

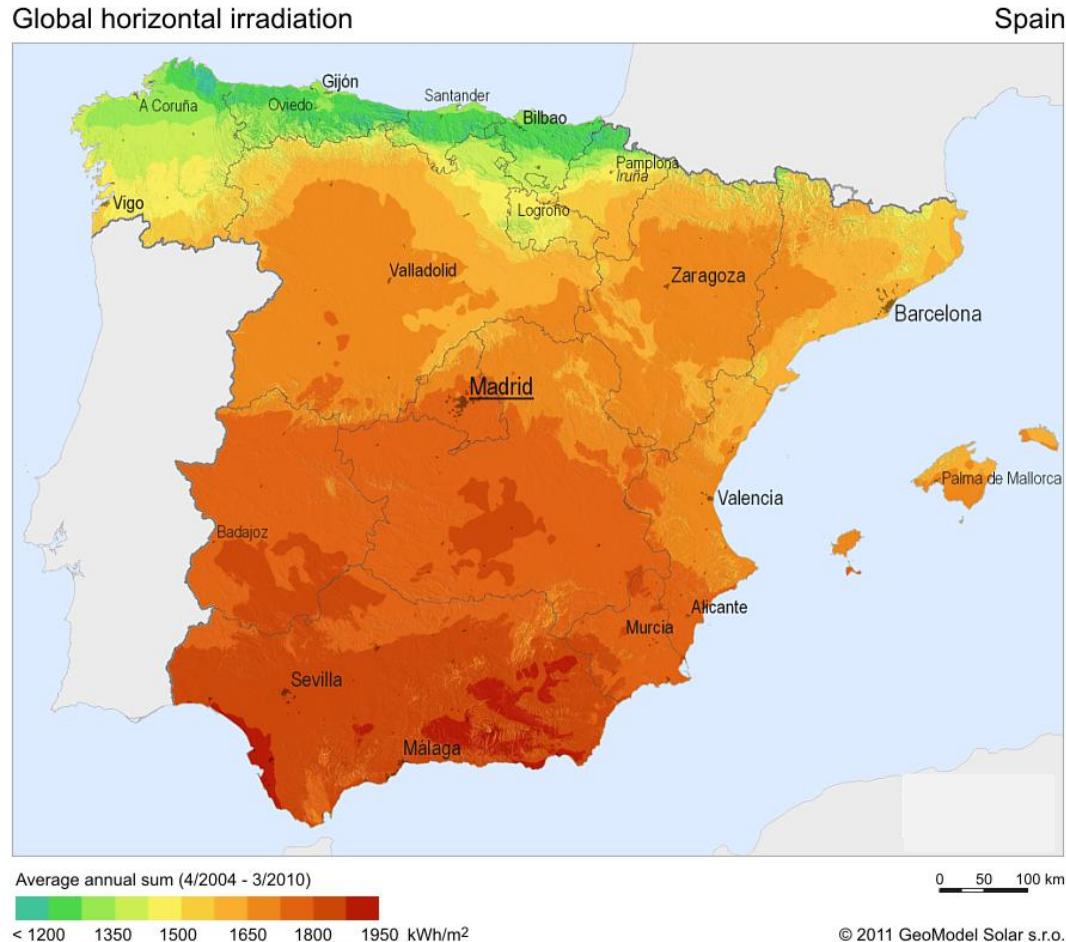
# Artificial photosynthesis: Towards efficient Solar-to-H<sub>2</sub> Conversion with metal oxide semiconductors

**Sixto Giménez**

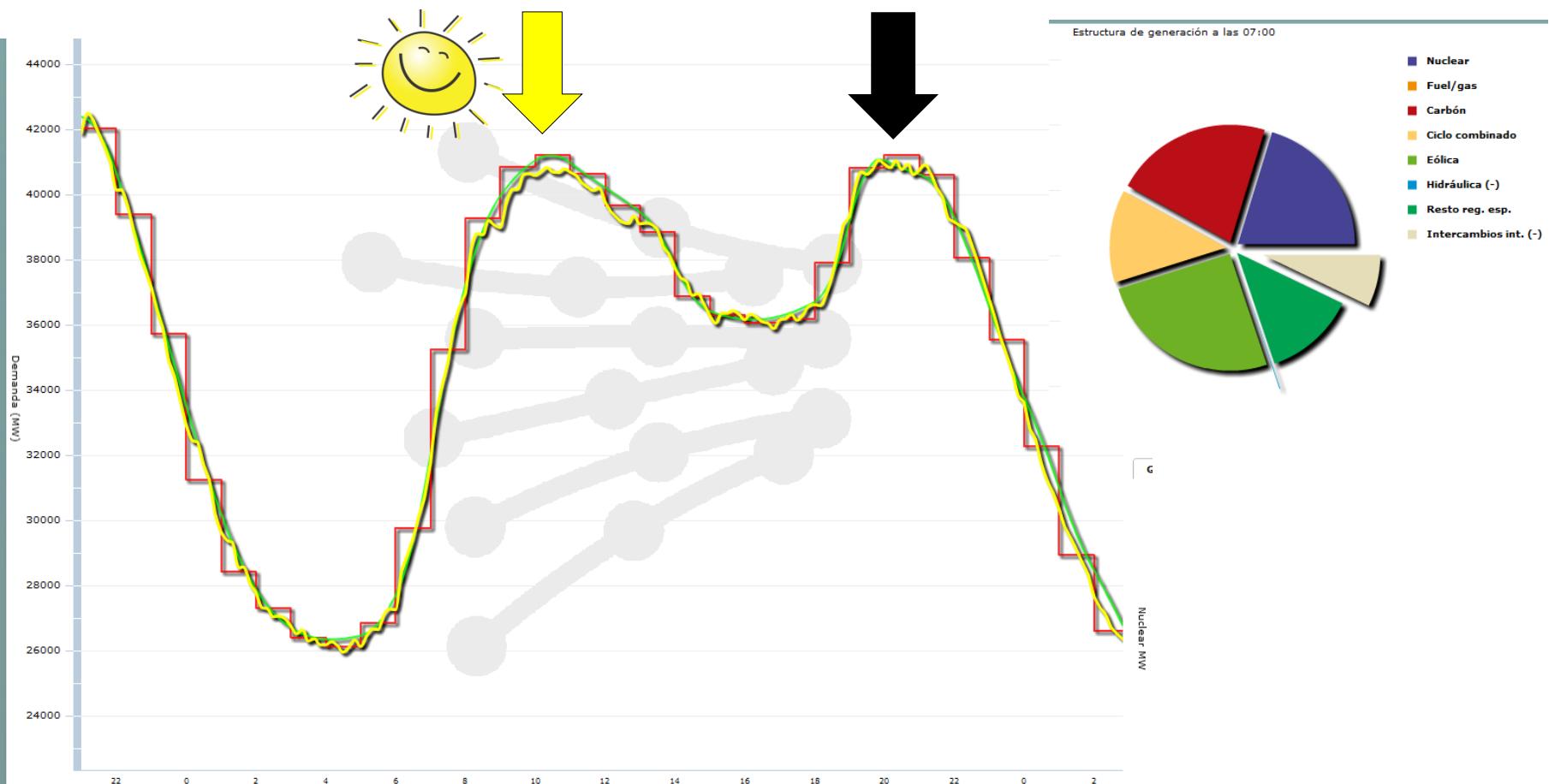
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# Introduction

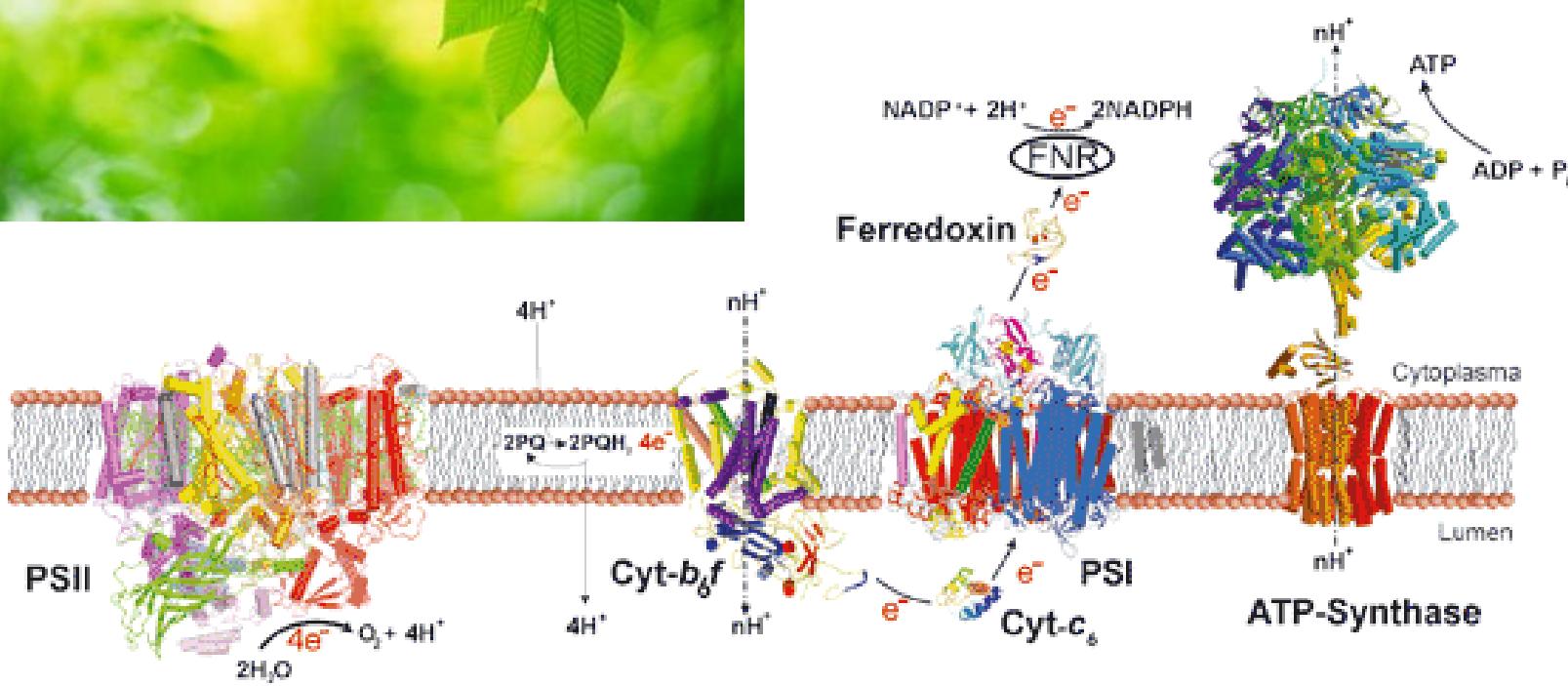
Global horizontal irradiation



# Energy demand in Spain



# Natural photosynthesis



# Solar energy storage

Mimicking nature is one of the most successful strategies in the history of science and technology.



# Solar energy storage

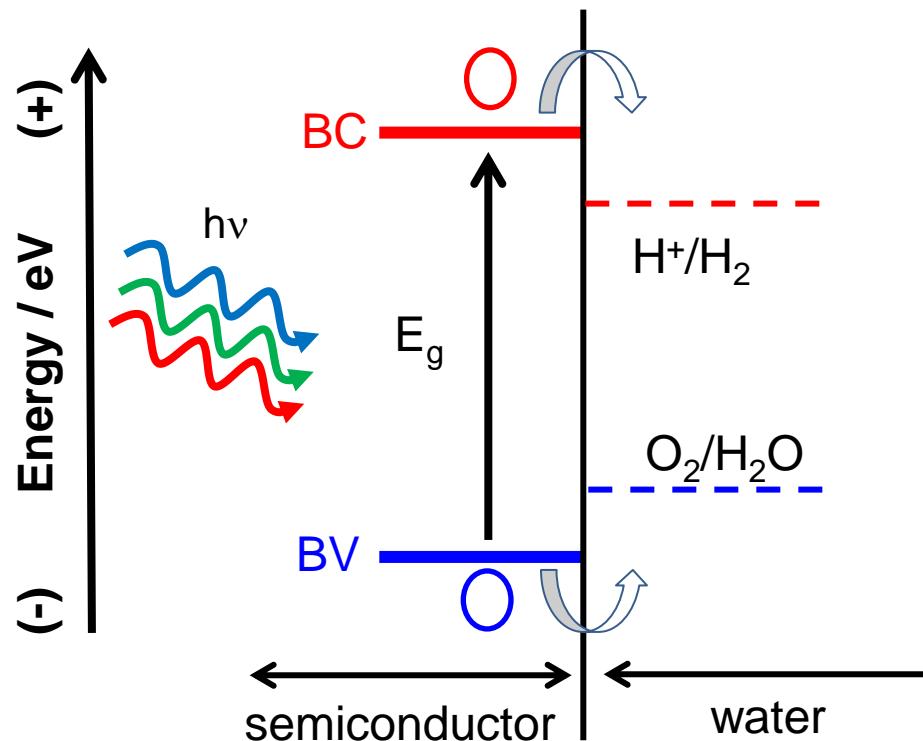
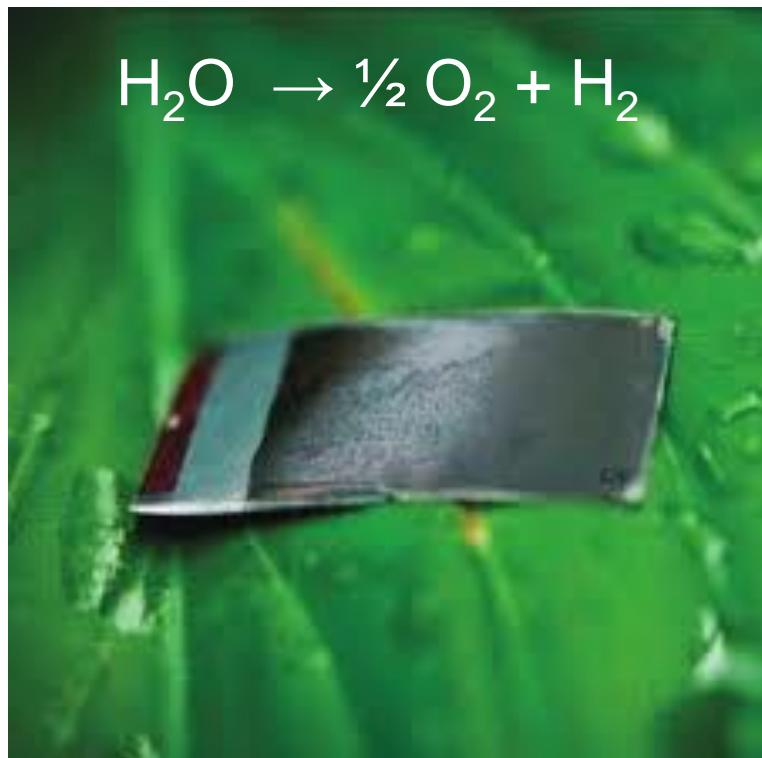
Mimicking nature is one of the most successful strategies in the history of science and technology.



# Artificial photosynthesis

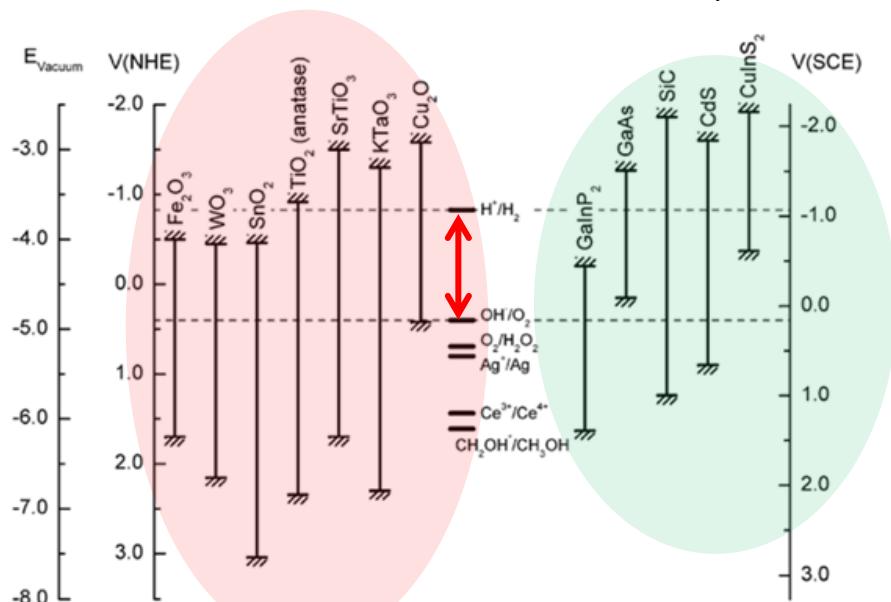
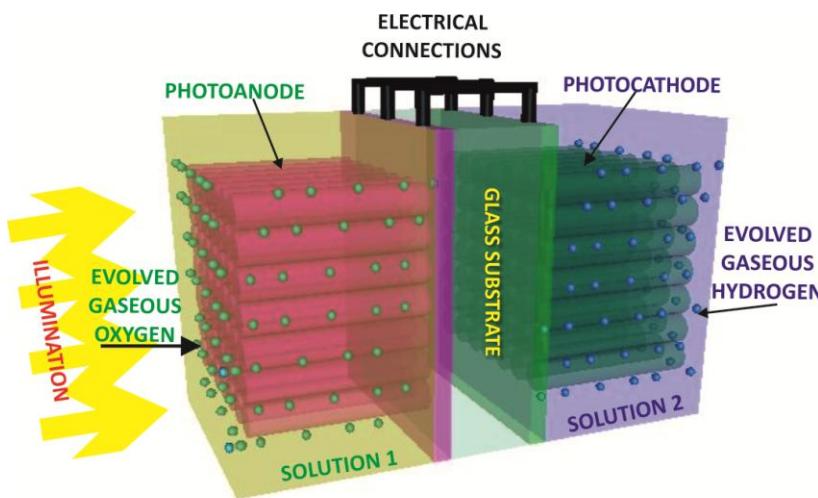
The aim of this technology is achieving a device able to efficiently transform solar radiation into fuels (i.e. H<sub>2</sub>).

The simplest approach involves the use of **semiconductor materials**, which upon illumination carry out the reactions of water oxidation and H<sub>2</sub> reduction.



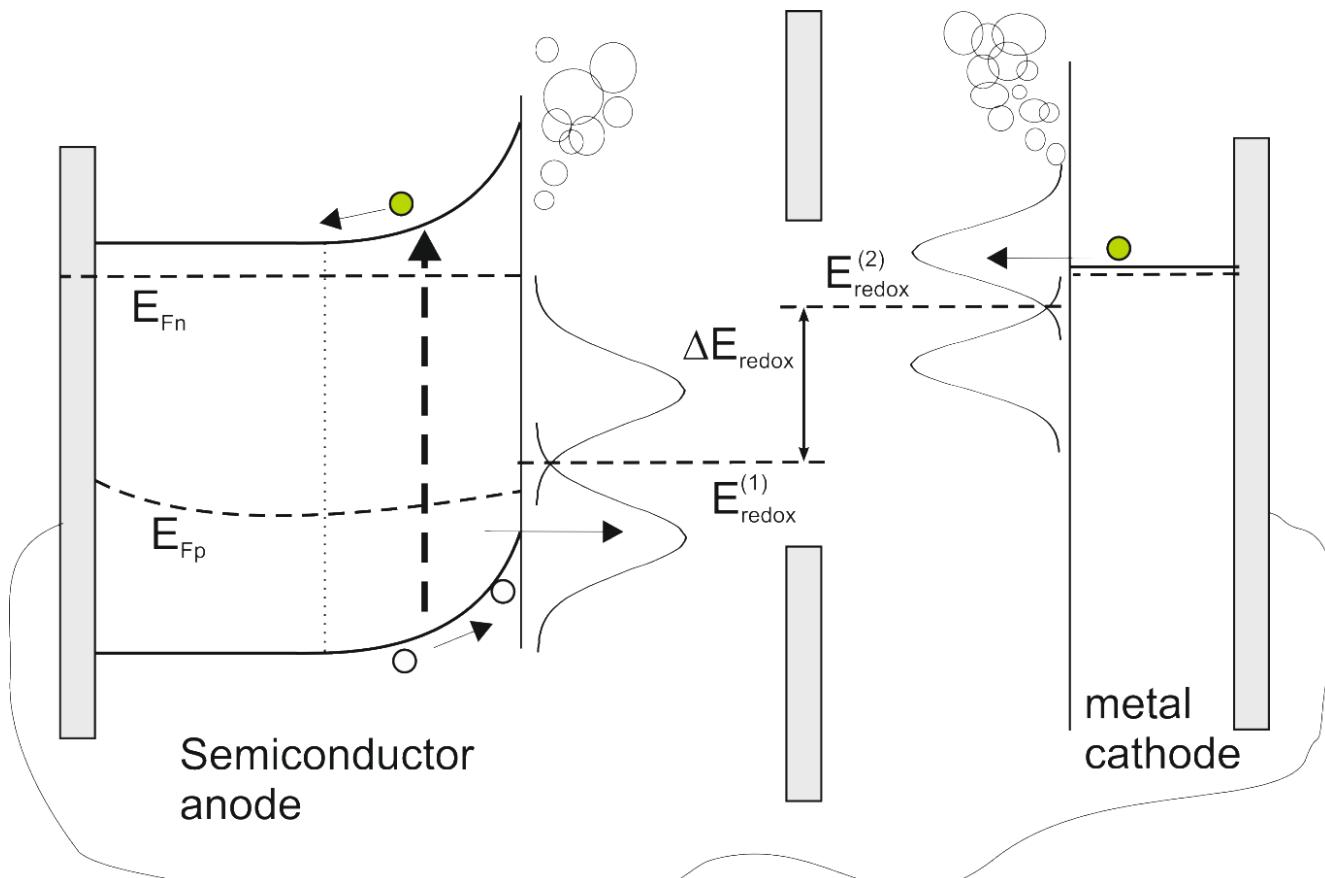
# Requirements for semiconductor materials

- Adequate bandgap for optical absorption (optimal 1.9 eV)
- Band edges straddling the  $\text{H}_2\text{O}/\text{O}_2$  y  $\text{H}^+/\text{H}_2$  potentials.
- Efficient carrier transport within the semiconductor material
- Low charge transfer resistance at the semiconductor/water interface (low overpotentials)
- Low cost



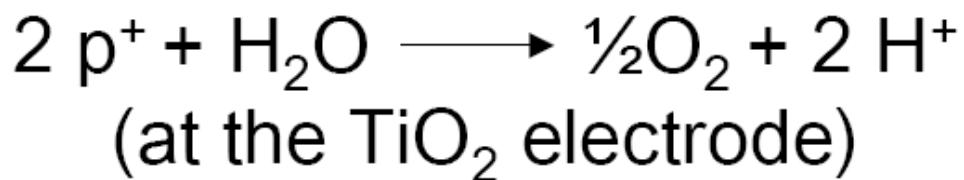
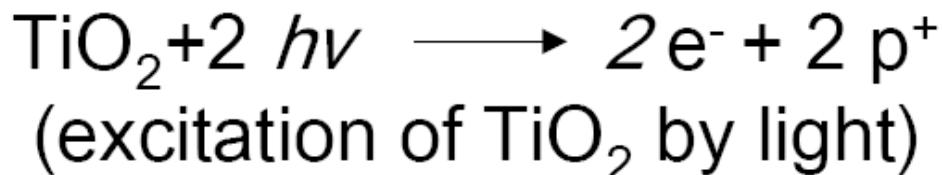
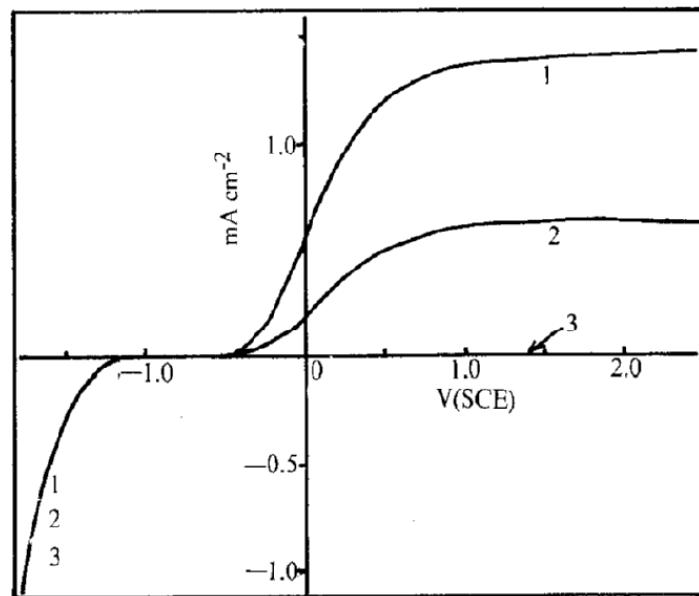
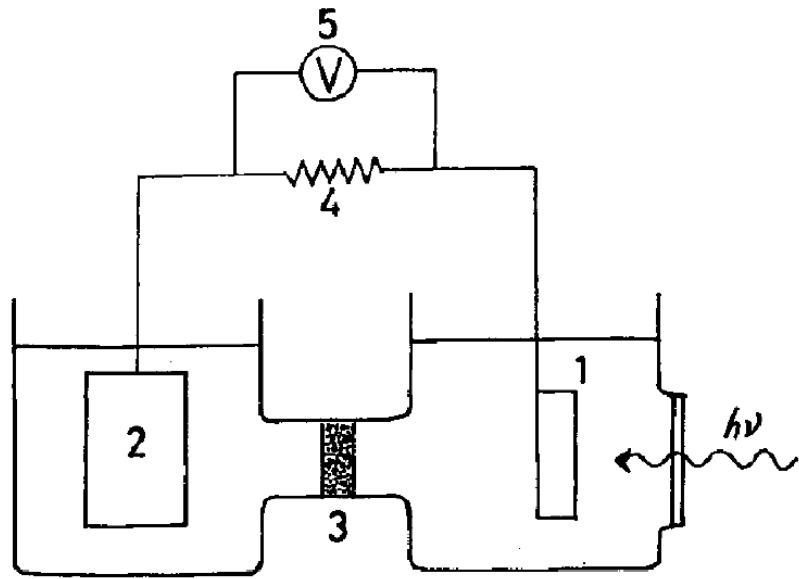
Van de Krol, *J. Mater. Chem.*, 2008, 18, 2311–2320  
 Michael G. Walter et al., *Chem. Rev.* 2010, 110, 6446–6473.

# Photoelectrochemical cell



How it works: Anode absorbs light and generates electron and hole. Holes in the VB react at the surface (i.e. with water to produce oxygen) electrons in CB are not able to generate H<sub>2</sub> in an efficient way. The anode is wired to a catalytic cathode (i.e. Pt) that generates the H<sub>2</sub> from protons libetated at the anode

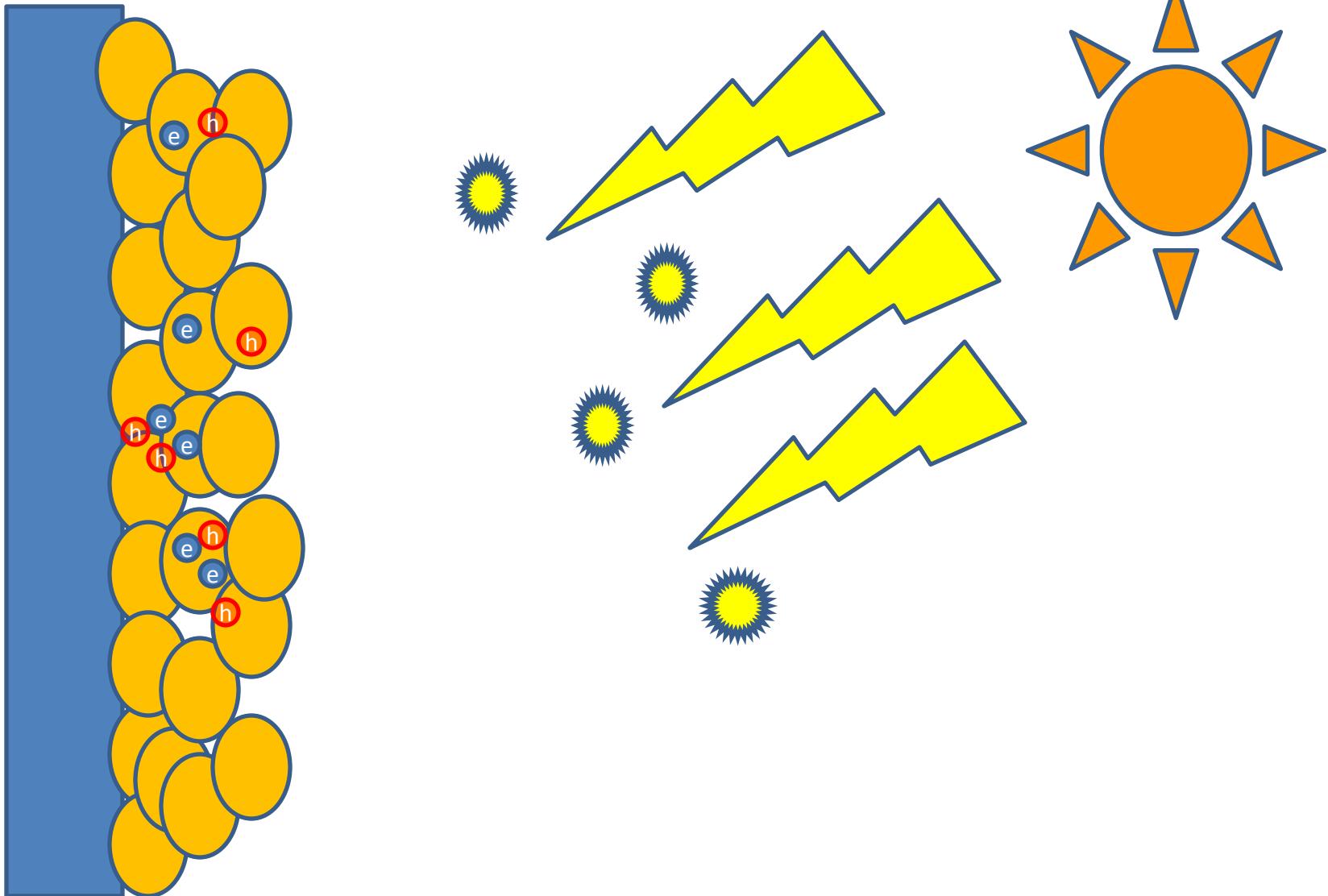
# Honda-Fujishima effect



The overall reaction is  

$$\text{H}_2\text{O} + 2 h\nu \longrightarrow \frac{1}{2}\text{O}_2 + \text{H}_2$$

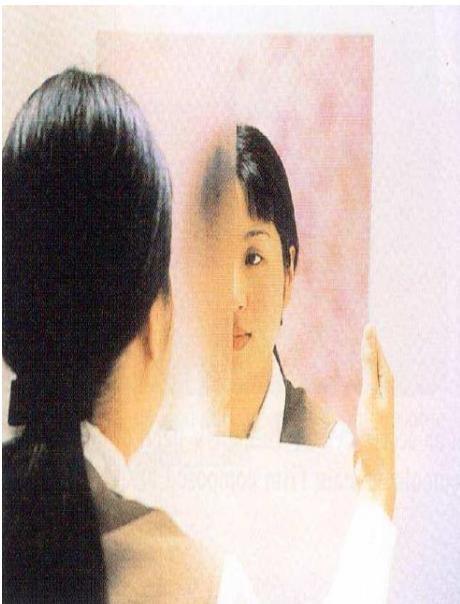
# Photocatalysis





GRUP DE DISPOSITIS  
FOTOVOLTAICS I  
OPTOELETROÔNICS

# Photocatalytic applications



CHINA NATIONAL GRAND THEATER / THE REAL PROJCO  
中国·国家大剧院·实境效果

National Grand Theater/Under Construcion  
中国·国家大剧院

# Hematite: $\alpha\text{-Fe}_2\text{O}_3$

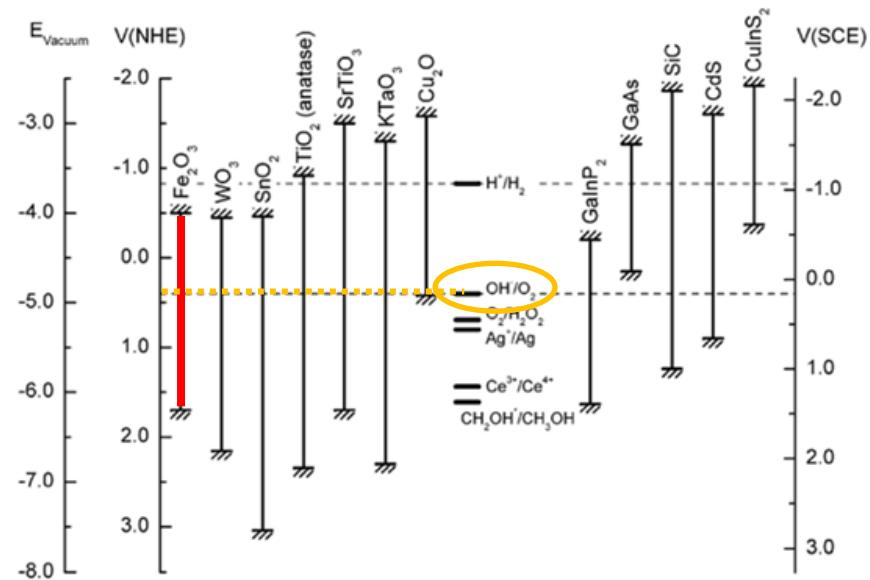


# Hematite

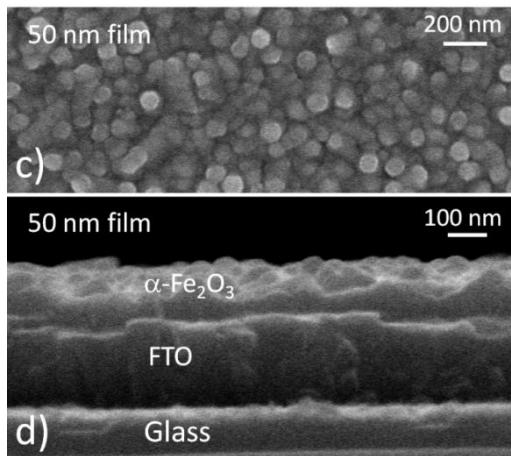
## PHOTOANODE

Hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) is a promising material as photoanode of electrochemical cells for water splitting.

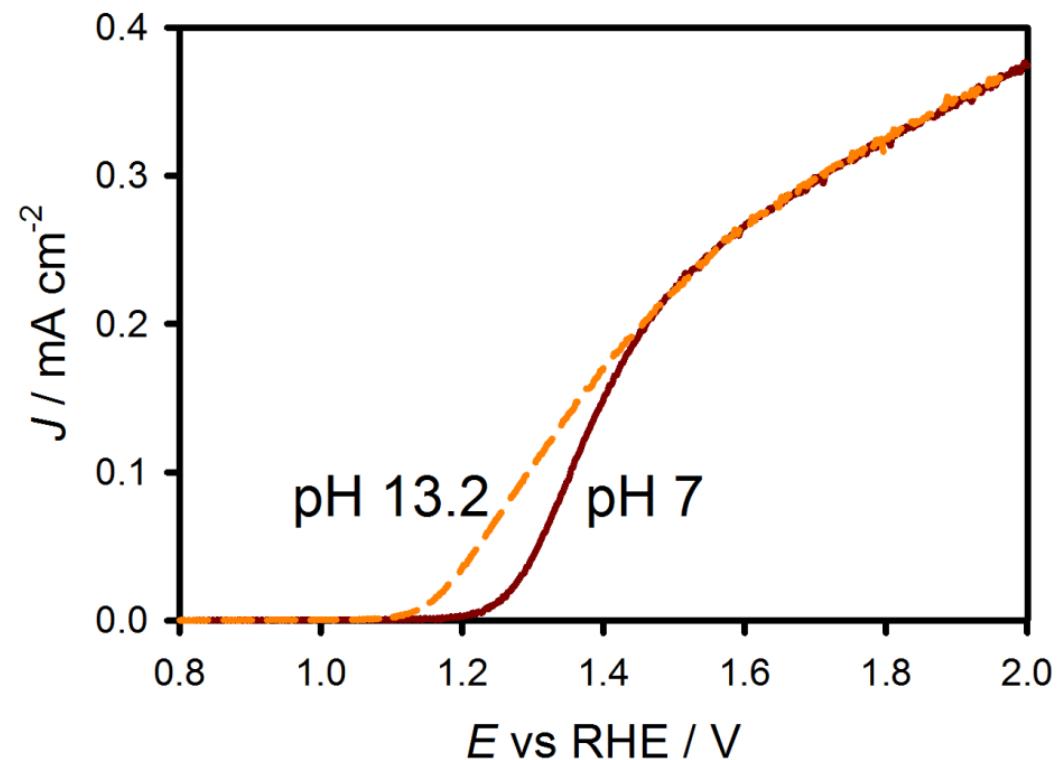
- Abundant
- Visible light absorption up to 590 nm
- Good stability in neutral and alkaline env
- Indirect bandgap semiconductor (low abs)
- Short carrier lifetime and low mobility of i
- Inadequate position of the CB edge for h<sup>-</sup>



# Photoelectrochemical behavior

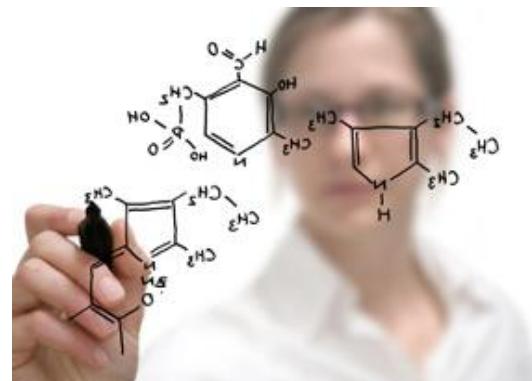
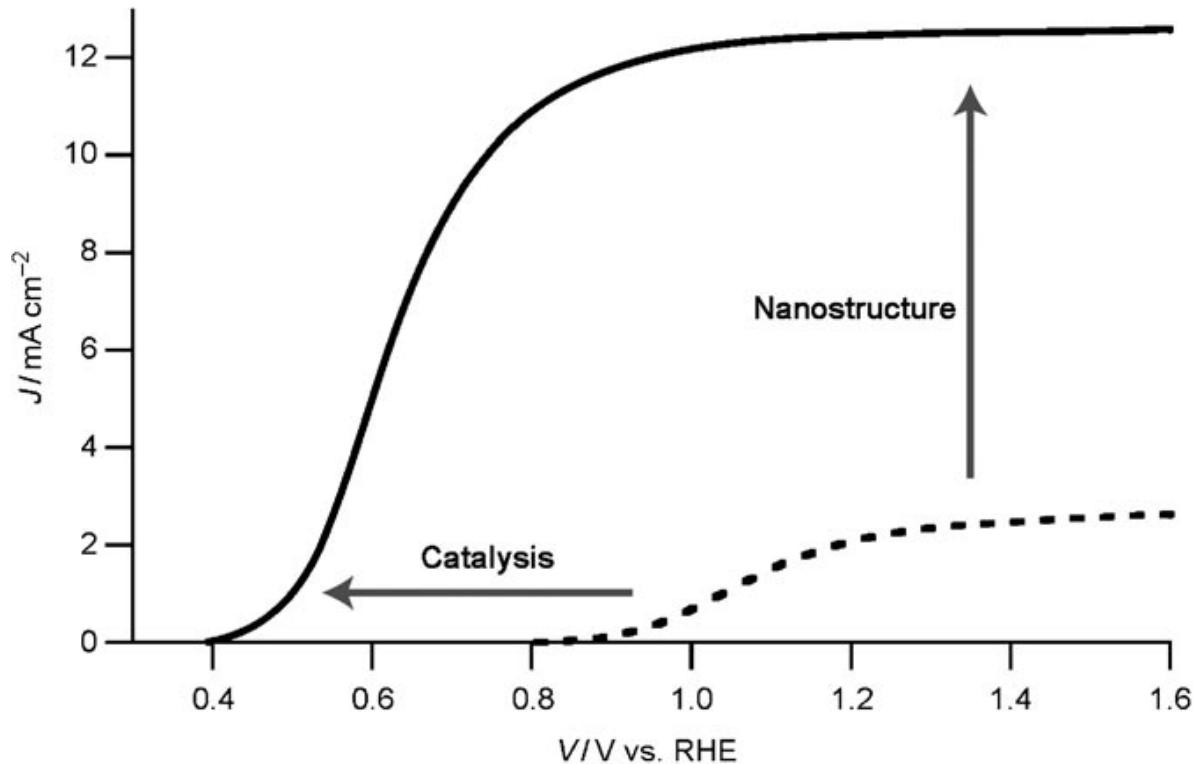


B.M. Klahr, A.B.F. Martinson, T.W. Hamann, Langmuir 2011, 27(1), 461–468



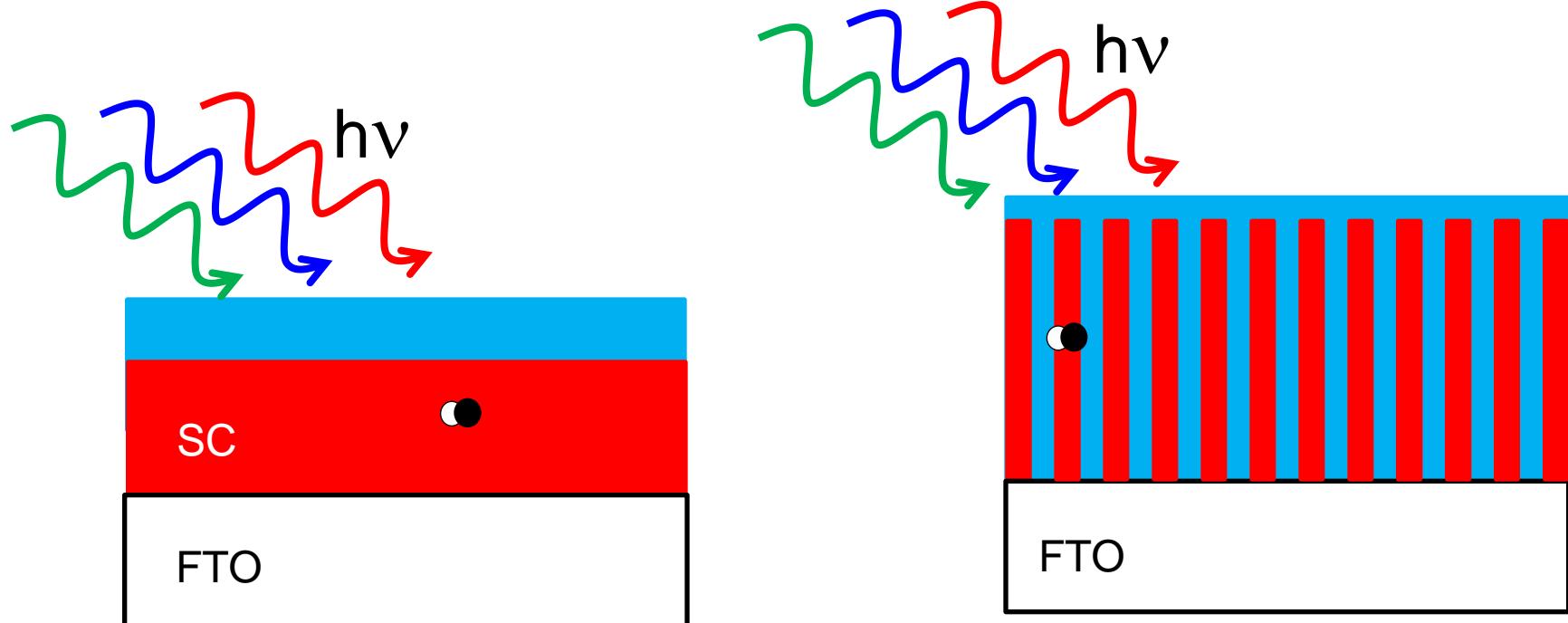
The curves vs RHE (100 mW·cm<sup>-2</sup> illumination) show remarkable overlap, demonstrating the consistency of hematite electrodes prepared via ALD.

# Effect of catalysts on $\text{Fe}_2\text{O}_3$



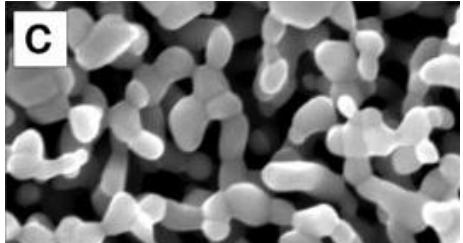
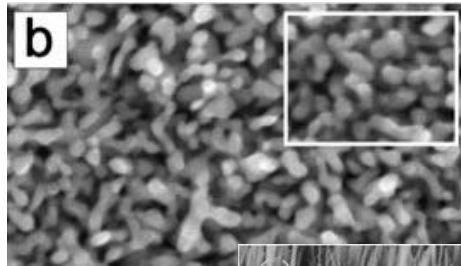
The objective is to obtain efficient electrodes. Two options available: (i) increasing contact surface and light absorption (nanostructures) to increase current; (ii) improve the charge transfer mechanisms using better reaction catalysts

# Nanostructuring

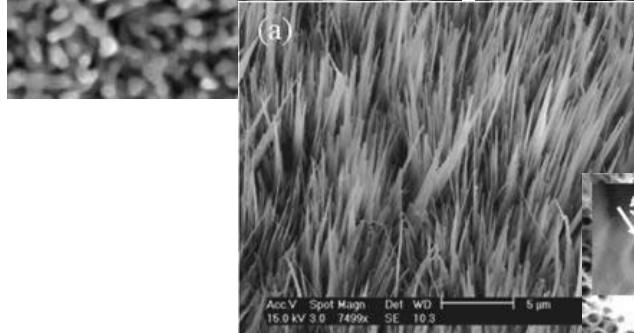


Orthogonalization between light absorption and carrier diffusion

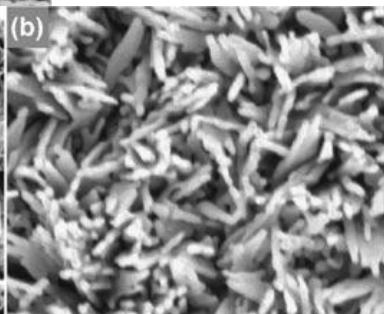
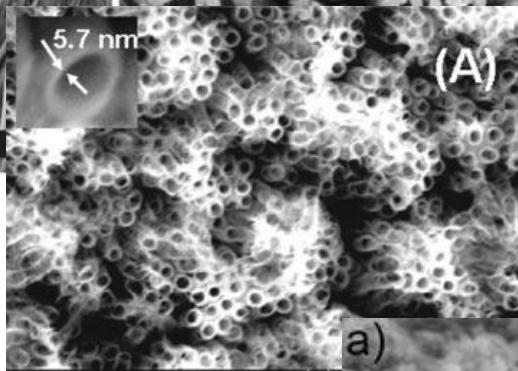
# Design of new materials



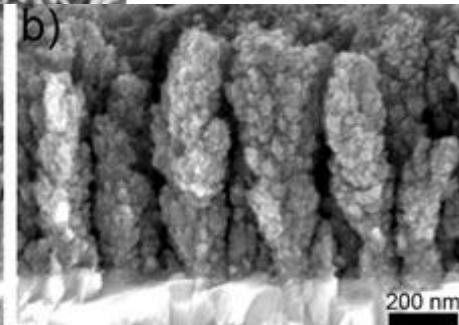
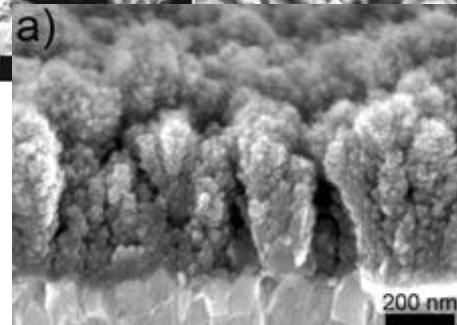
Nanoparticules



Nanowires



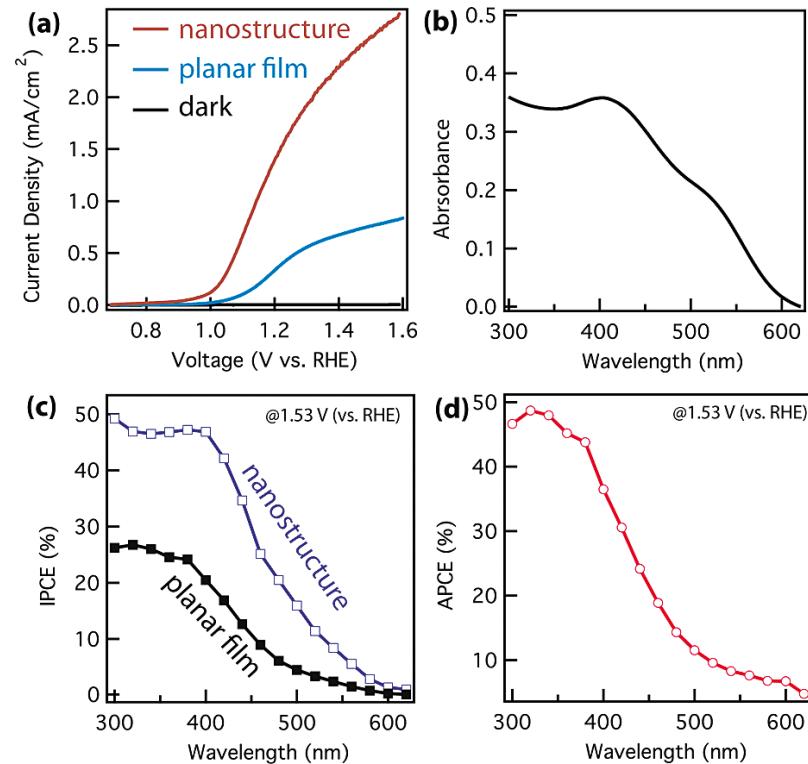
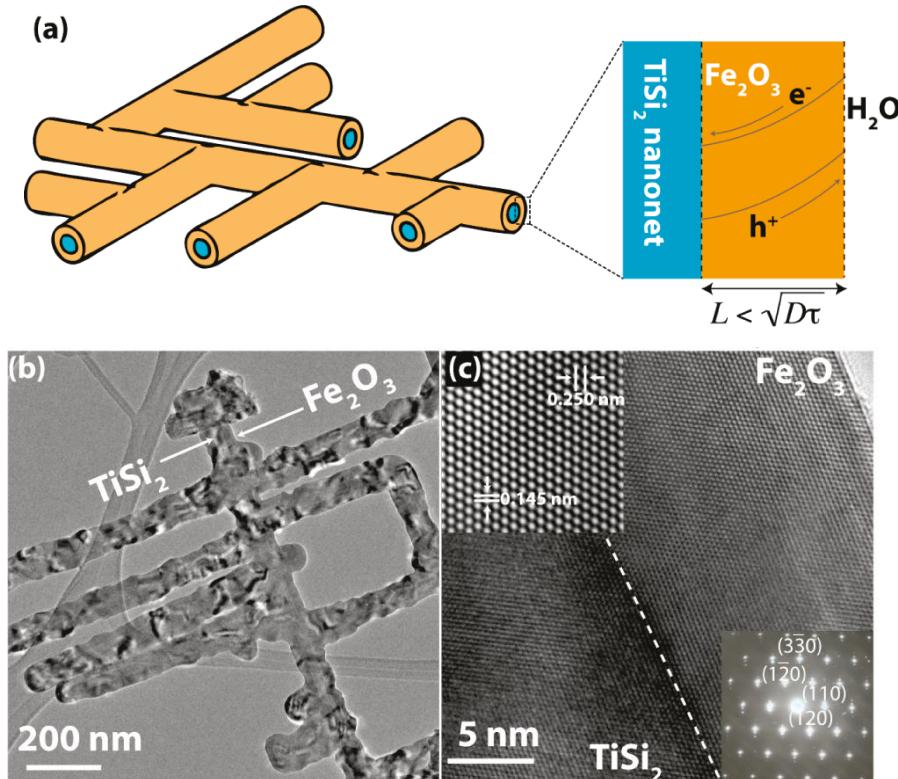
Nanotubes



Coliflowers

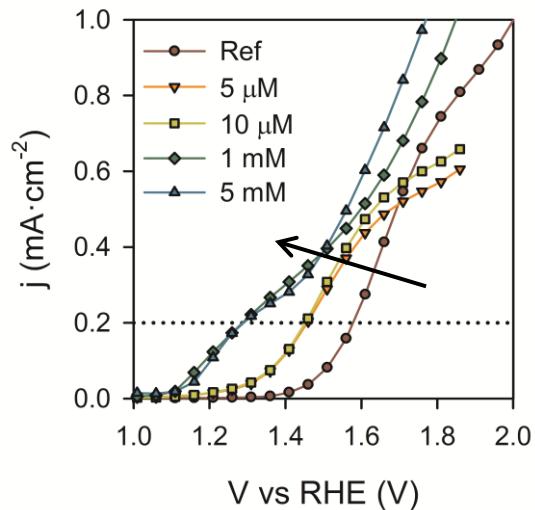
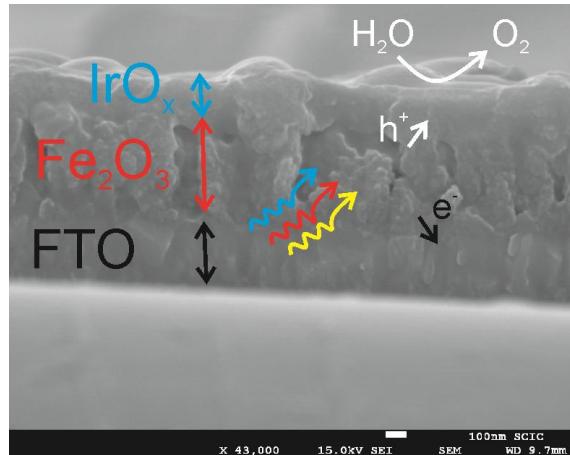
# Design of new materials

## TiSi<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub> heterostructures

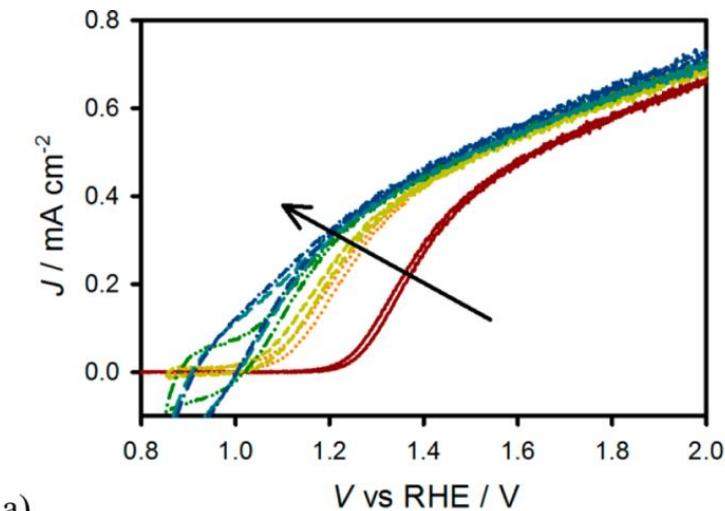
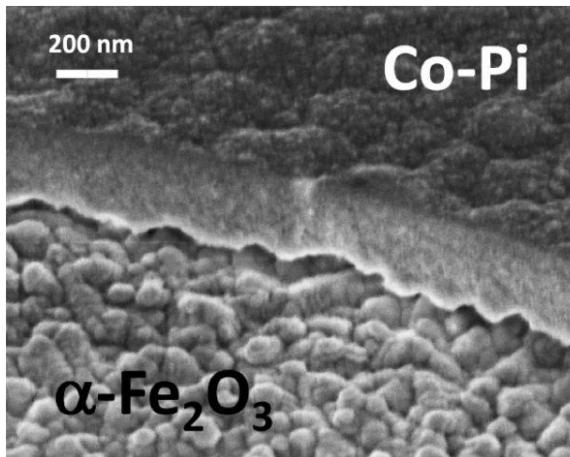


# Effect of catalysts on $\text{Fe}_2\text{O}_3$

$\text{IrO}_x$



Co-Pi

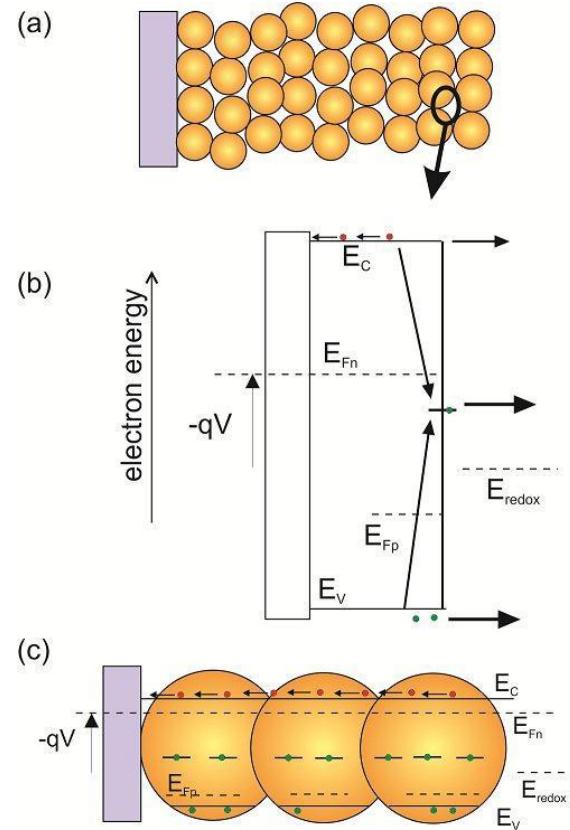
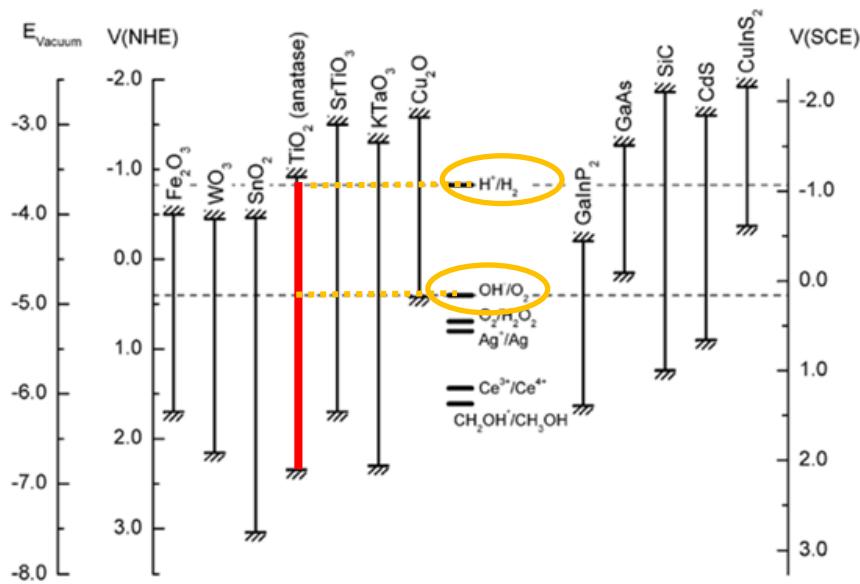


# Titanium dioxide



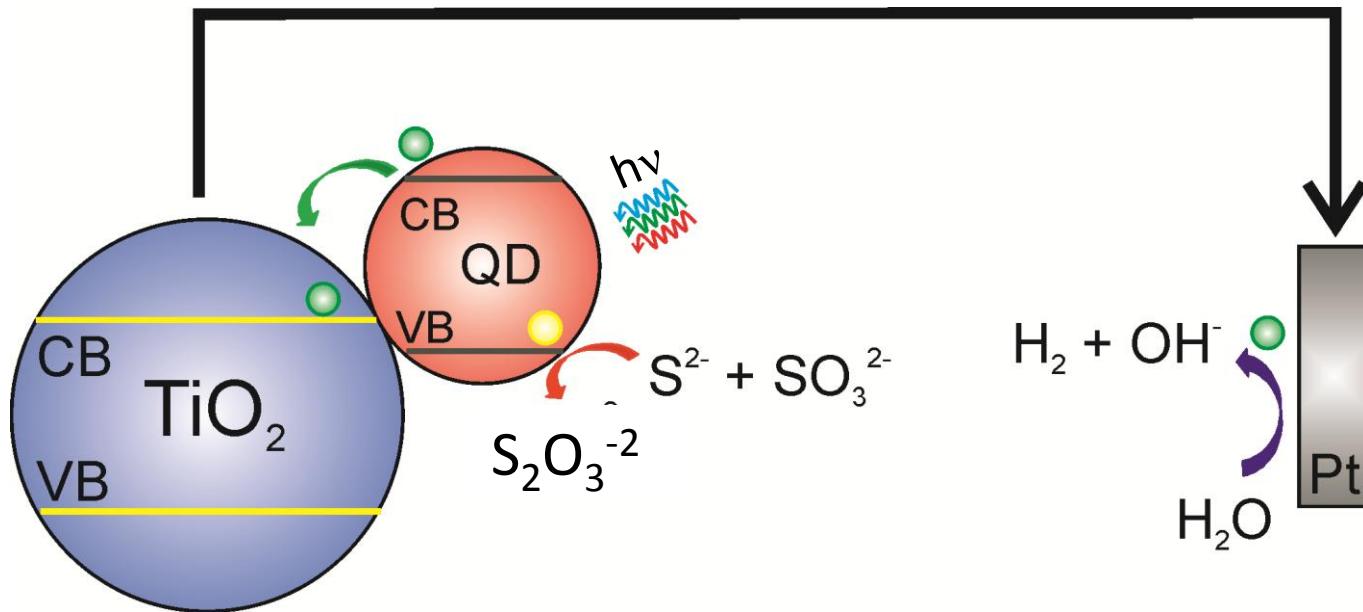
# Titanium dioxide

## PHOTOANODE



$\text{TiO}_2$  is a well studied material for photocatalytic applications, but its large bandgap precludes this material for its use as efficient photoanode in water splitting devices.

# QDs based heterostructures for unassisted solar H<sub>2</sub> generation



P. Rodenas, et al., Adv. Ener. Mat. (2013) 3 (2) 176–182

R. Trevisan et al., J. Phys. Chem. Lett. (2013) 4 (1) 141-146

V. González-Pedro et al., J. Phys. Chem. C (2014) 118, 891–895

# Confinamiento cuántico

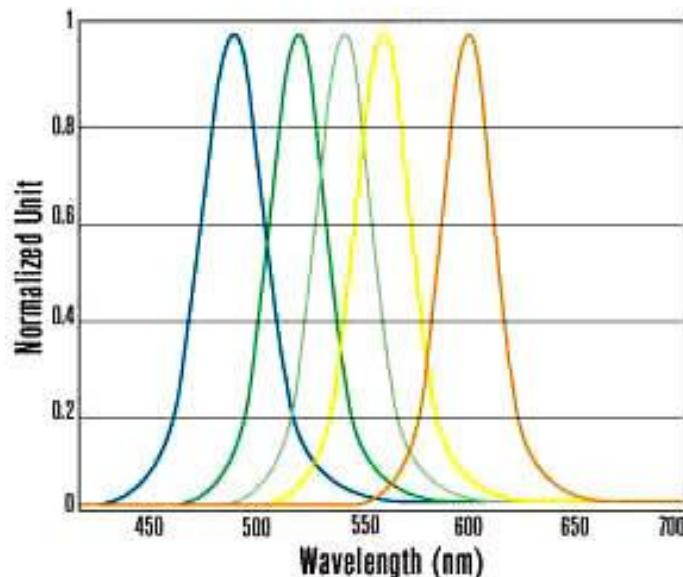
## Propiedades de los puntos cuánticos:

Ajuste del ancho de banda mediante control de tamaño

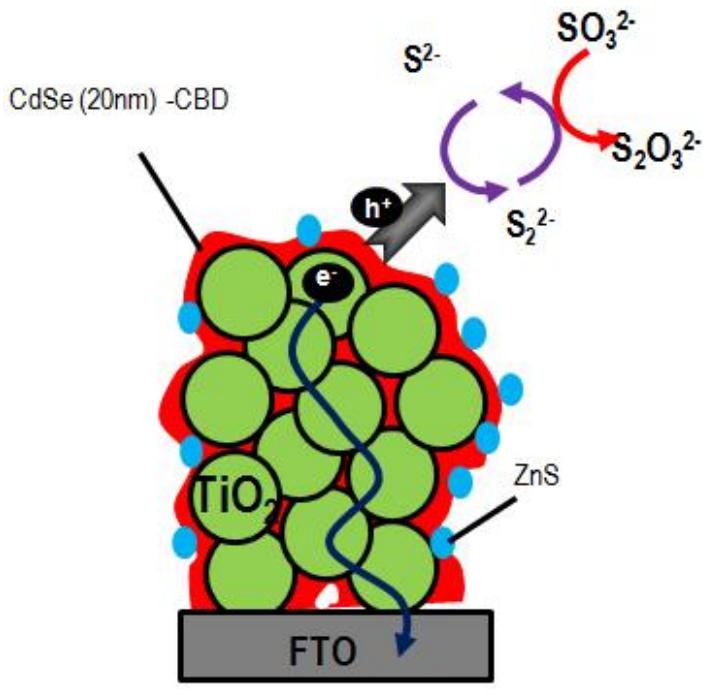
Coeficiente de extinción molar ↑↑

Momento dipolar intrínseco ↑↑

Generación múltiple de excitones

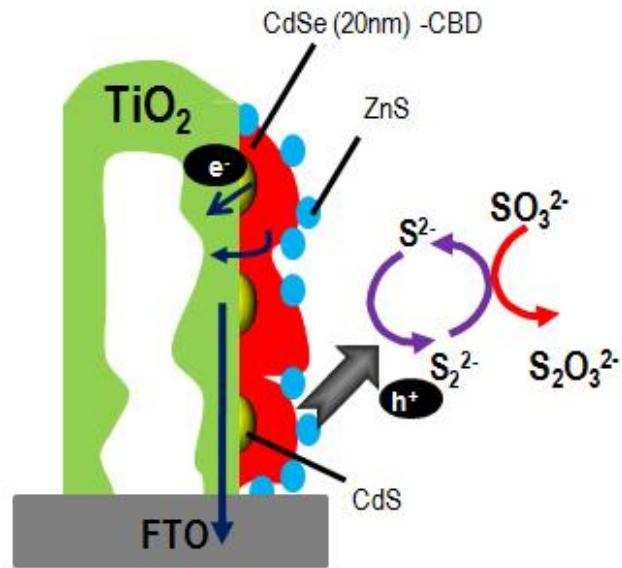


# QDs based heterostructures for unassisted solar H<sub>2</sub> generation



Random electron transport

TiO<sub>2</sub> Nanoparticulate

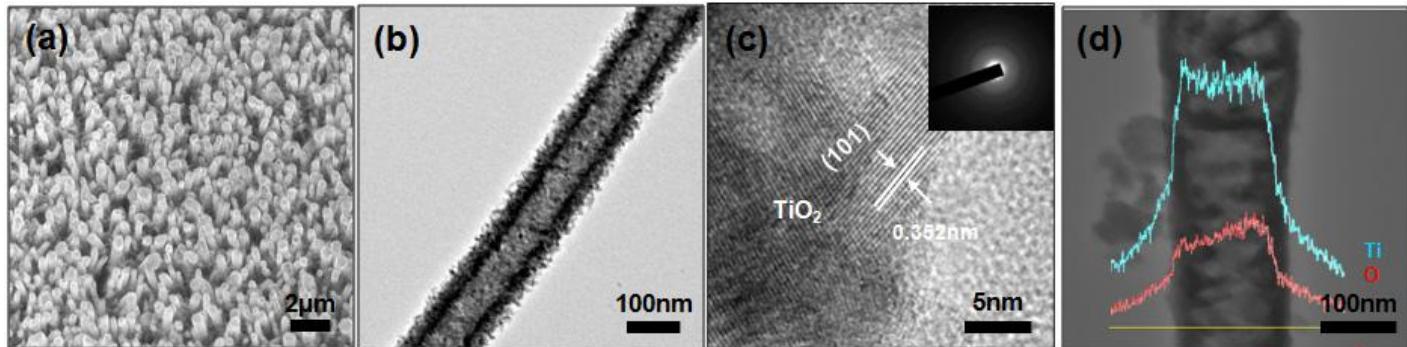


Fast electron transport

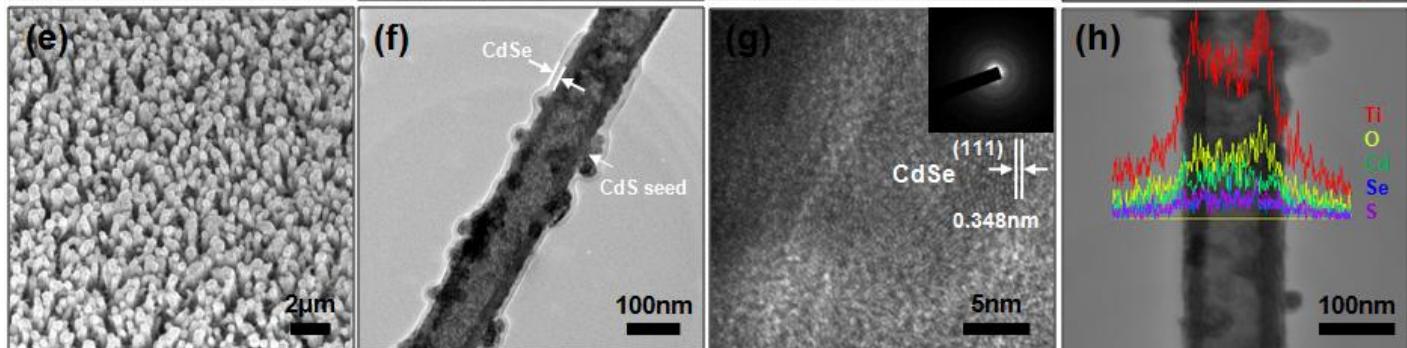
TiO<sub>2</sub> Nanowire

# Structural characterization

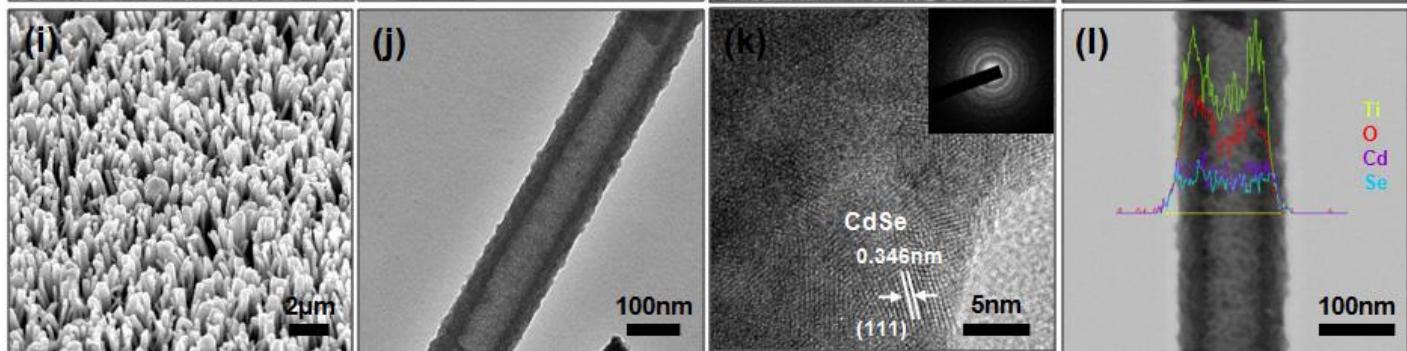
$\text{TiO}_2$



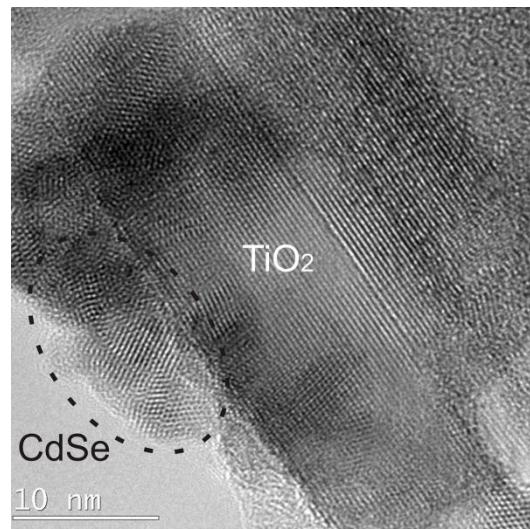
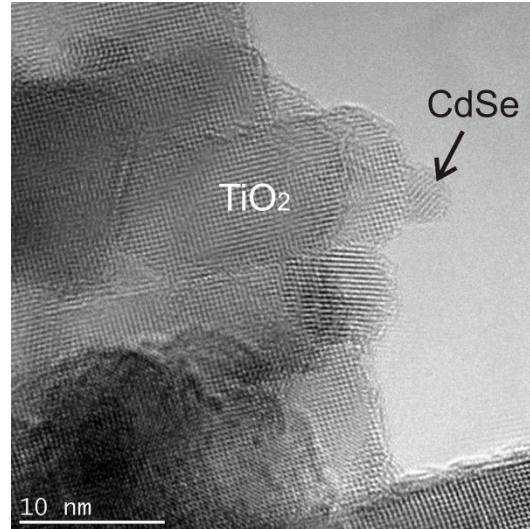
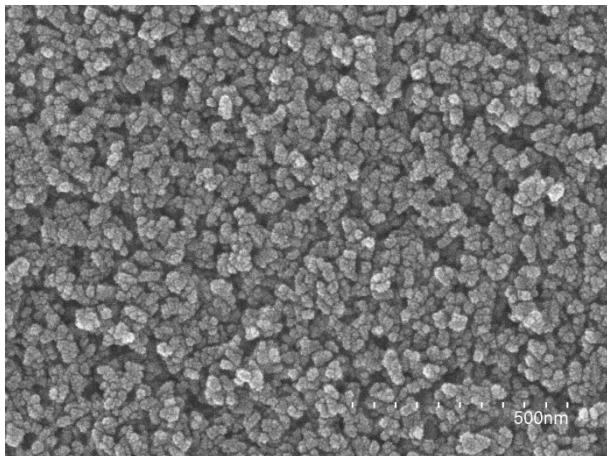
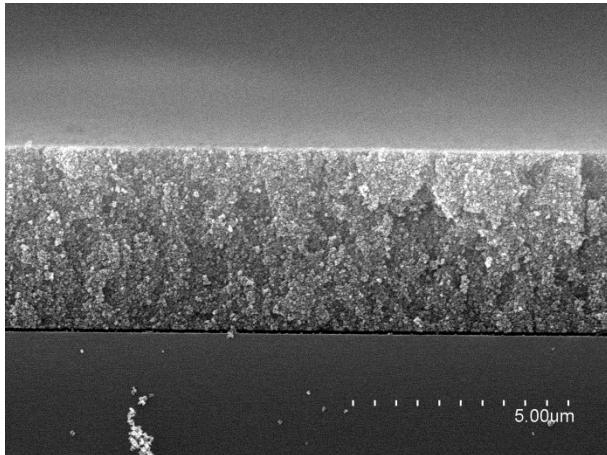
$\text{TiO}_2/\text{CdS}/\text{CdSe}$   
**SILAR**



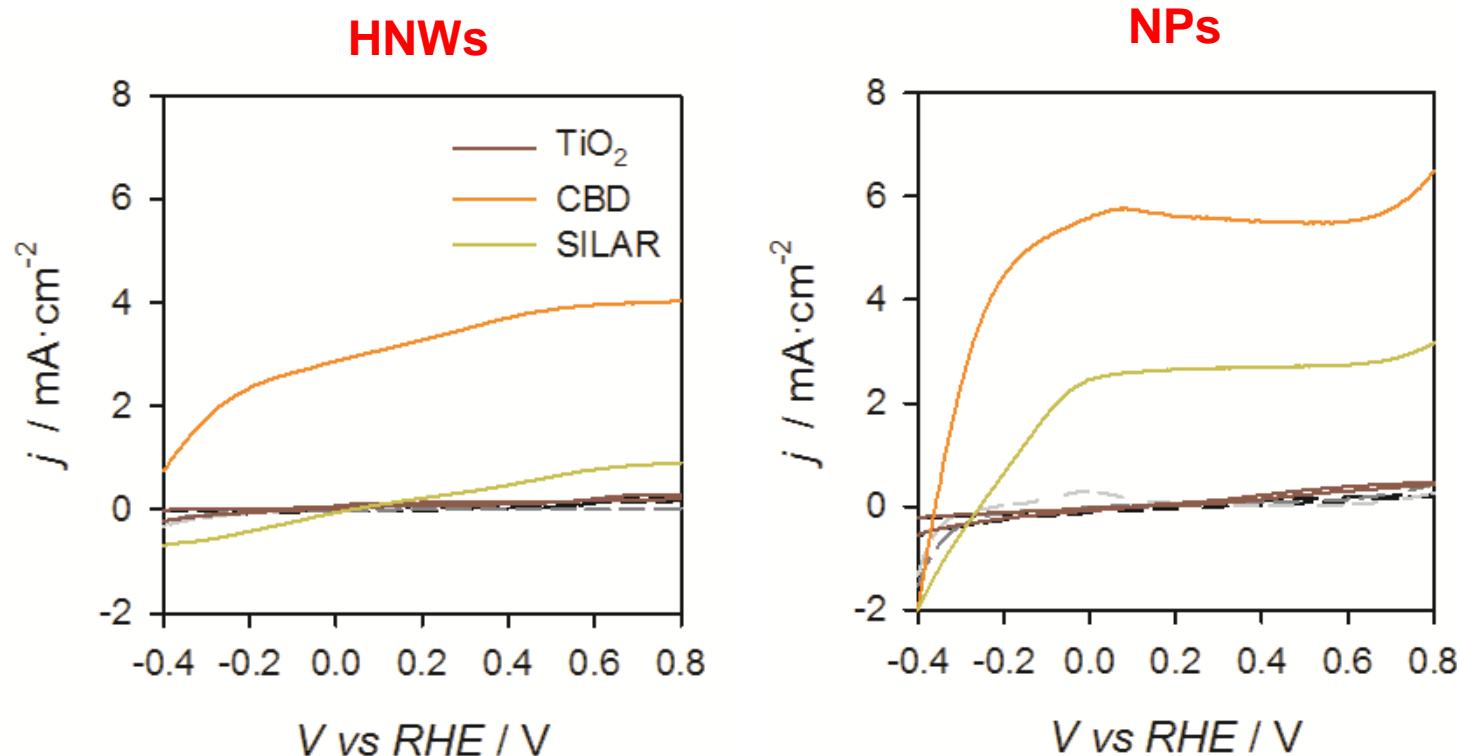
$\text{TiO}_2/\text{CdS}/\text{CdSe}$   
**CBD**



# TiO<sub>2</sub> nanoparticulated films

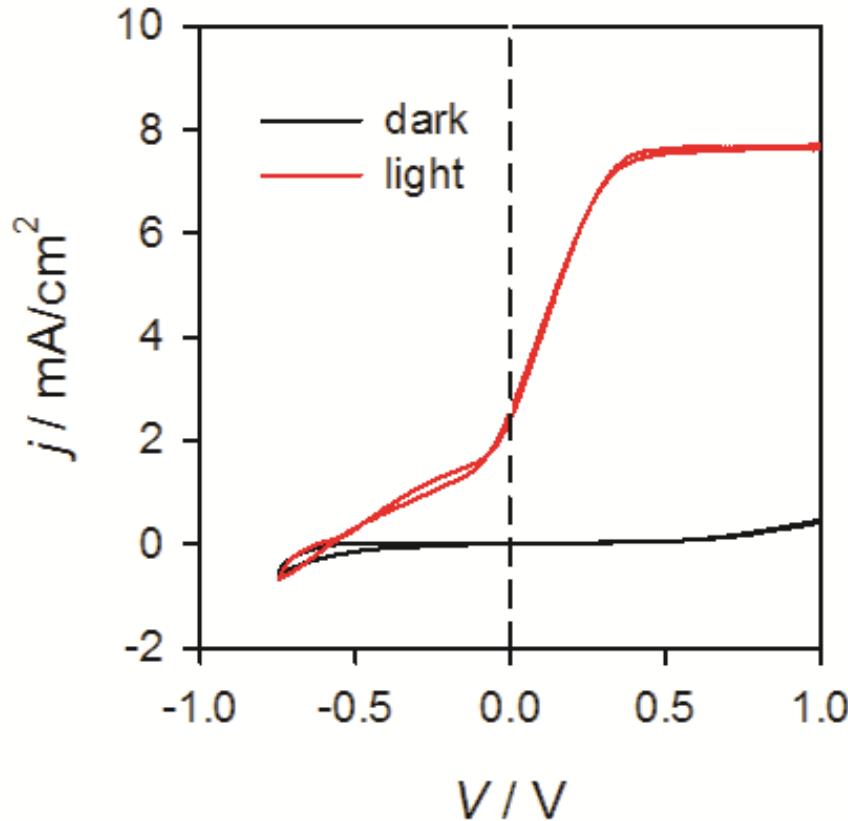


# Photoelectrochemical characterization



Photocurrents of **4 mA·cm<sup>-2</sup>** and **6 mA·cm<sup>-2</sup>** have been obtained in a three-electrode configuration **for HNWs and NPs**, respectively. The contribution of  $\text{TiO}_2$  to the photocurrent is negligible.

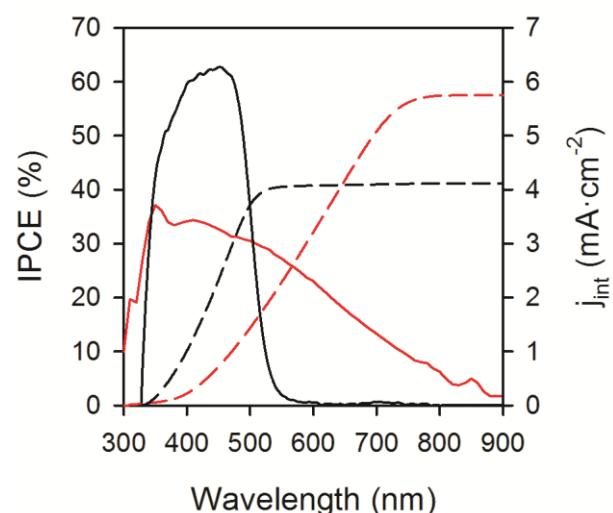
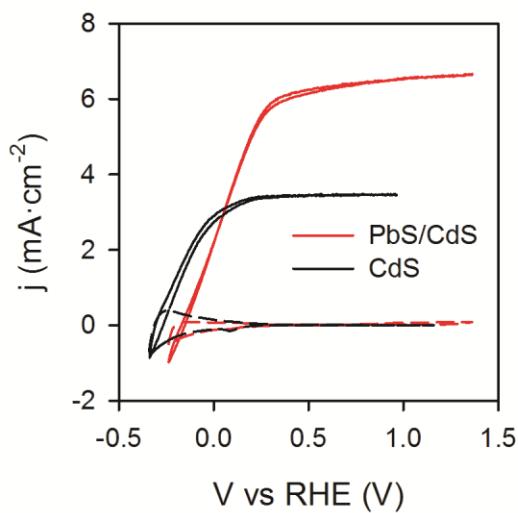
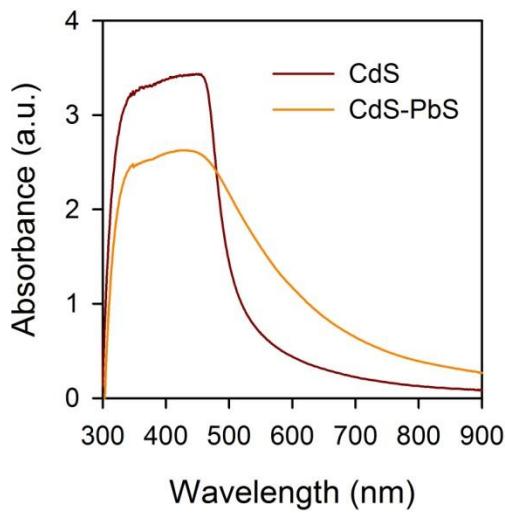
# Photoelectrochemical characterization



For an optimized NP photoelectrode, **8 mA·cm<sup>-2</sup>** have been obtained in a two-electrode configuration.

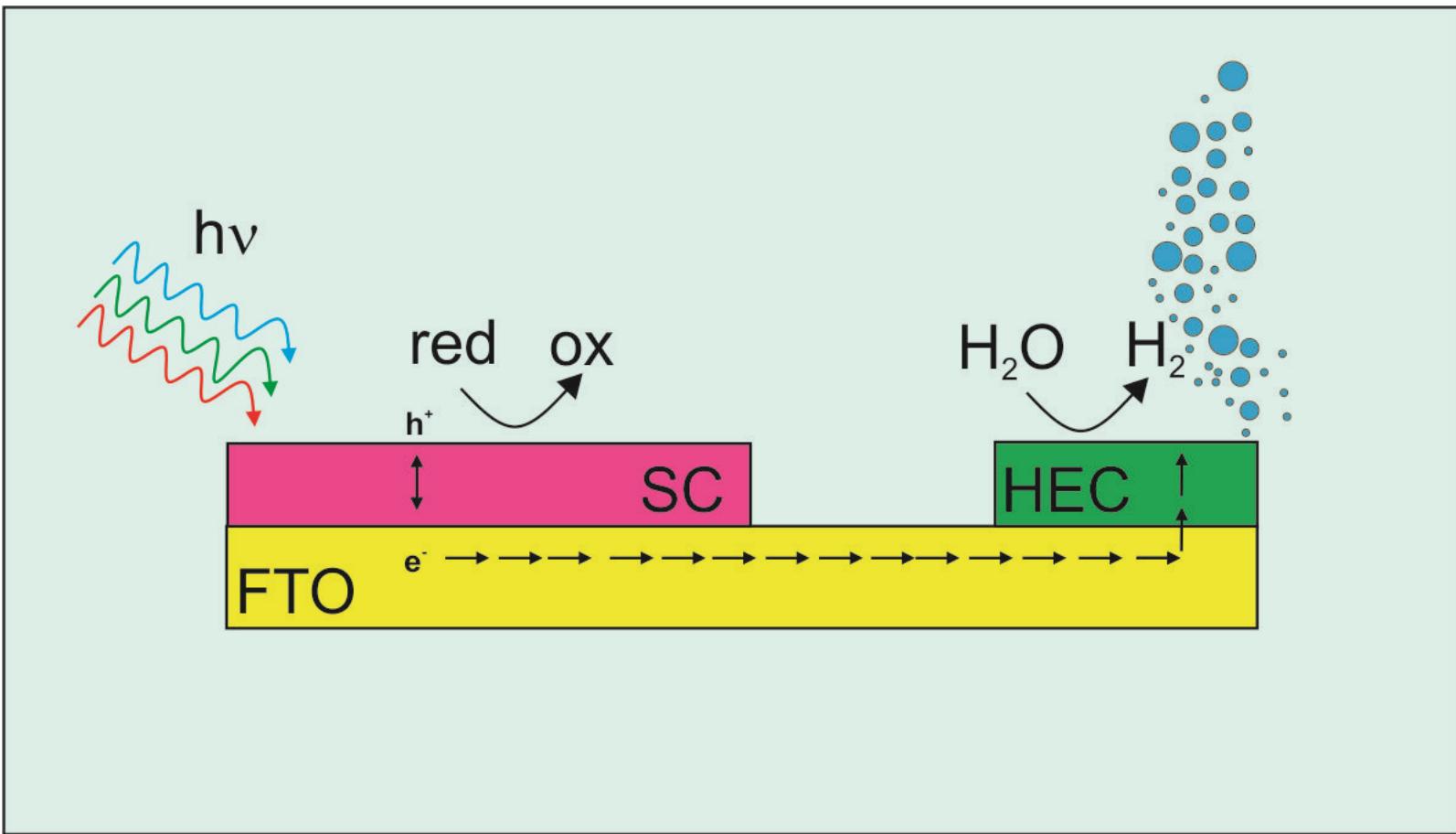
**At zero bias, 2 mA·cm<sup>-2</sup> have been obtained (unassisted H<sub>2</sub> generation).**

# Harnessing IR photons for H<sub>2</sub> generation

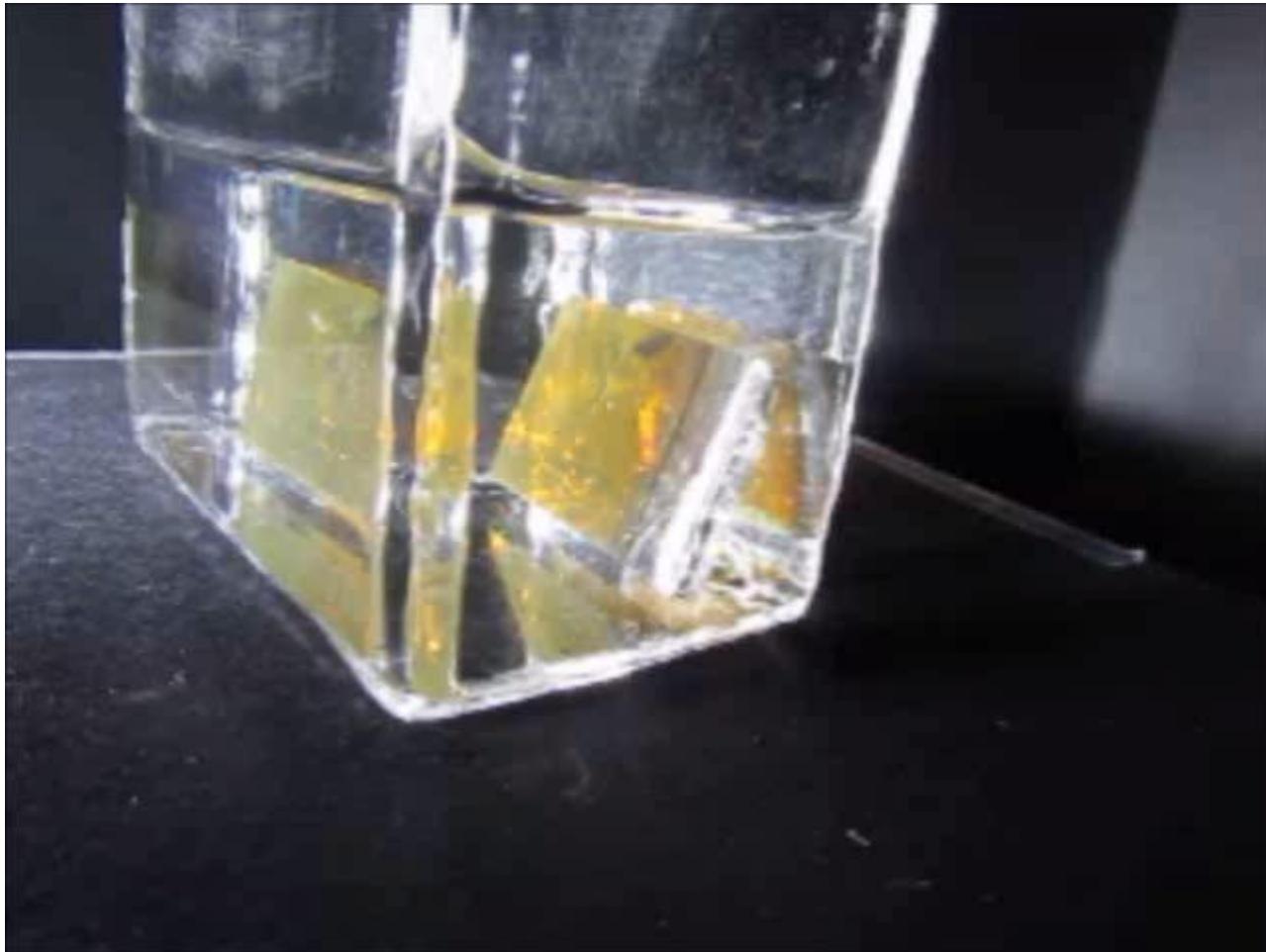


PbS clearly enhances the light absorption in the IR region, which is reflected into higher photocurrents under simulated solar illumination and **higher IPCE values in the IR**.

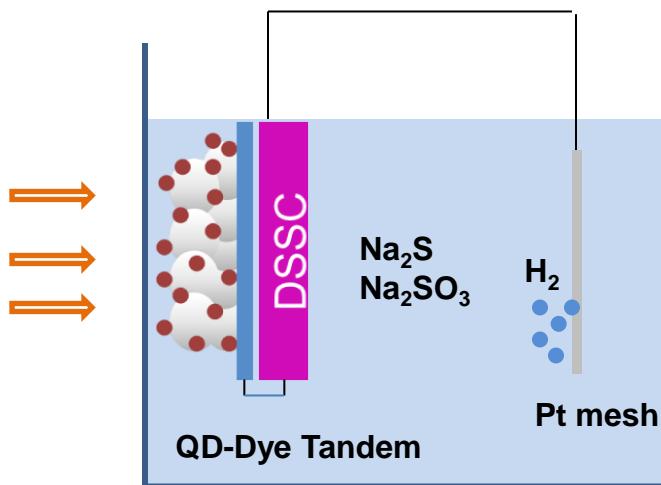
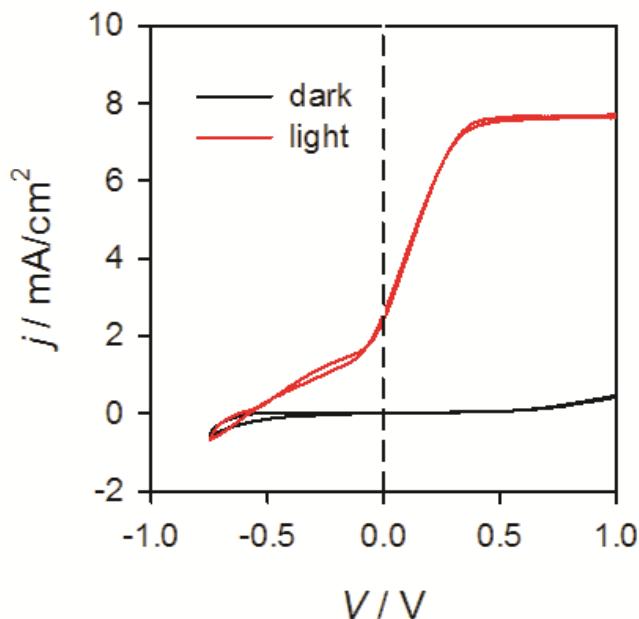
# QDs based artificial leaf



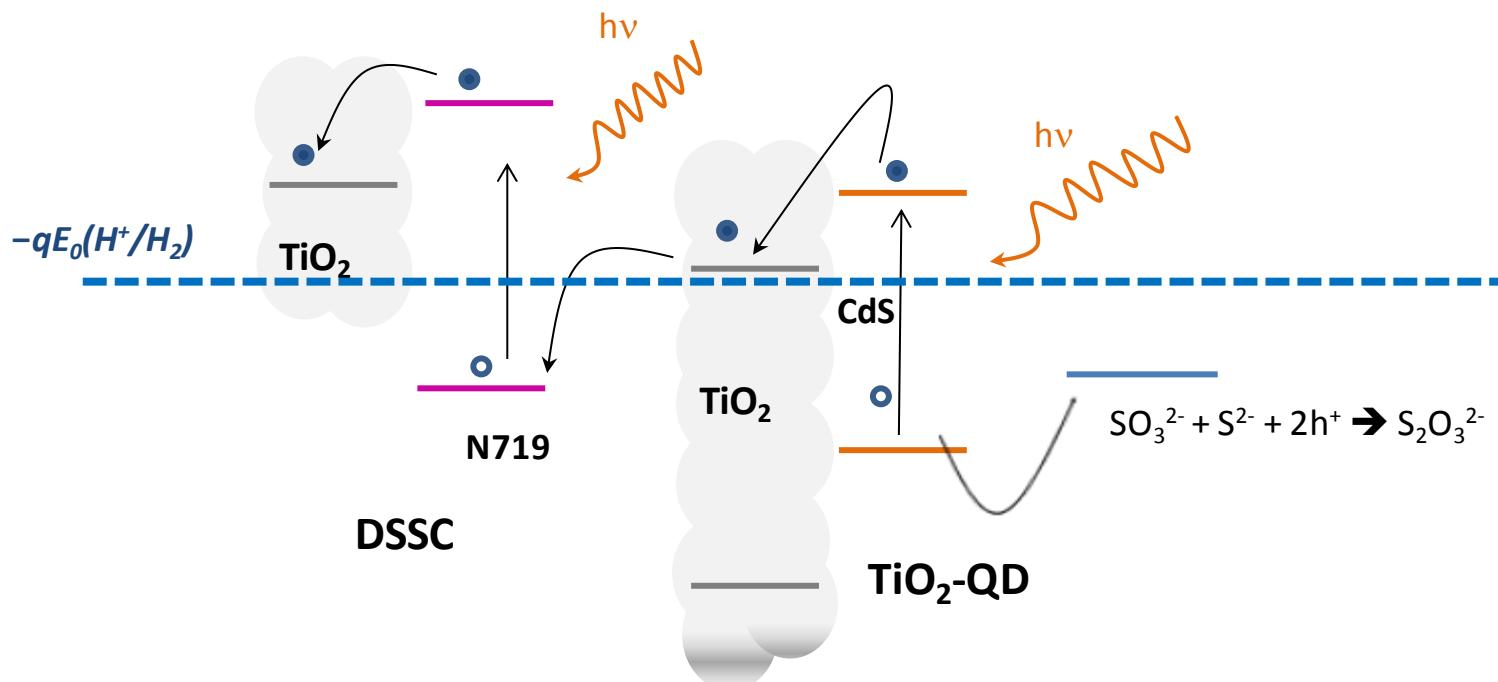
# QDs based artificial leaf



# Tailored QD-Dye based tandem device for unassisted $H_2$ generation

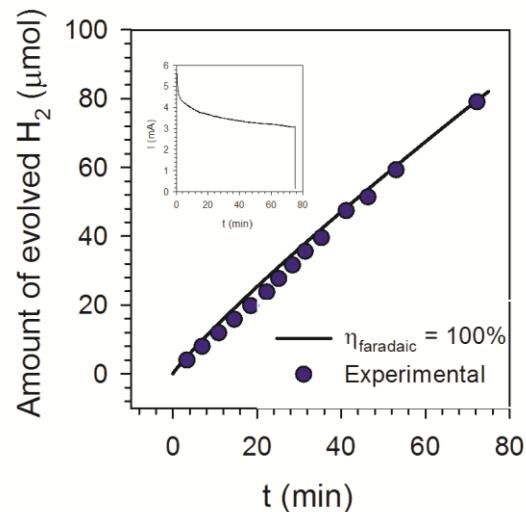
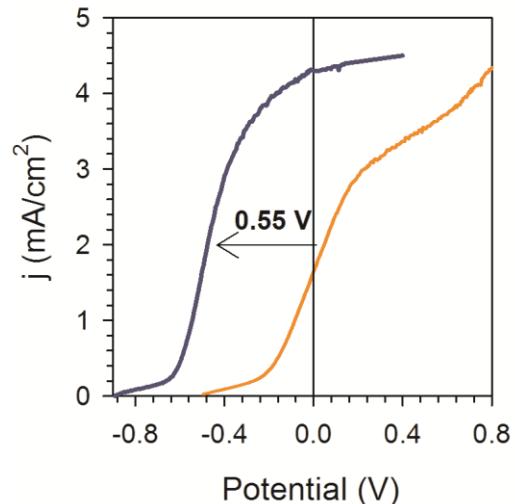
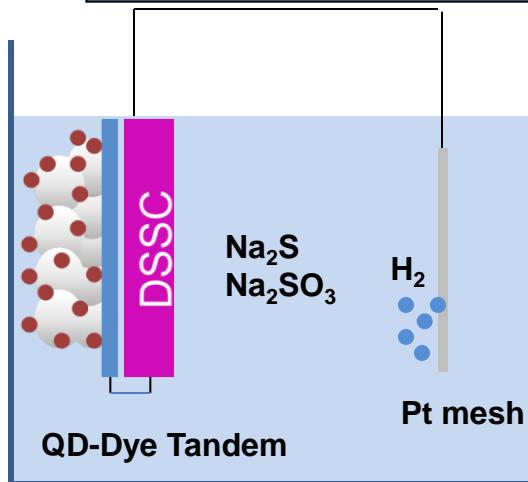


# Tailored QD-Dye based tandem device for unassisted H<sub>2</sub> generation



A solar cell provides the extra energy needed to complete hydrogen production reaction. Cells are connected in tandem configuration to minimize area used.

# Tailored QD-Dye based tandem device for unassisted H<sub>2</sub> generation



$$STH = \frac{\Delta G_{H_2}^0 R_{H_2}}{P_{total} A}$$

Sample	$J_{op}$ (mA/cm <sup>2</sup> )	$I_{op}$ (mA)	$R_{H_2}$ (nmol/s)	STH (%)
TiO <sub>2</sub> -CdS	$1.64 \pm 0.2$	$0.41 \pm 0.05$	$2.09 \pm 0.26$	$0.34 \pm 0.04$
Tandem	$3.8 \pm 0.6$	$0.94 \pm 0.16$	$4.9 \pm 0.8$	$0.78 \pm 0.04$

# Acknowledgements

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