

# RATOCAT: Rational design of highly effective photocatalysts with atomic-level control

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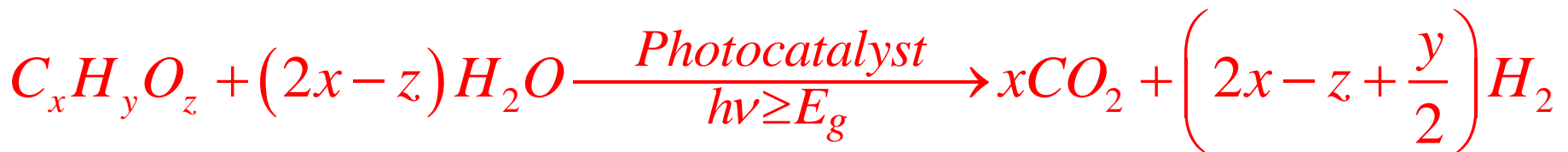
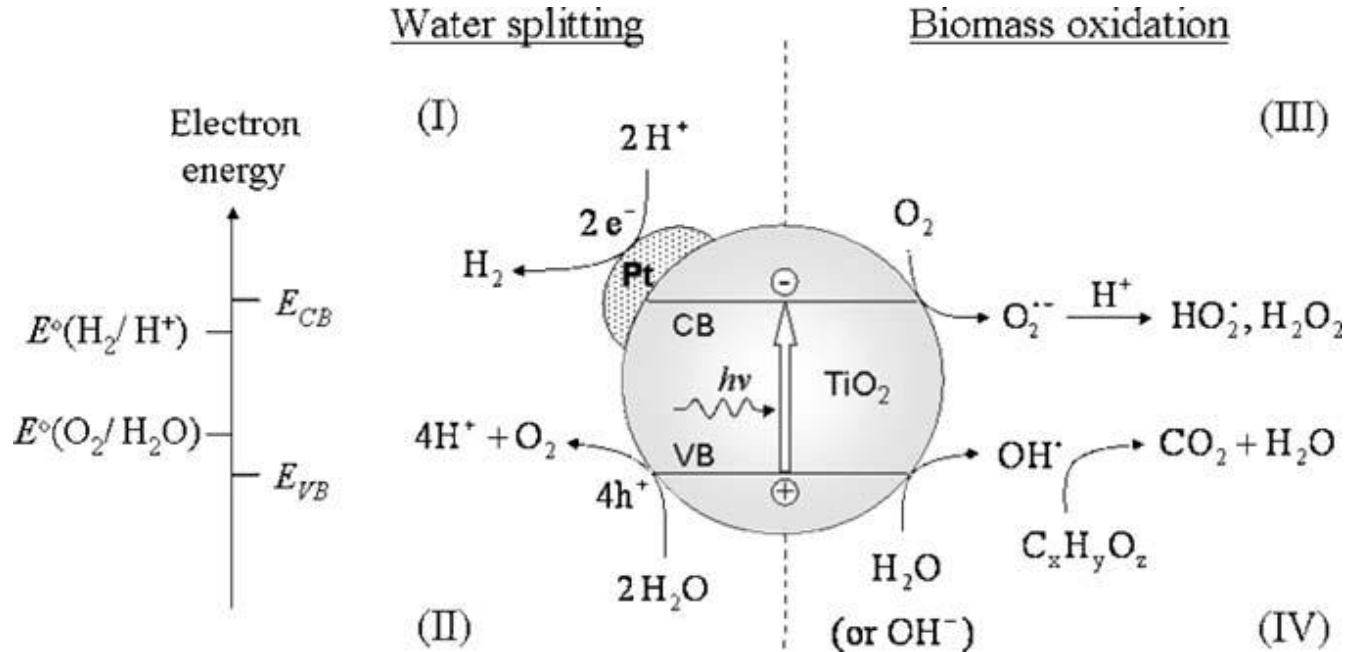
**J.R. van Ommen.** Delft University of Technology, The Netherlands



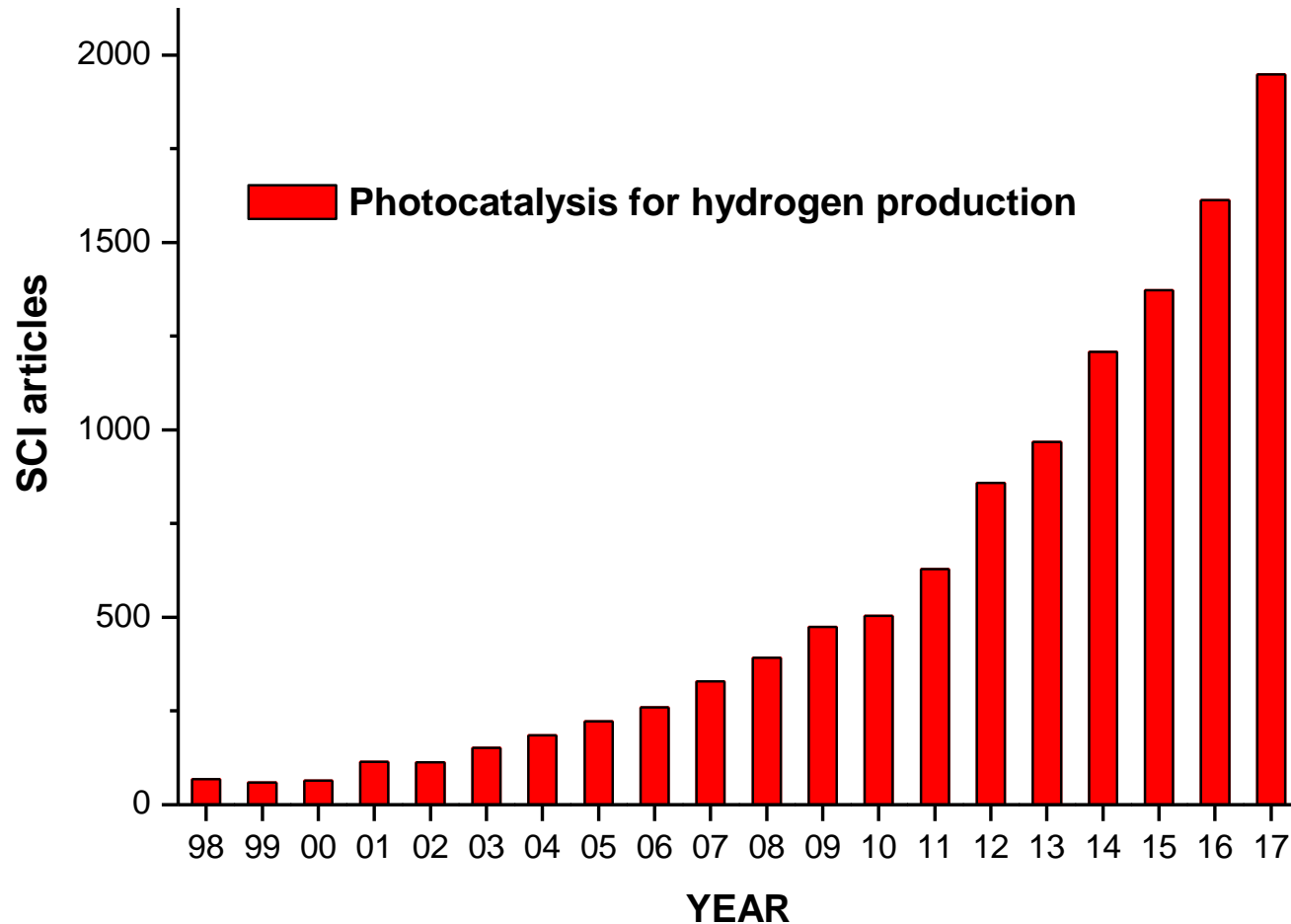
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# Photoreforming of organic aqueous pollutants



# Photoreforming of organic aqueous pollutants



Source: [www.scopus.com](http://www.scopus.com)

RATOCAT (Funding: ERA-NET for materials research and innovation) will develop and demonstrate highly effective photocatalysts for solar-powered hydrogen generation, through a rational approach to designing both the catalyst material and its production process with atomic-level control.

## Increase efficiency and reduce costs in three ways:

1. Absorption of the **visible-light solar spectrum** by tailoring surface-modified catalyst materials;
2. Surface modification of catalyst powders with non-critical materials via a **deposition process that is scalable** to the manufacturing environment;
3. **Wastewater as the feedstock** for hydrogen.

# RATOCAT Partners

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## University College Cork (Tyndall-UCC)

### Role in the project:

- (i) Project coordination.
- (ii) Simulation of new photocatalysts based on surface modification with metal oxide nanoclusters to predict optimum photocatalysts for experimental study at ICMSE (CSIC).
- (iii) Simulation of surface chemical reactions during atomic layer deposition of catalysts. Optimise the deposition process at TU-Delft.

## Plataforma Solar de Almeria (PSA), CIEMAT

### Role in the project:

Testing of new nanomaterials under solar irradiation at pilot plant scale.

## Delft University of Technology

### Role in the project:

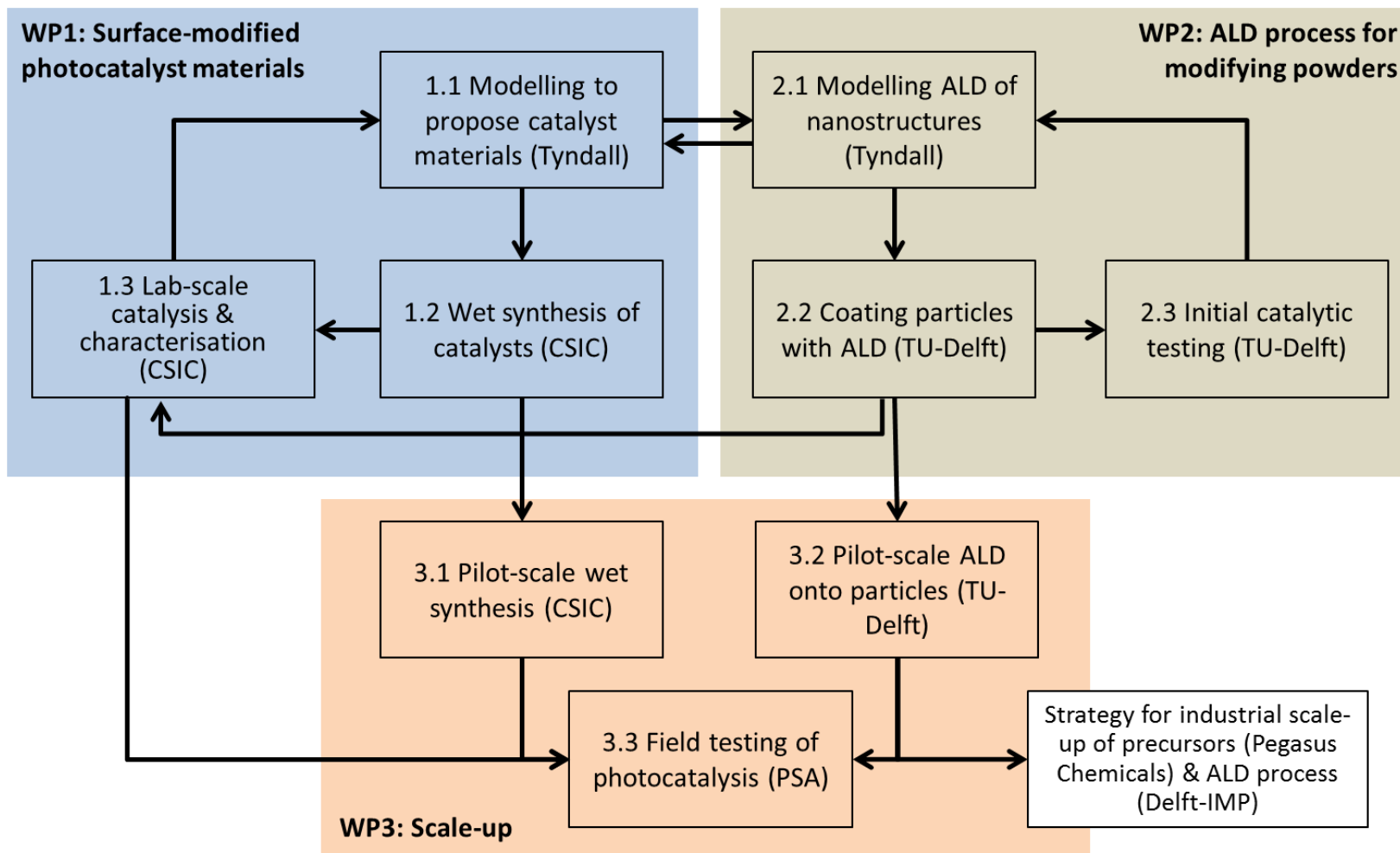
Develop an ALD process for deposition of oxide, non-oxide nanocluster modifiers onto TiO<sub>2</sub> powders.

## Instituto de Ciencia de Materiales de Sevilla, Consejo Superior de Investigaciones Científicas (CSIC)

### Role in the project:

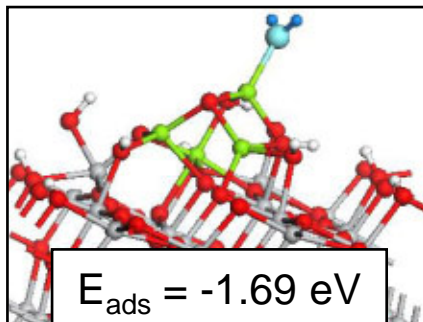
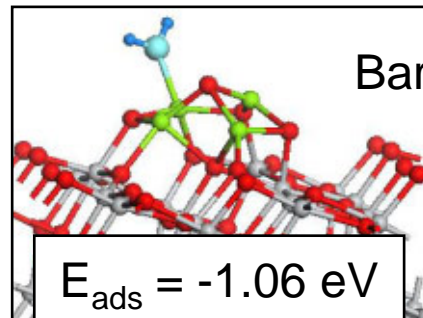
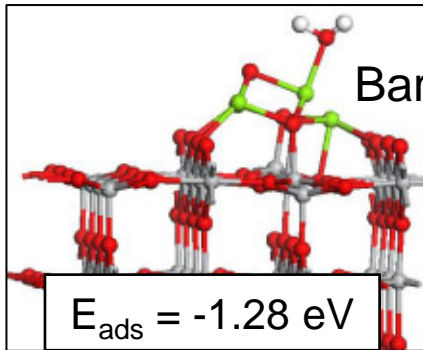
- (i) Preparation of powdered catalysts,
- (ii) Physicochemical characterization of catalysts and probing structural and surface properties by means of advanced characterization technique
- (iii) Photocatalytic test at lab scale.

# RATOCAT Workplan

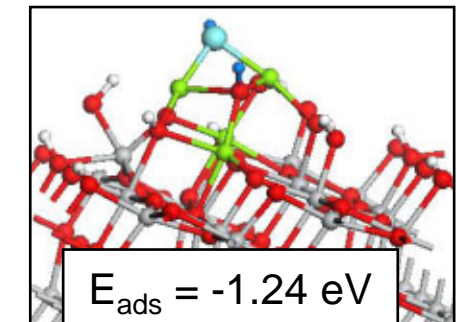
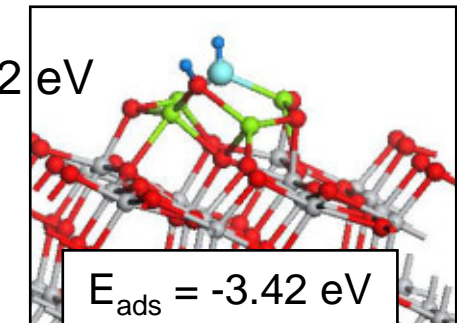
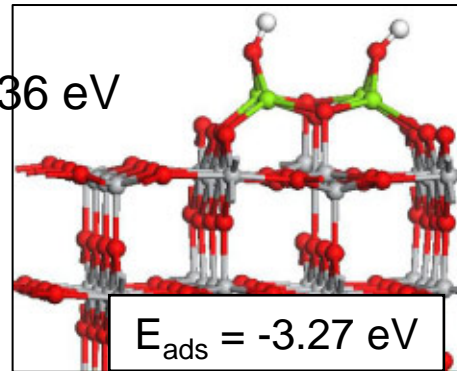


# Results of Simulation Work Water Oxidation

## Molecular



## Dissociated



H<sub>2</sub>O at **Mg<sub>4</sub>O<sub>4</sub>**-modified  
**bare** (o-)rutile (110).

H<sub>2</sub>O at **Mg<sub>4</sub>O<sub>4</sub>**-modified  
**bare** (o-)anatase (101).

H<sub>2</sub>O at **Mg<sub>4</sub>O<sub>4</sub>**-modified  
**hydroxylated** (OH-)anatase  
(101).

Determine water oxidation  
pathway/energetics

# Results of Simulation Work Water Oxidation

From literature, investigate modifying  $\text{TiO}_2$  with nanoclusters of **metal chalcogenides** (sulphides, selenides)

Descriptor for H evolution:

Compute adsorption free energy of H atom at catalyst

$$\Delta G^{\text{H-ads}} = \Delta E^{\text{H-ads}} + 0.24 \text{ eV}$$

Aim for  $\Delta G \sim 0 \text{ eV} \pm 0.2 \text{ eV}$

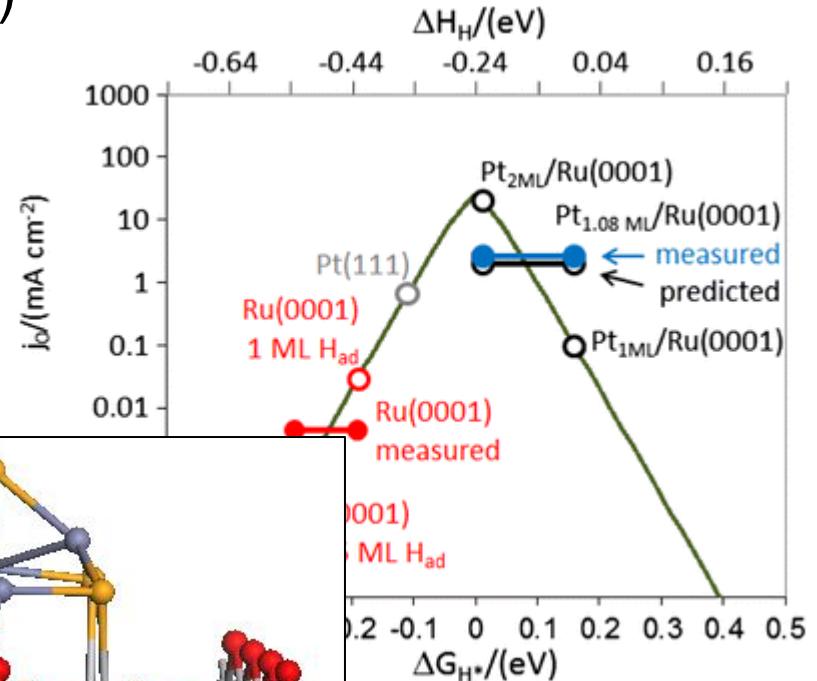
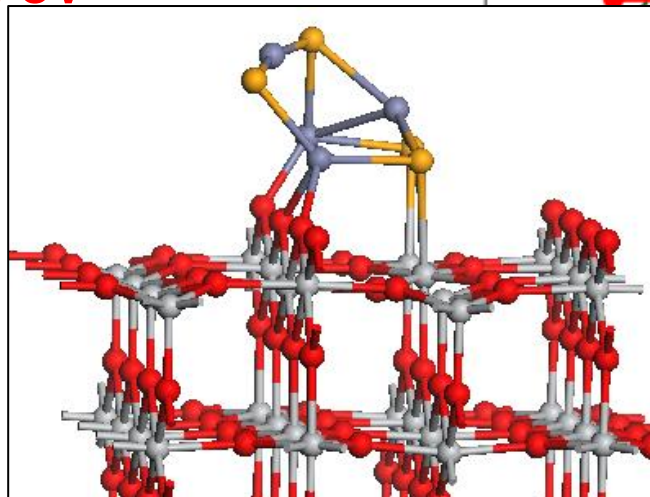
**Model Systems:**

$\text{Sn}_4\text{Se}_4$ -rutile-(110)

$\text{Sn}_4\text{S}_4$ -rutile-(110)

$\text{Zn}_4\text{Se}_4$ -rutile-(110)

$\text{Zn}_4\text{S}_4$ -rutile-(110)



# Results of Simulation Work H<sub>2</sub> Evolution

	$\Delta G^{\text{H-ads}} 25\% \text{ H}$	$\Delta G^{\text{H-ads}} 50\% \text{ H}$	$\Delta G^{\text{H}_2\text{O}}$
Sn <sub>4</sub> Se <sub>4</sub> -r110	-0.19	0.1	-0.68
Sn <sub>4</sub> S <sub>4</sub> -r110	-0.92	-0.17	-0.74
Zn <sub>4</sub> Se <sub>4</sub> -r110	0.15	0.17	-0.76
Zn <sub>4</sub> S <sub>4</sub> -r110	-0.39	0.24	-0.69

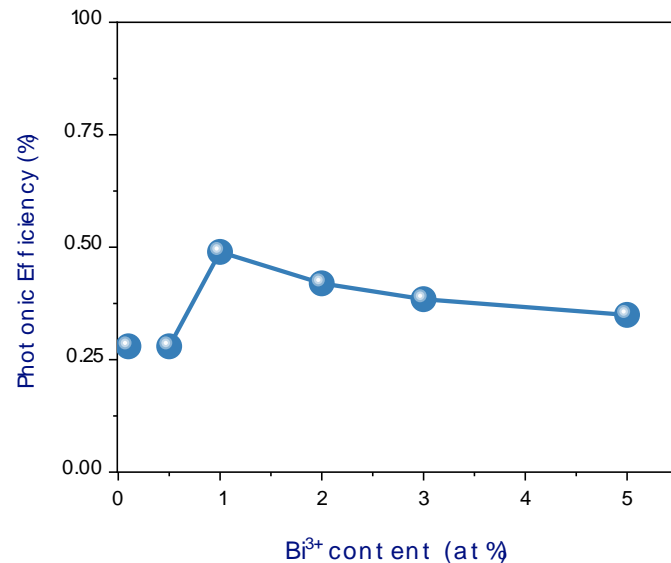
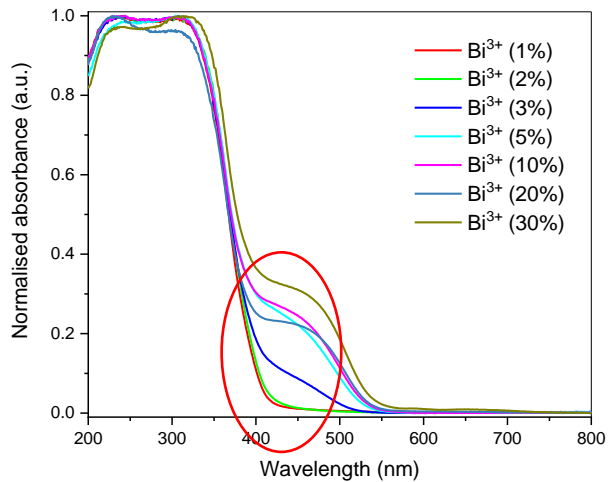
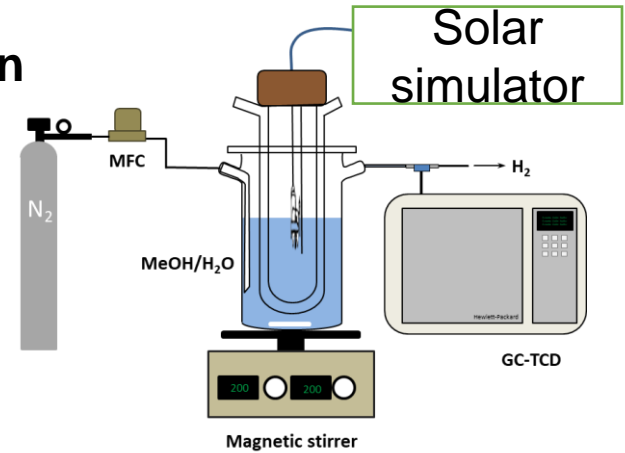
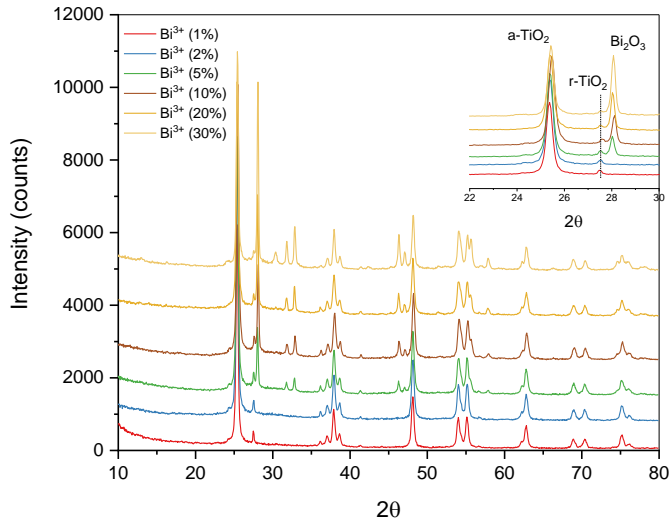
H adsorption  
**too strong**  
for sulphide  
modifiers.

H adsorption  
**favourable**  
for selenide  
modifiers as  
< 0.2

Water adsorbs only in  
molecular form for each  
modified surface.

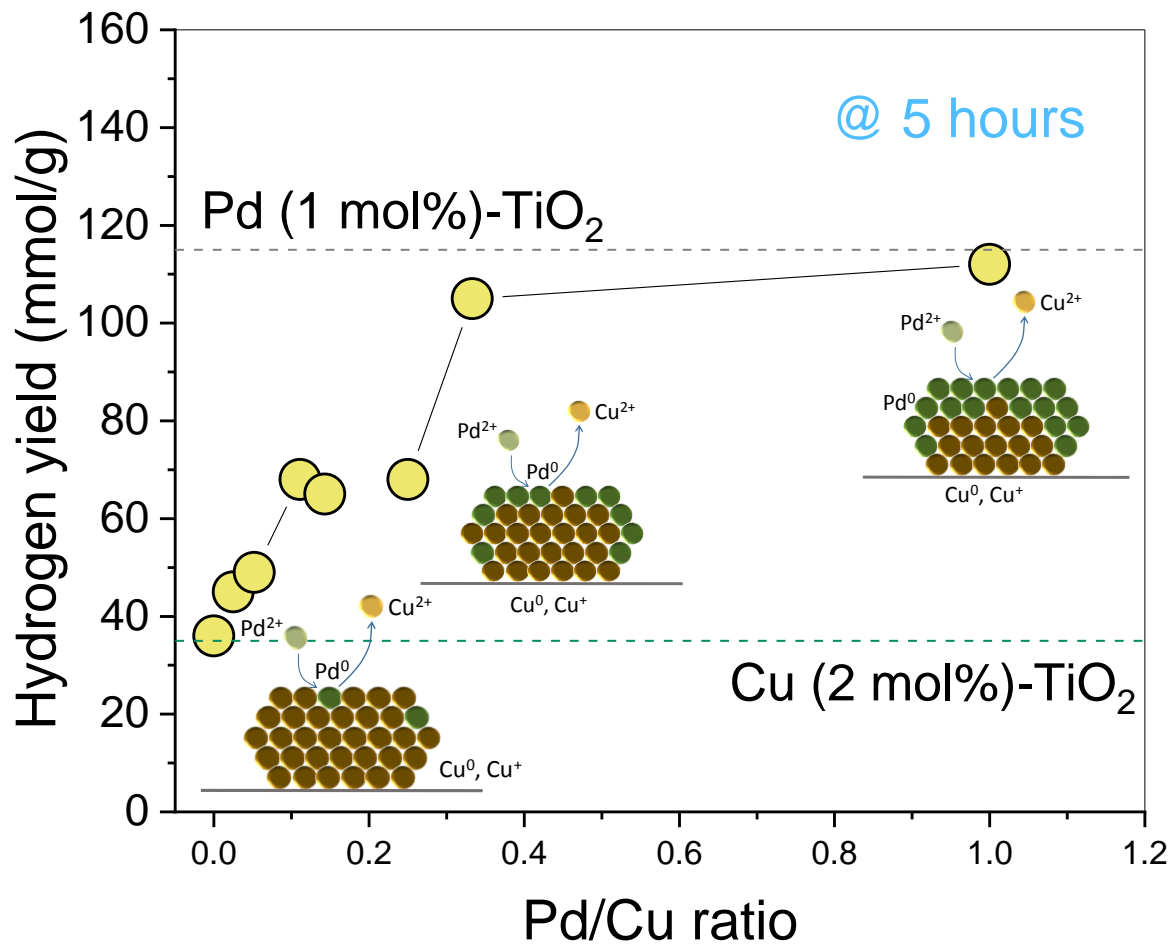
# Results of H<sub>2</sub> photocatalytic evolution

## Bismuth-modified TiO<sub>2</sub> for Hydrogen Evolution Reaction



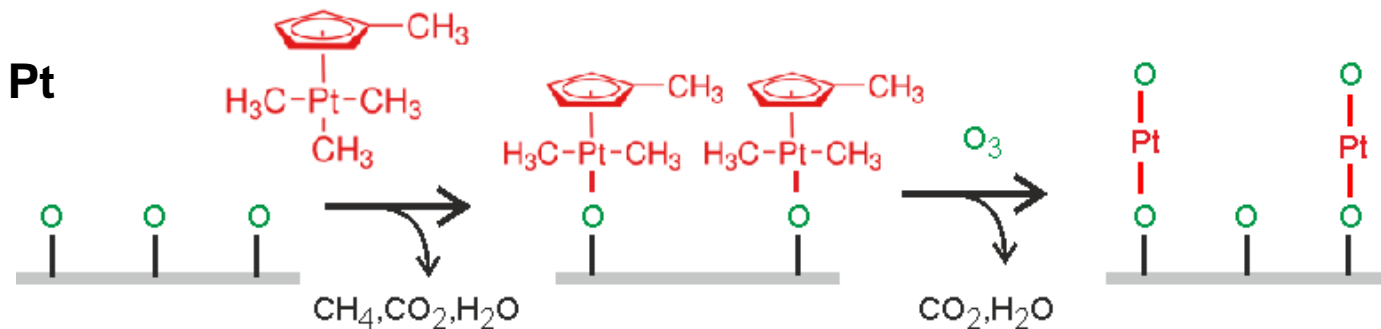
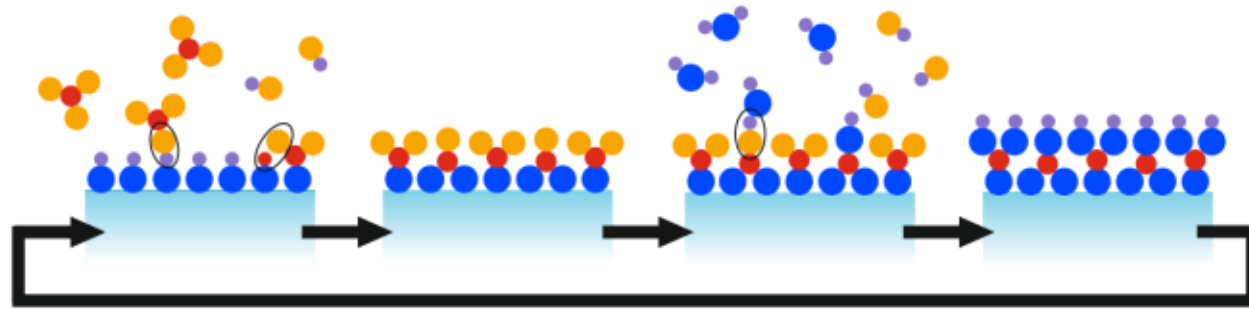
# Results of H<sub>2</sub> photocatalytic evolution

## Cu-Pd Co-catalyst on TiO<sub>2</sub> for Hydrogen Evolution Reaction



# Gas phase coating of objects via ALD

ALD = Atomic layer deposition



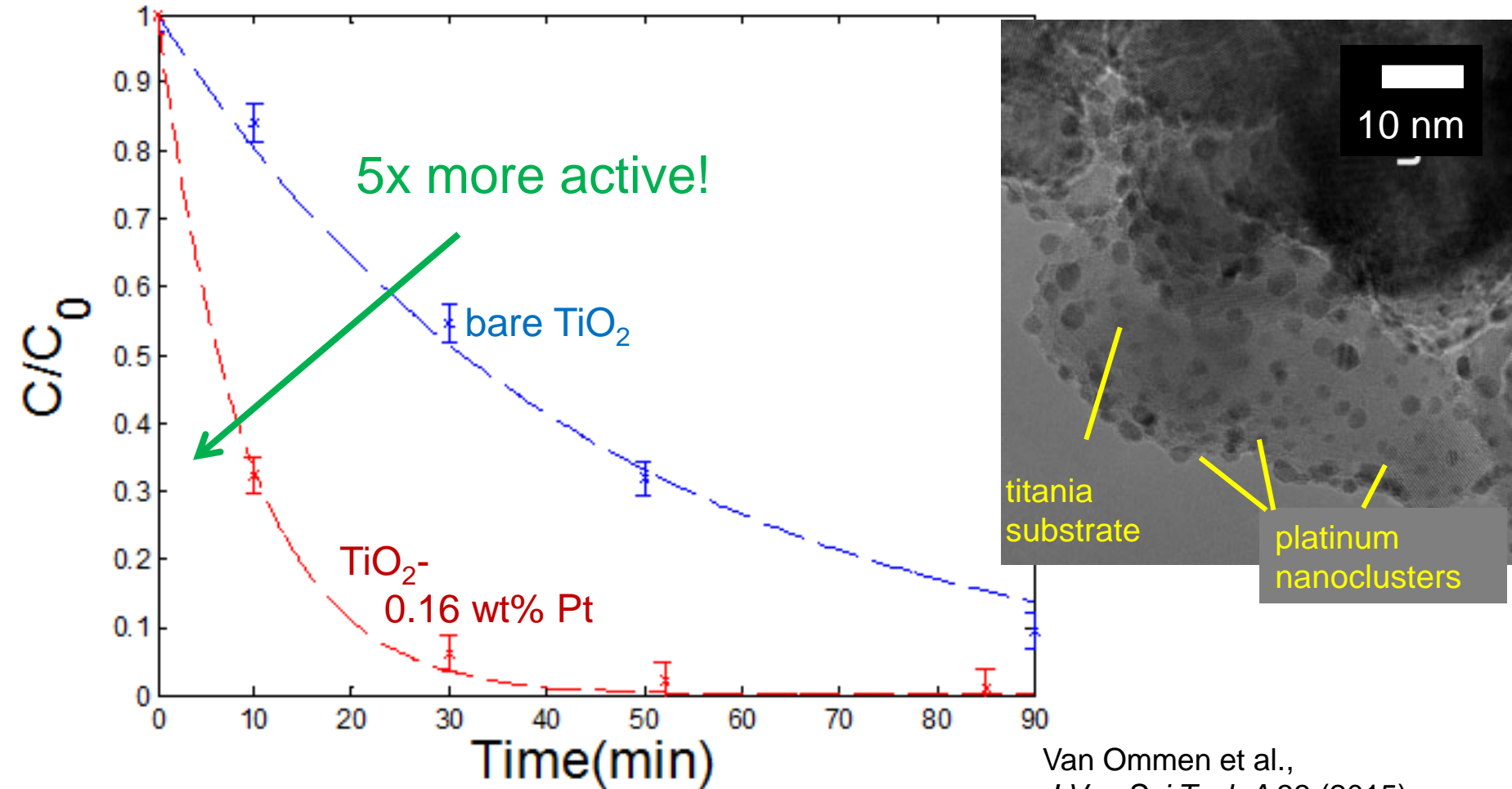
Many materials possible:

Other oxides such as  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{ZrO}_2$ , ...

Other metals such as  $\text{Co}$ ,  $\text{Cu}$ ,  $\text{Ru}$ ,  $\text{Pd}$ ,  $\text{W}$ , ...

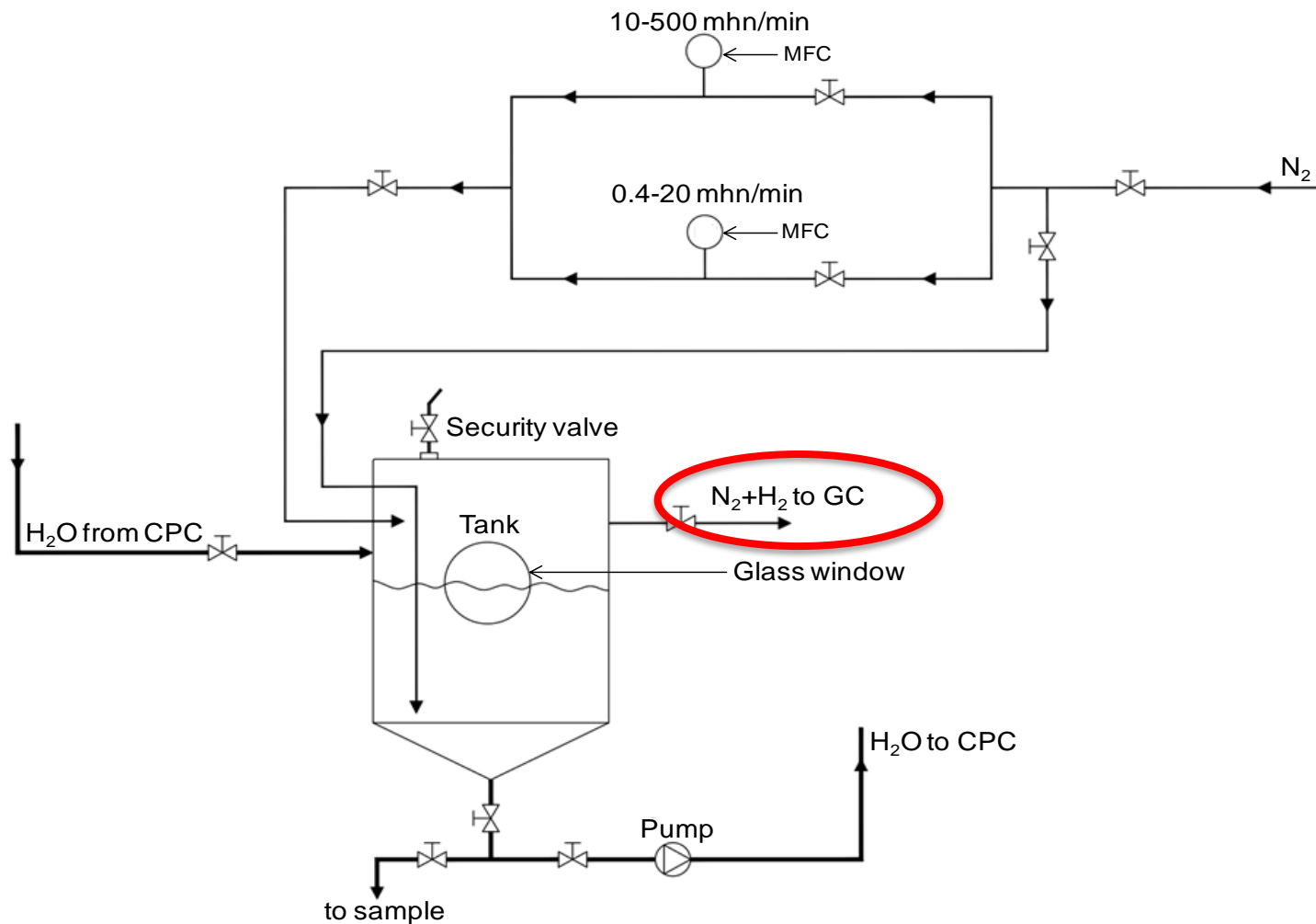
Other materials such as  $\text{BN}$ ,  $\text{AlN}$ ,  $\text{TiN}$ ,  $\text{SiC}$ ,  $\text{MgF}_2$ ,  $\text{ZnS}$ , ...

# Gas phase coating of objects via ALD

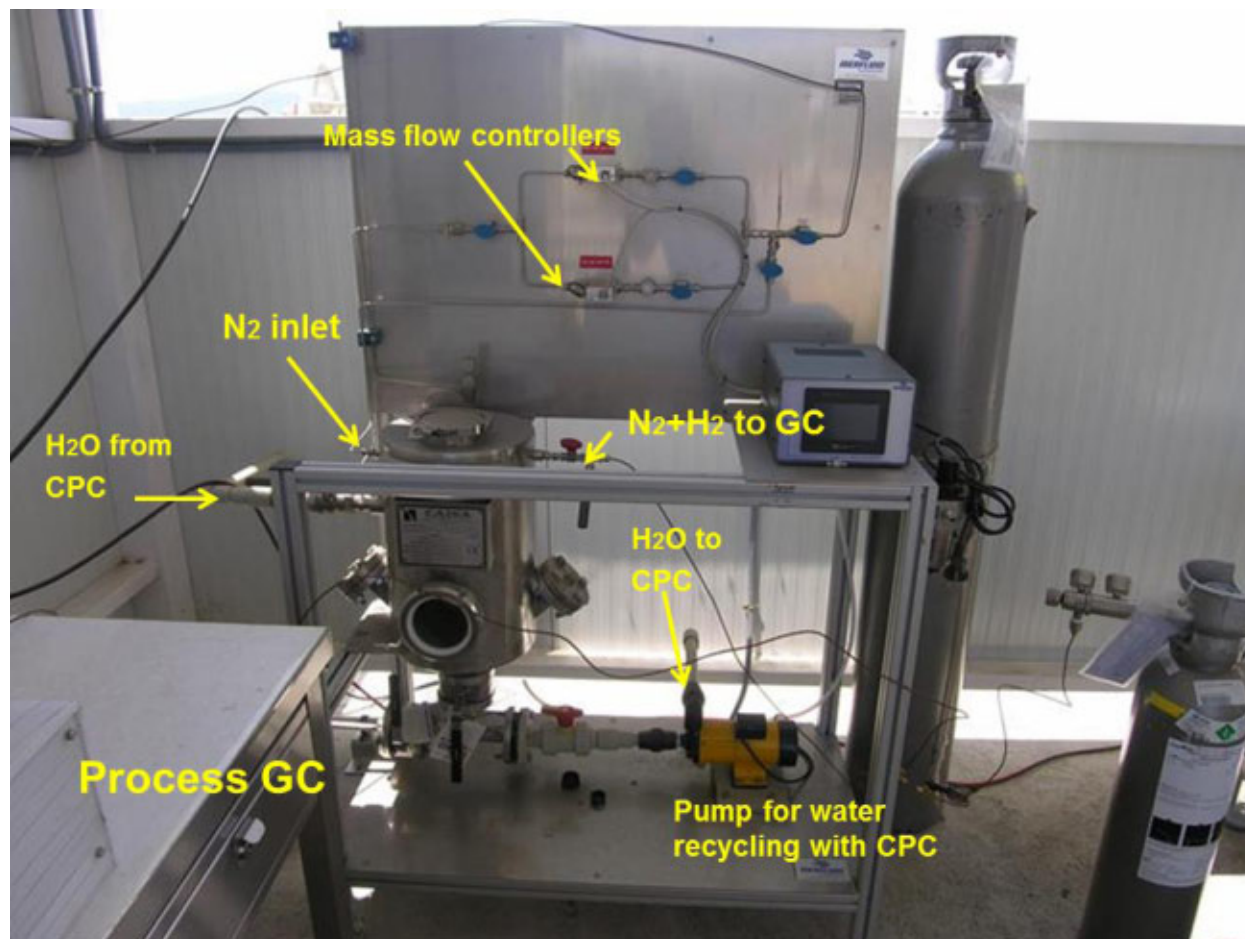


Van Ommen et al.,  
*J Vac Sci Tech A* 33 (2015)  
021513

# Testing of new nanomaterials under solar irradiation at pilot plant scale



# Testing of new nanomaterials under solar irradiation at pilot plant scale



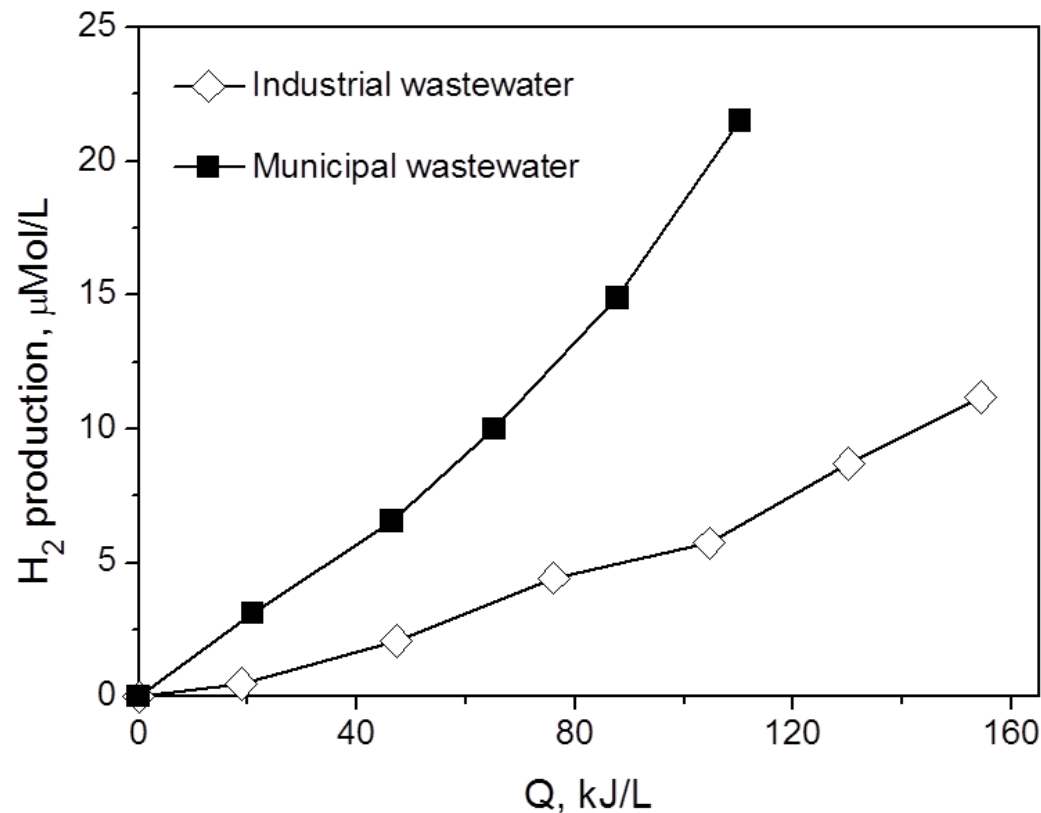
- Stainless steel tank of 27 L
- Centrifugal pump with a flow rate of 20 L/min

# Testing of new nanomaterials under solar irradiation at pilot plant scale



- 16 Pyrex glass tubes (inner Diameter 28.45 mm, outer diameter 32.0 mm, length 1530.0 mm) mounted on a fixed platform tilted  $37^\circ$  (local latitude).
- Total area irradiated of  $2.1 \text{ m}^2$
- Total irradiated volume of 14.24 L.
- Total slurry volume of 25 L
- Catalyst conc. in the range of 0.1-0.3 g/L.

# Testing of new nanomaterials under solar irradiation at pilot plant scale



**H<sub>2</sub> production vs. energy accumulated into the photoreactor (305-550 nm).** 25 L of 0.2 g·L<sup>-1</sup> Au/TiO<sub>2</sub> slurries. In both cases pH was adjusted to 3. Total irradiation time of 5 h.

**Other examples could be found in:**

*Int. J. Hydrogen Energy.* **41** (2016) 11933–11940

*App. Catal. B: Environ.*, **229** (2018) 15–23.

# RATOCAT Project

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**Thank you very much  
for your attention.**

**Questions?**