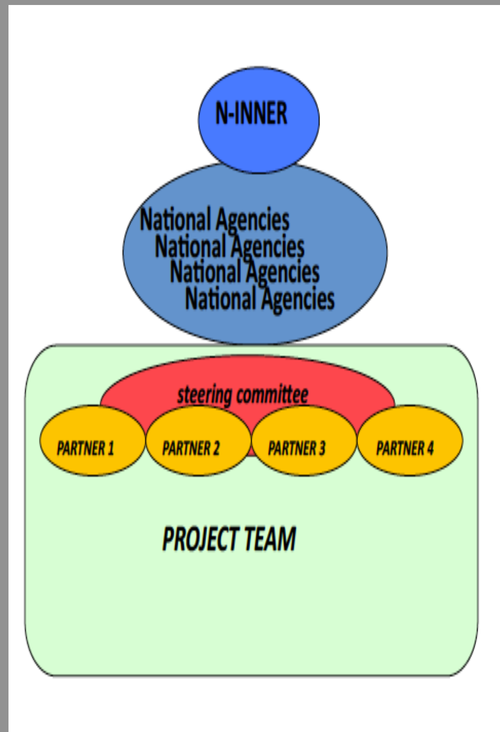
***University of Oslo (UiO), Department of Physics,***
***Centre for Material***
***Science and Nanotechnology, Oslo, Norway***
***PI: Prof. Andrej Kuznetsov***
*Telephone: +4722852870*
*E-mail: andrej.kuznetsov@fys.uio.no*

• København:

***Technical University of Denmark (DTU), Danish National Research Foundation's, Center for Individual Nanoparticle Functionality,***
***Department of Physics, Kongens Lyngby, Denmark***
***PI: Prof. Ib Chorkendorff***
*Telephone: +4545253170*
*E-mail: ibchork@fysik.dtu.dk*

• Reykjavík:

***Science Institute of University of Iceland (SIUI) Reykjavik, Reykjavik, Iceland***
***PI: Prof. Hannes Jonsson***
*Telephone: +3548923560*
*E-mail: hj@hi.is*



SOLAR HYDROGEN

# 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***

•Peter Kluepfel

•Simon Kluepfel

•Hildur Gudmundsdottir

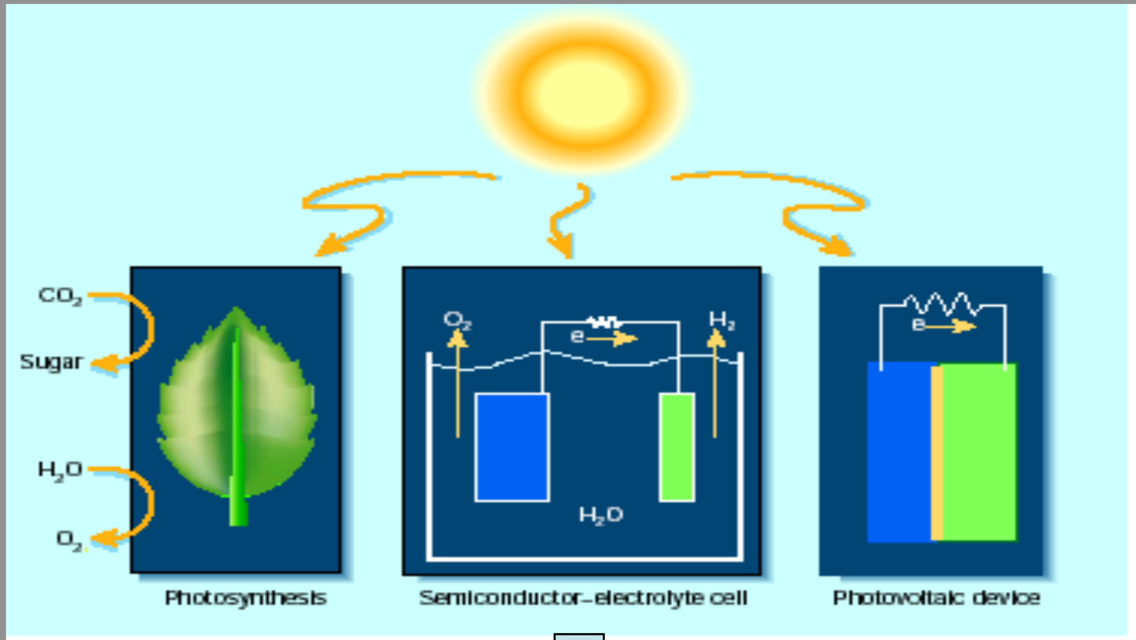
•*Post Doc*

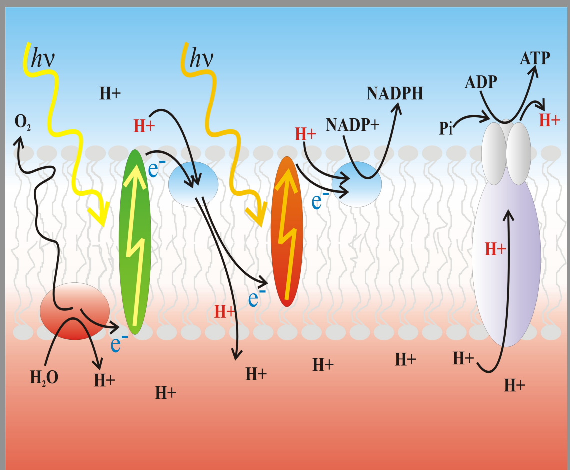
•Andri Arnaldsson

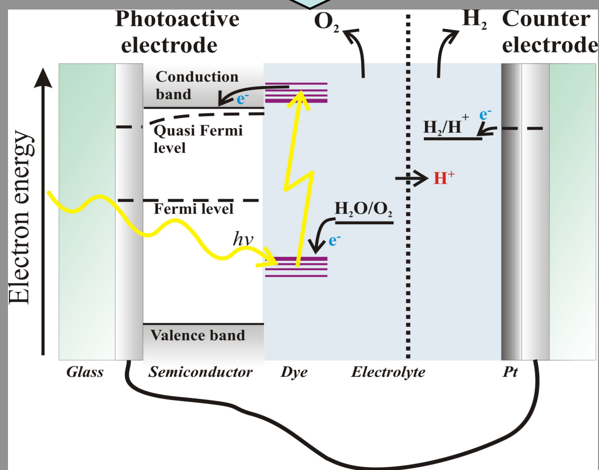
* *Funded at least partly from the project*

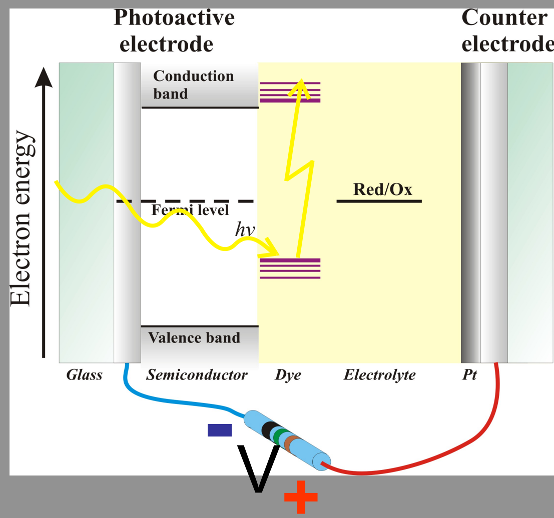
\+ *Collaboration and consulting*

# SOLAR ENERGY CONVERSION SCHEMES



SOLAR HYDROGEN

## Aim

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

## Background

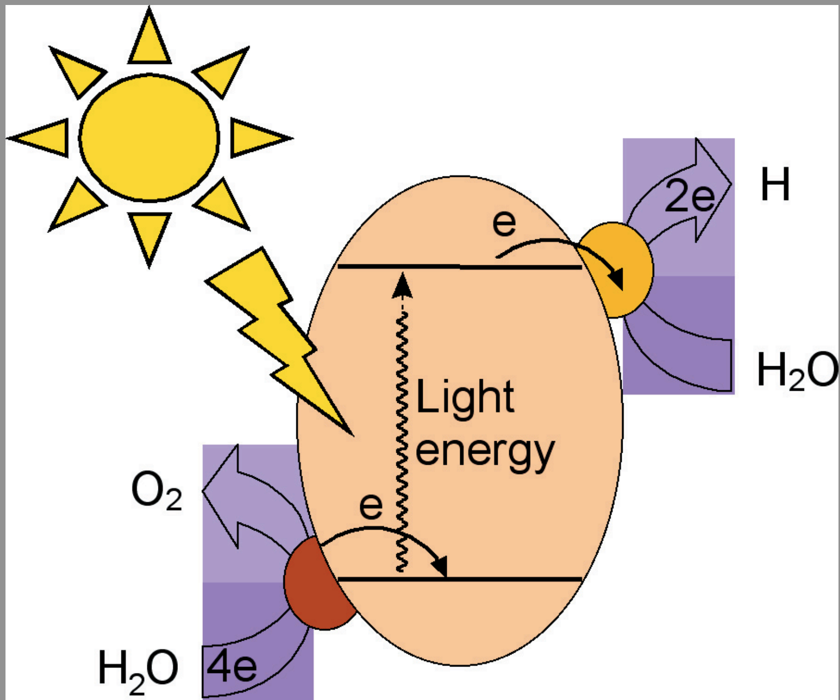
*Sunlight photons have enough energy to split water to hydrogen and oxygen. The efficiency of energy transfer can be orders of magnitudes higher than the natural photosynthesis.*

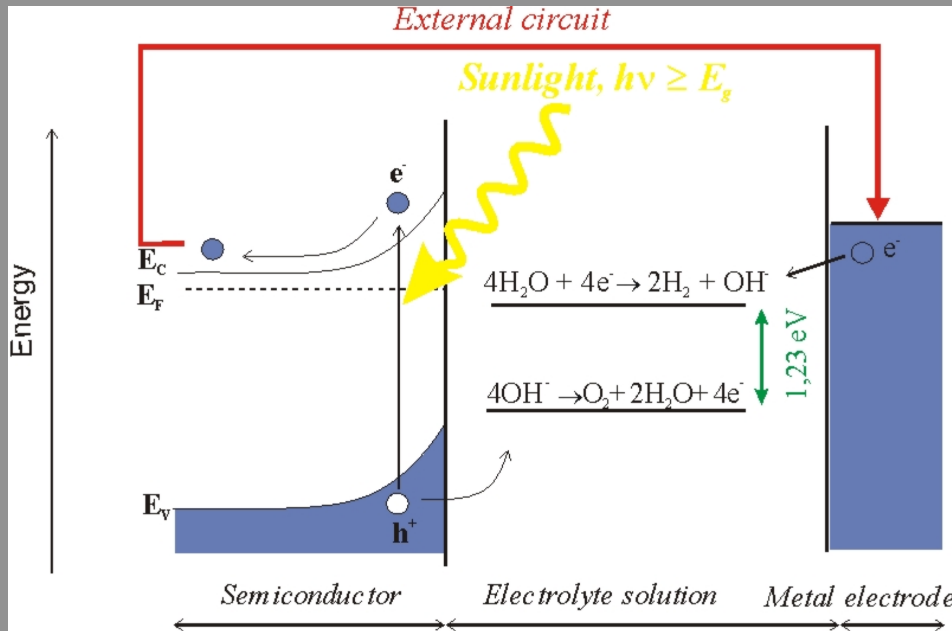
## Leading idea

*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"***



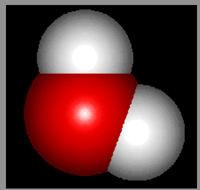



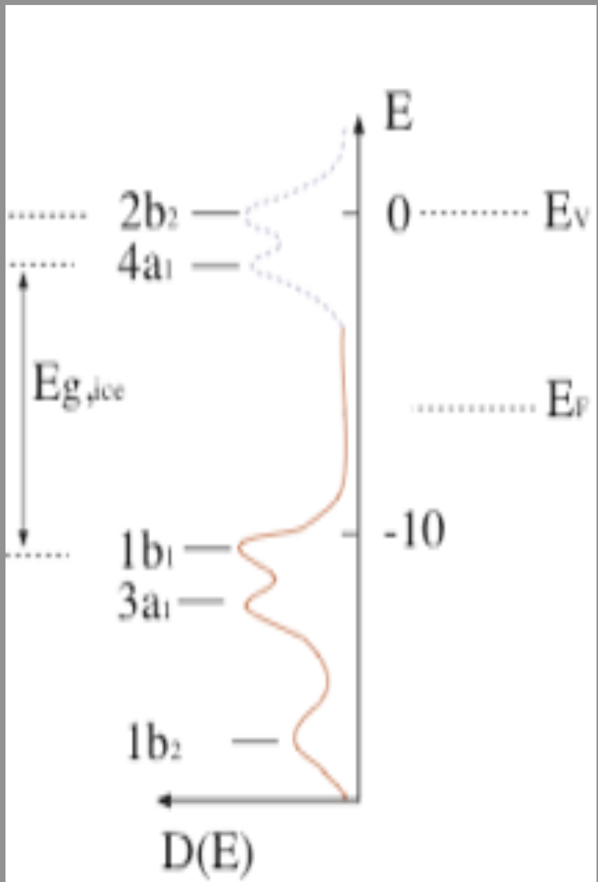

*Schematic of the catalytic water splitting process*

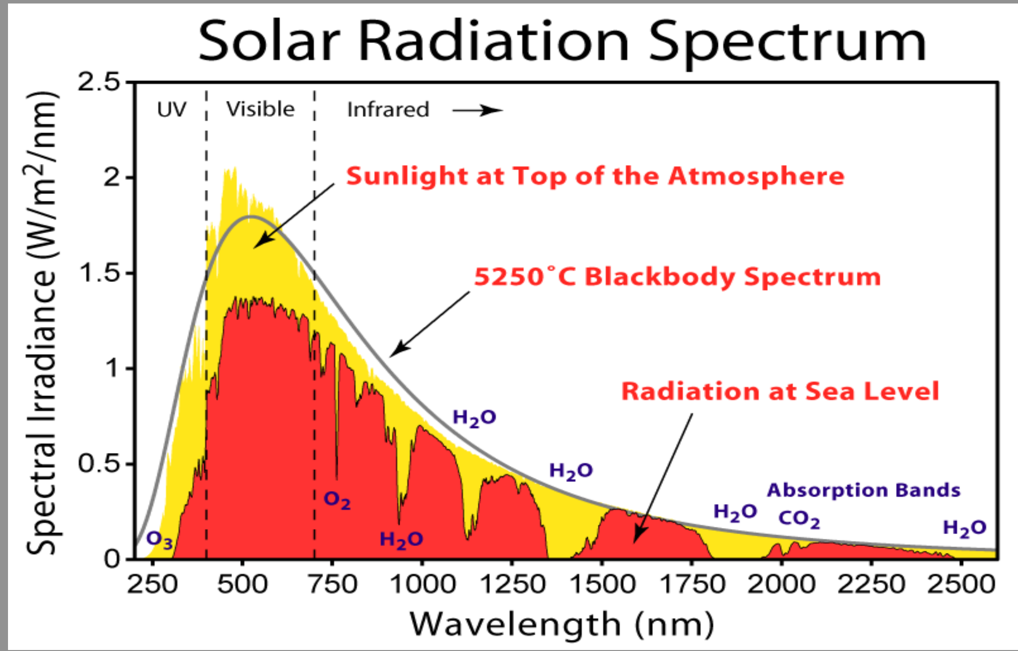
- **Fujishima and Honda** [*Nature* **238** (1972) 37].
- **Production of $H_2$ and $O_2$** from water with a photoelectrochemical cell consisting of a **Pt** and **$TiO_2$** electrodes under a small electric bias.

*"The absorption spectrum of the system must overlap the emission spectrum of the sun".*

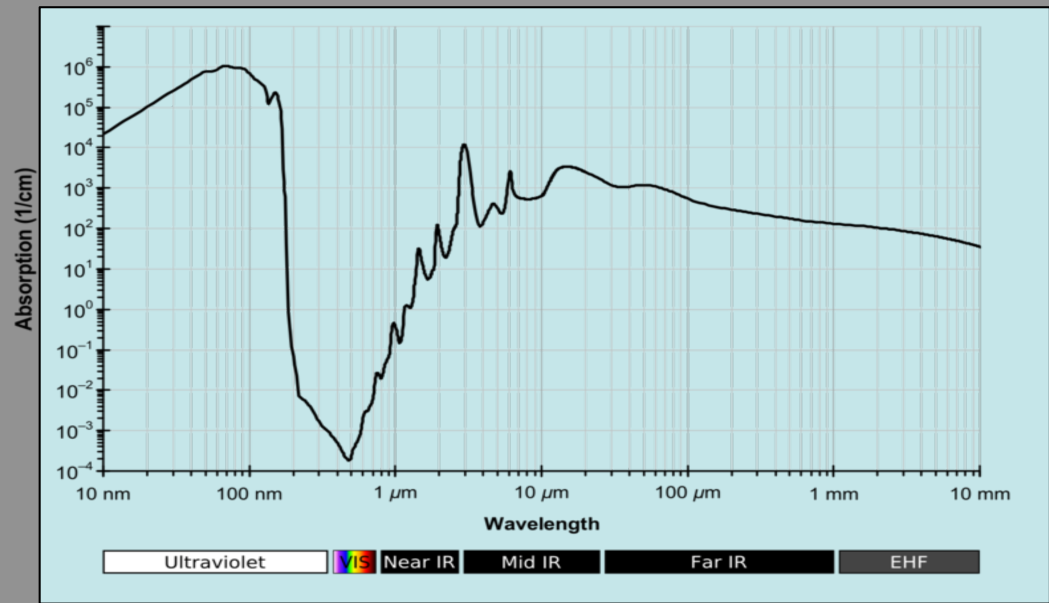
# $H_2O$ photodissociation






Water Absorption Spectrum



SOLAR HYDROGEN

"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 $H_2O$ again;
- Difficulties of matching the semiconductor band-edge energies with the $H_2$ and $O_2$ evolution reactions;
- Corrosion resistivity;
- .......

SOLAR HYDROGEN

**"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.

SOLAR HYDROGEN

**"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 4$^{th}$ 2009.

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

•**Raja Sellapan**, AP, CTH, Sweden, Lic Thesis title: Fabrication and characterization of composite TiO2/Carbon nanofilms with enhanced photocatalytic activity.", defended on April 29, 2011.

•**Vishnu Vishukathan,** DF, UIO, Norway, Thesis title: "ZnO and ZnCdO metal organic chemical vapor deposition: epitaxy, defects, and band gap engineering, defended on June 16, 2011.

# Results: Publications

1. Tuning light absorption by band gap engineering in ZnCdO as a function of MOVPE-synthesis conditions and annealing, V.Venkatachalapathy, A.Galeckas, R.Sellapan, D.Chakarov and A.Yu.Kuznetsov, Journal of Crystal Growth, 314, 301 (2011) 2. Understanding of phase separation in ZnCdO by combination of structural and optical analysis, V.Venkatachalapathy, M.Trunk, T.Zhang, A.Azarov, A.Galeckas and A.Yu. Kuznetsov, Phys. Rev. B 83, 125315 (2011)

3. Temperature dependence of surface plasmon mediated near band-edge emission from Ag/ZnO nanorods, Y. P. Liu, Y. Guo, J. Q. Li, M.Trunk, A. Yu. Kuznetsov, J. B. Xu, Z. X. Mei, and X. L. Du, Journal of Optics 13, 75003 (2011).

4. Testing ZnO based photoanodes for PEC applications, M.Trunk, A.Sobas, V.Venkatachalapathy, T.Zhang, A.Galeckas, A.Yu.Kuznetsov, Energy Procedia, accepted

5. Mechanism of enhanced photocatalytic activity of composite $TiO_2$/carbon nanofilms, R.Sellappan, A.Galeckas, V.Venkatachalapathy, A.Yu.Kuznetsov, and D.Chakarov, Applied Catalysis B: Environmental, doi:10.1016/j.apcatb.2011.05.036 6. Cd diffusion and thermal stability of CdZnO/ZnO heterostructures, A.Yu. Azarov, T. Zhang, B.G. Svensson, and A.Yu. Kuznetsov, Appl.Phys.Lett., 99, 111903 (2011).

7. Surface/strain energy balance controlling preferred orientation of CdZnO film, T.C.Zhang and A.Yu.Kuznetsov, J.Appl.Phys, accepted

7. Time-resolved spectroscopy of carrier dynamics in graded ZnCdO multilayered structures, M. Trunk, V. Venkatachalapathy, T.C. Zhang, A. Azarov, A. Galeckas, and A. Kuznetsov, Appl.Phys.Lett., submitted

8. H. Jónsson, Proceedings of the National Academy of Sciences 108, 944 (2011).

9. P. J. Klüpfel, S. Klüpfel, K. Tsemekhman and H. Jónsson, Lecture Notes in Computer Science (in press).

10. S. Klüpfel, P. J. Klüpfel, and H. Jónsson, Phys. Rev. A (submitted).

11. A.Valdes, J.Brillet, M.Graetzel, H.A.Hansen, H.Jonsson, P.Klupfel, S.Klupfel, G.-J. Kroes, F. Le Formal, I.C. Man, R.S. Martins, J.K. Nørskov, J.Rossmeisl, K. Sivula and M. Z ä ch, Energy & Environmental Science (submitted, 2011).

S. In, Y. Hou, B. Abrams, P. C. K. Vesborg, and I. Chorkendorff, Controlled Directional Growth of $TiO_2$ Nanotubes Using Molecular Oxygen as a Catalyst, *J. Electrochem. Soc.* 157 (2010) E69-E74.

P. C. K. Vesborg, S. In, J. L. Olsen, T.R. Henriksen, B. L. Abrams, Y. Hou, A. Kleinman-Shwarsctein, O. Hansen and I. Chorkendorff, Quantitative measurement of photocatalytic CO-oxidation as a function of light intensity and wavelength over TiO2 nanotube thin films in micro-reactors, *J. Phys.Chem.C* 114 (2010) 11162-11168.

S. In, M. G. Nielsen, P.C. K. Vesborg , Y. Hou, B. L. Abrams, T.R. Henriksen, O. Hansen, and I. Chorkendorff, "Photocatalytic methane decomposition over vertically aligned transparent TiO2 nanotube arrays", Chem. Commun. 47 (2011) 2613–2615.

Y. Hou, B. L. Abrams, P-C.K. Vesborg, M. E. Björketun, K.Herbst, L. Bech, A. M. Setti, C. D. Damsgaard, T.Pedersen, O. Hansen, J. Rossmeisl, S.Dahl, J. K. Nørskov,, and I. Chorkendorff, "Bioinspired Co-catalysts Bonded to a Silicon Photocathode for Solar Hydrogen Evolution " Nature Materials 10 (2011) 434-438.

Y. Hou, B. L. Abrams, P-C.K. Vesborg, M. E. Björketun, K.Herbst, L. Bech, T.Pedersen, O. Hansen, J. Rossmeisl, S.Dahl, J. K. Nørskov,, and I. Chorkendorff, Photoelectrocatalysis and electrocatalysis on cubane-like cluster-decorated silicon electrodes (*in preparation)*

*S. In, P.C. K. Vesborg, B.L. Abrams, Y. Hou, and I. Chorkendorff., "Does nitrogen doping of TiO2 nanotubes really enhance the visible light photooxidation of organics?", Journal of Photochemistry and Photobiology A: Chemistry 222 (2011) 258-262.*

*B. L. Abrams, Y. Hou, P. C.K. Vesborg, S. In, C. Damsgaard, O. Hansen, K. Herbst, and I. Chorkendorff, "Materials for photoelectrocatalytic hydrogen production", EPO Patent Application No.: 10000303.7 and USA Provisional Patent Application No.: 61/294866 (2010).*

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

Ib Chorkendorff (invited talk, Summer School), Catalysts for producing Solar Fuels, Materials for the hydrogen economy, 17-21 August, 2010, Reykjavik, Iceland

Ib Chorkendorff (invited talk), New catalysts for production solar fuels, 18th International Conference on Photocatalysis and Solar Energy Storage, July 25-30, 2010, Seoul, Korea

Peter Vesborg (oral presentation), Photocatalytic measurements in μ-reactors, 18th International Conference on Photocatalysis and Solar Energy Storage, July 25-30, 2010, Seoul, Korea.

Yidong Hou (poster presentation), Bioinspired Co-catalysts Bonded to a Silicon Photocathode for Solar Hydrogen Evolution, 14th Nordic Symposium on Catalysis, August 29-31, 2010, Helsingør, Denmark.

Raja Sellappan, Jiefang Zhu, Hans Fredriksson, Rafael S. Martins, Michael Zäch and Dinko Chakarov, Preparation and characterization of $TiO_2$/Carbon composite thin films with enhanced photocatalytic activity, Submitted to Journal of Molecular Catalysis, August 2010.

**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

***Results***- Conferences, invited talks, workshops

**‘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.

SOLAR HYDROGEN

*Dissemination+*

**About 40 (25+15) publications and invited talks!**

## *Milestones: what is achieved*

-The newl 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.

SOLAR HYDROGEN

# *What is going on!*

-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 resuults more publications
-and patent(s).
**-We have created strong and successful team/network (!!!)**
**-We have ideas and direction, want to explore MORE!**
**-Industry!**

SOLAR HYDROGEN

**“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:

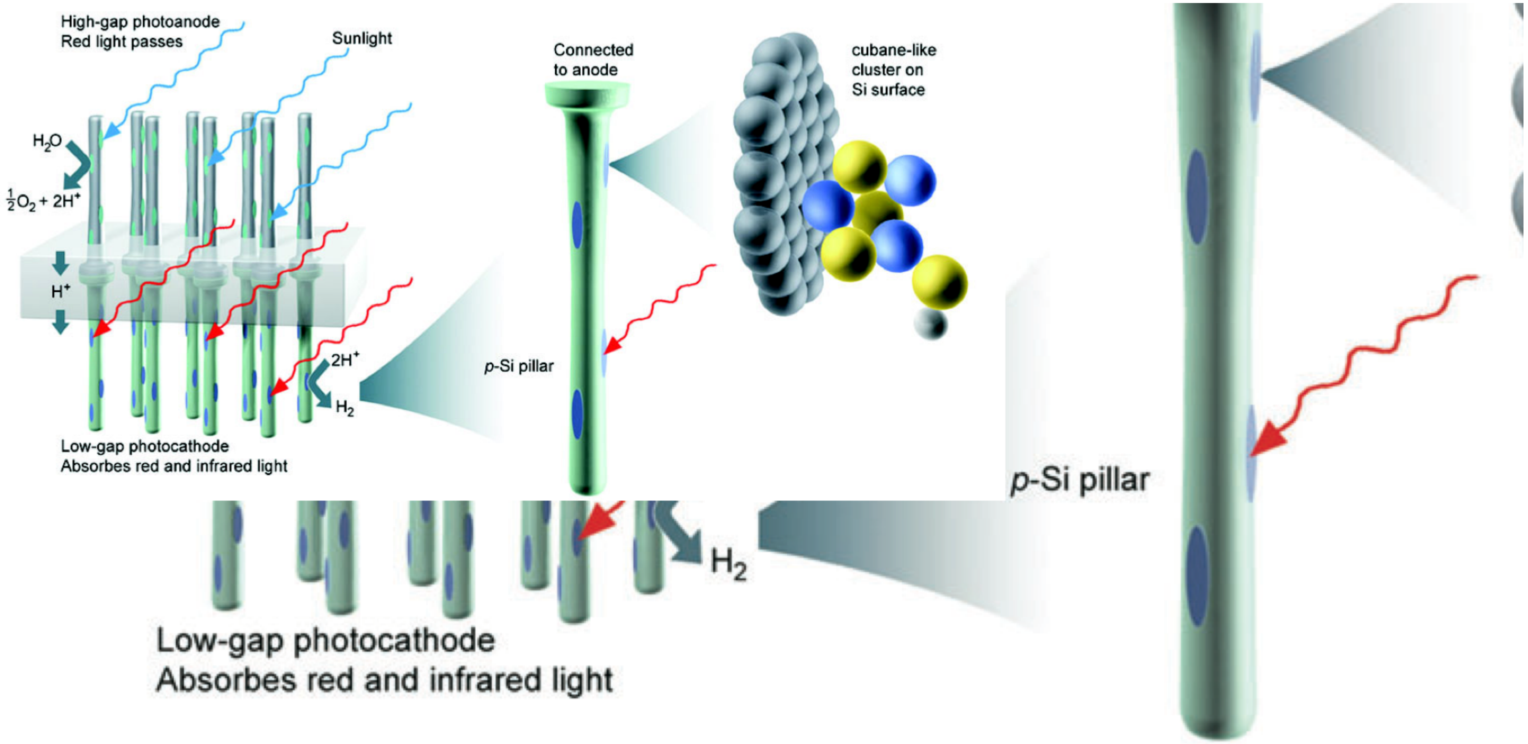
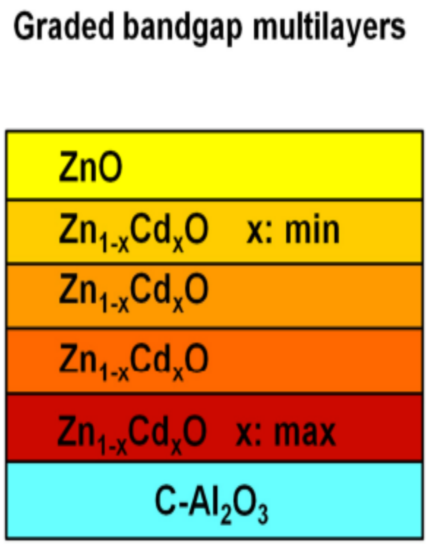
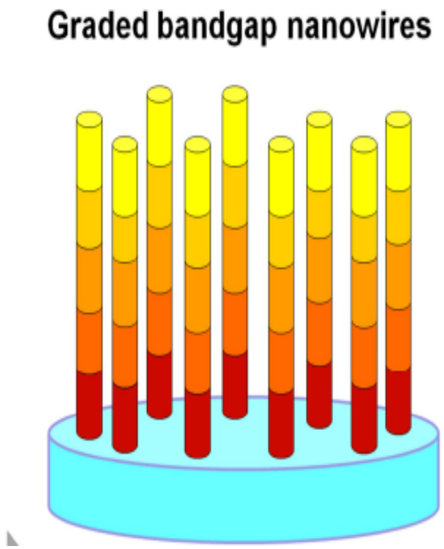


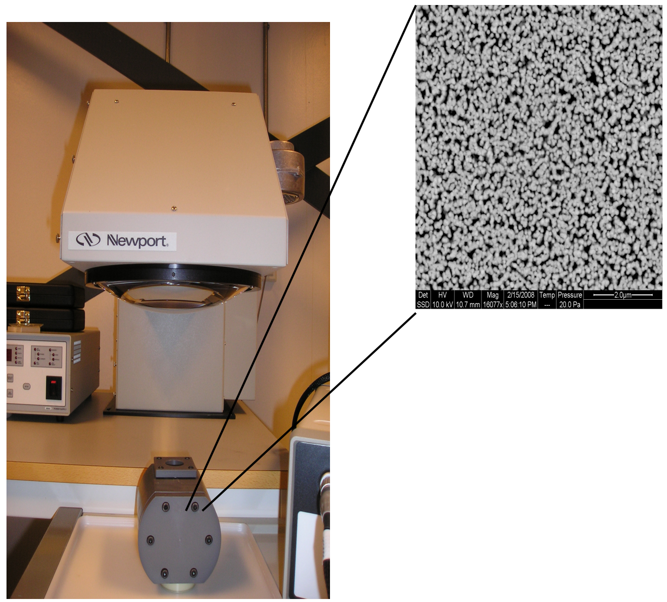

**Fig. 1.** Schematic of the tandem "chemical solar cell”. To the left, the entire system is shown where pillars are embedded in a proton conducting membrane. The solar light is incident from above and the blue part of the spectrum is absorbed by the anode used for oxidizing water into molecular oxygen and protons.
The protons migrate through the membrane and are reduced at the cathode side by $Mo_3S_4$ 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 $Mo_3S_4$ clusters and excited by the red part of the solar spectrum.

SOLAR HYDROGEN

# RESULTS: at UiO



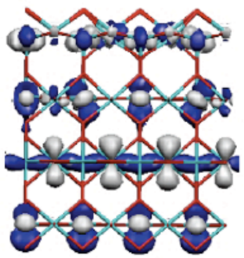

**Bandgap engineered samples prepared at MINA lab, Oslo.**

SOLAR
HYDROGEN

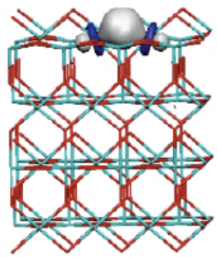
**Development of Theoretical Tools for Studies of Electronic Excitations and Trapped Holes**

**Peter Klüpfel, Simon Klüpfel, Hannes Jónsson**

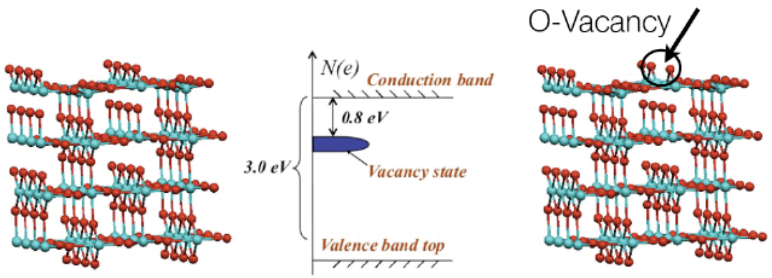
**Univ. of Iceland**



UNIVERSITY OF ICELAND



Oxygen-Vacancy State in $TiO_2$

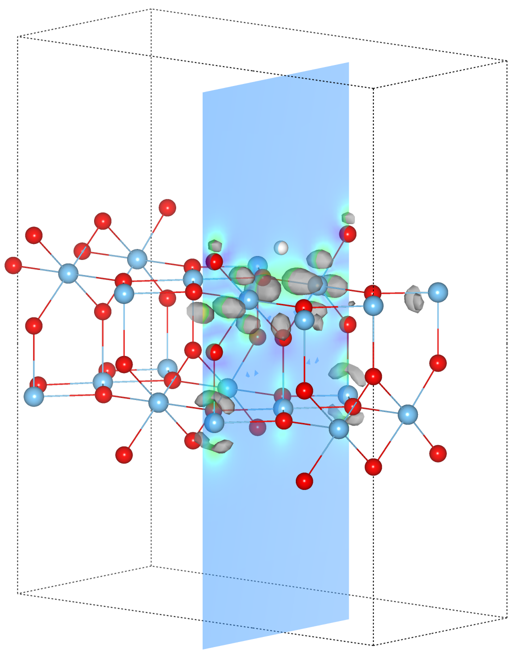



**Vacancy states (within the band-gap) can be created by removing an Oxygen atom from the ideal periodic structure of $TiO_2$**

experimentally identified: 0.8eV below conduction band

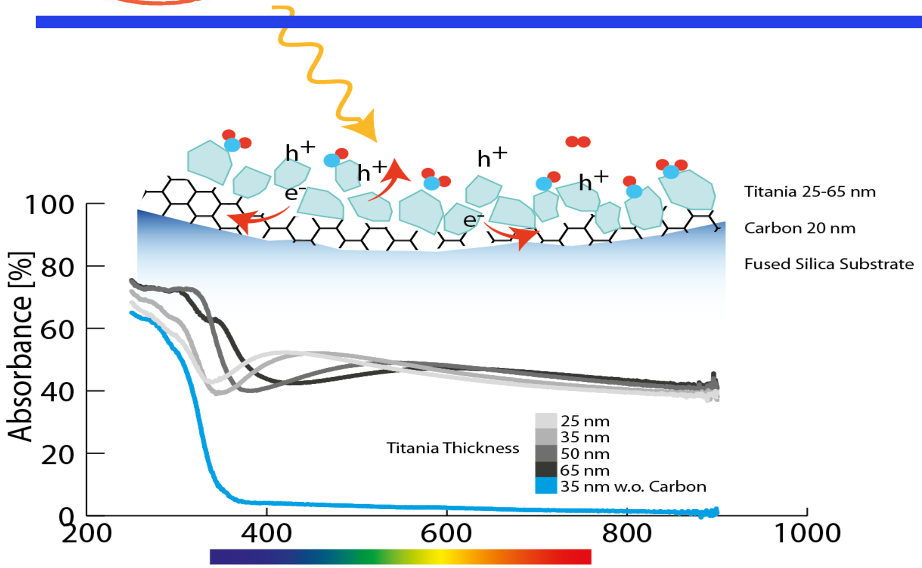
# ***RESULTS:*** *at UI*

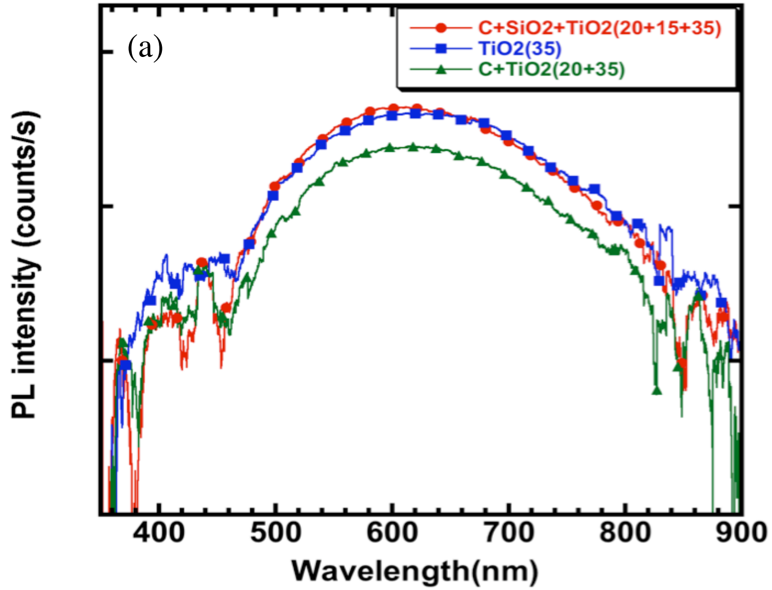
Characterization of the electronic defect states

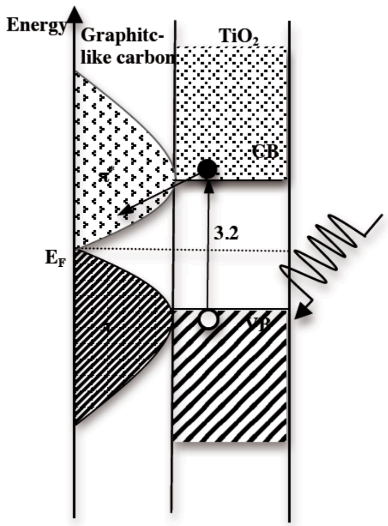


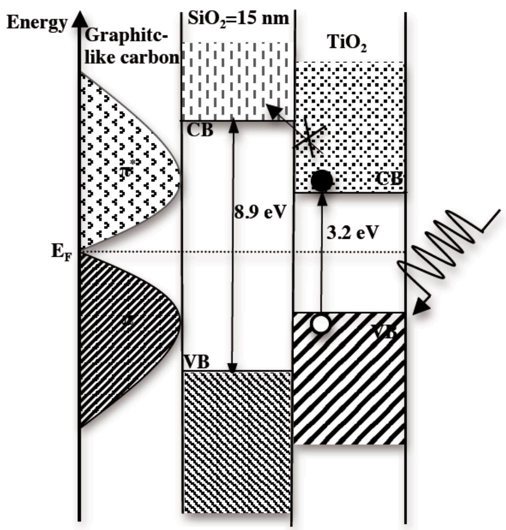
SOLAR HYDROGEN

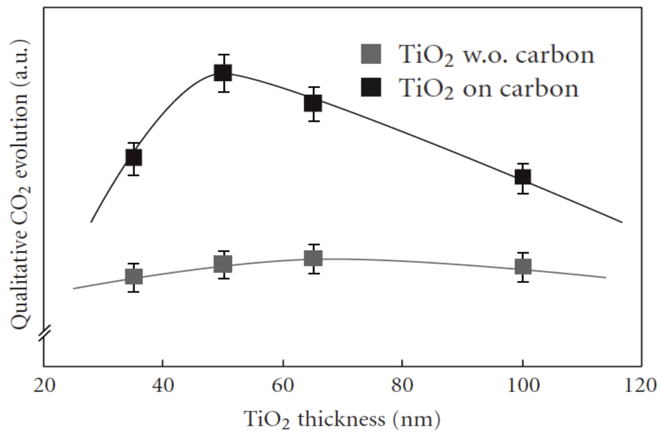
# *RESULTS:* at Chalmers




**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.**

SOLAR HYDROGEN

# 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,

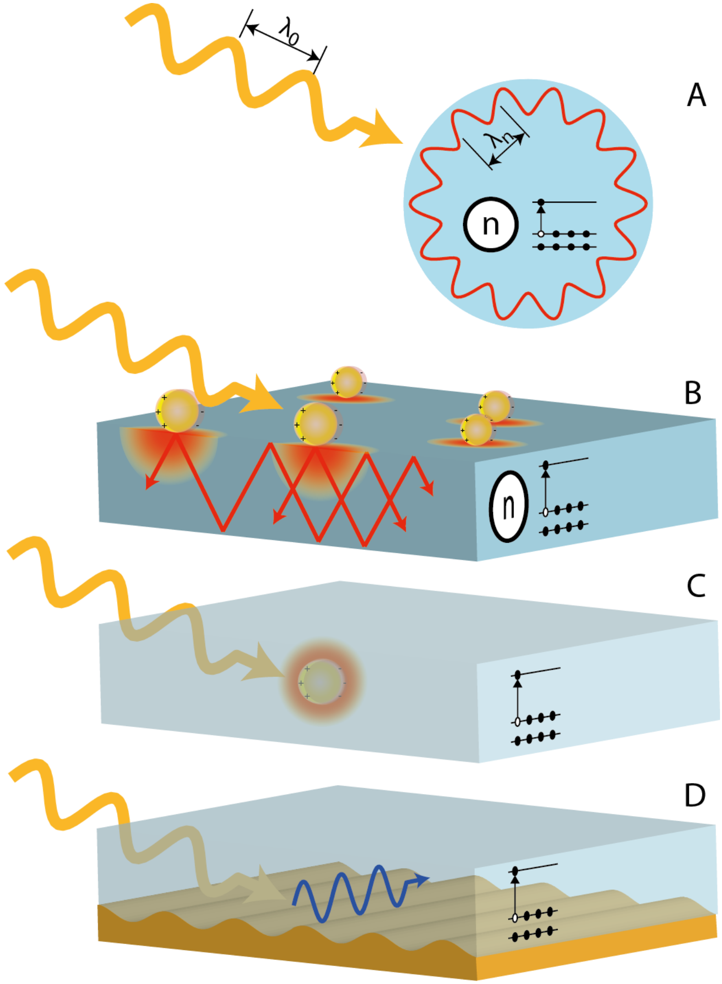
**(ii) Its generic character**,

(iii) collaboration with EU and national projects with similar activities.

SOLAR
HYDROGEN


Tank you for the ”initiative”!

Thanks for the attention!




→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.