INSTITUTO DE CATÁLISIS Y PETROLEOQUÍMICA

Laccase-Catalyzed Bioelectrochemical Oxidation of Water Assisted with Visible Light

Marcos Pita, Cristina Tapia, Sergey Shleev, José Carlos Conesa, Antonio L. De Lacey

Funding

- MINECO/FEDER CTQ2015-71290-R and ENE2013-46624-C4-1-R
- CSIC PIE 201560I018
- FP7-PEOPLE-2013-ITN-607793

UNIÓN EUROPEA
"Una manera de hacer Europa"

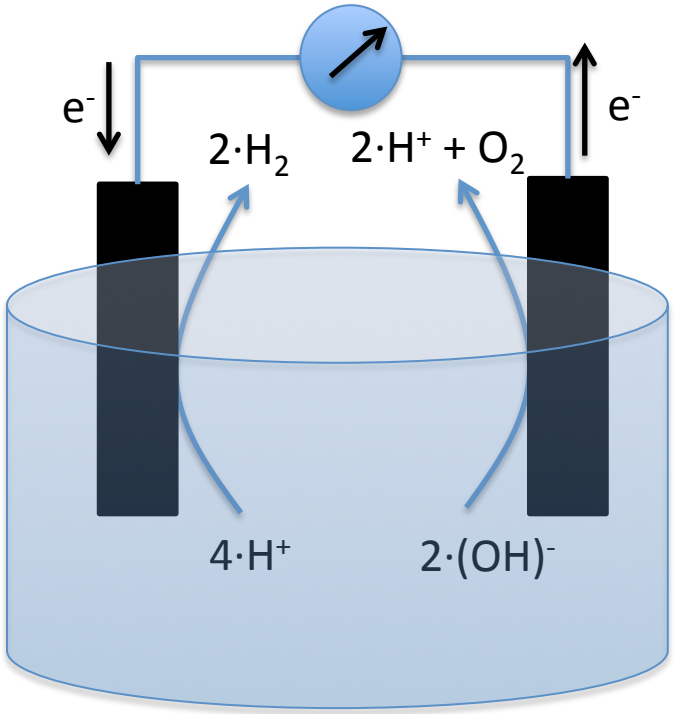
Water Splitting

- Goal: obtain H_2 and O_2 from H_2O through a sustainable synthesis route.
- High energy demanding process.
- Appropriate catalysts are key to the process.

$$2 \cdot H_2O \xrightarrow{E} 2 \cdot H_2 + O_2$$

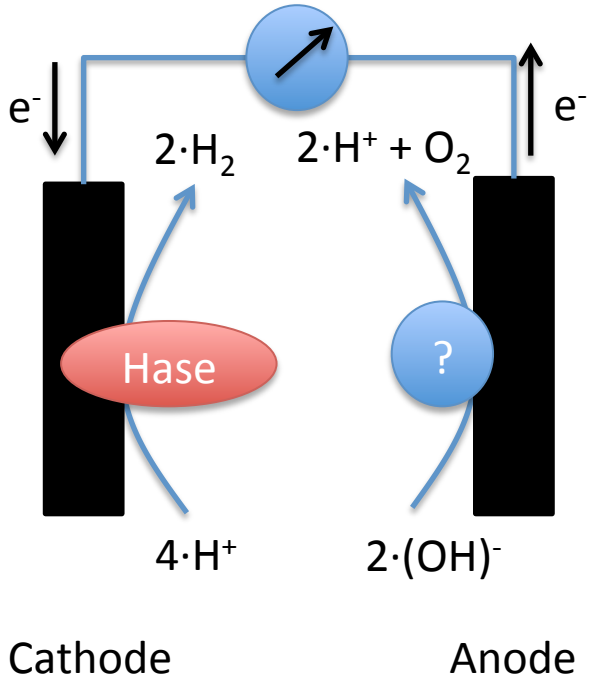
Electrochemical Water Splitting

- Goal: obtain H_2 and O_2 from H_2O through a sustainable synthesis route.
- High energy demanding process.
- Appropriate catalysts are key to the process.
- Electrochemistry can supply enough energy, although the overpotentials are high.
- Research focus on either electrode, as their behavior and mechanisms differ.



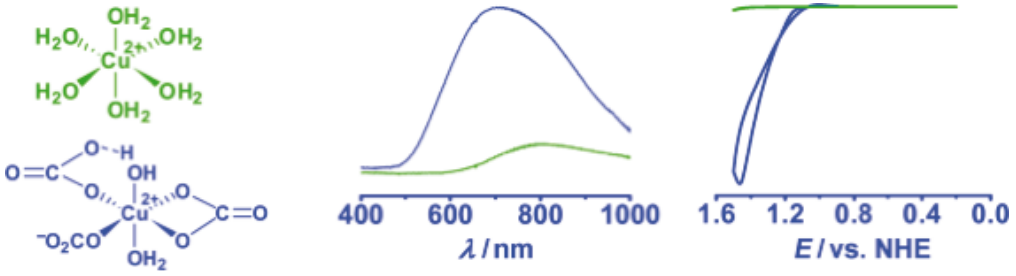
Bioelectrochemical Water Splitting

- Catalytic processes allow minimizing the overpotential challenge.
- Appropriate biocatalysts are key to the process: Hydrogenase for the anode; enzyme candidate for the cathode?
- O_2 evolution is not a natural-occurring reaction except for photosynthetic routes (PSI, PSII).



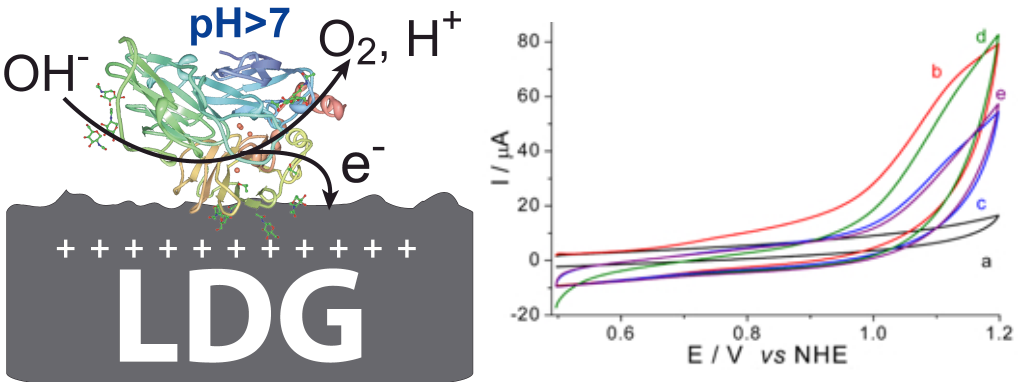
Bioelectrochemical O_2 Evolution

- Cu complexes have been reported as electrocatalysts for O_2 evolution.



Chen, Z.; Meyer, T.J. Angew. Chem. Int. Ed. 2013, 52, 700-703.

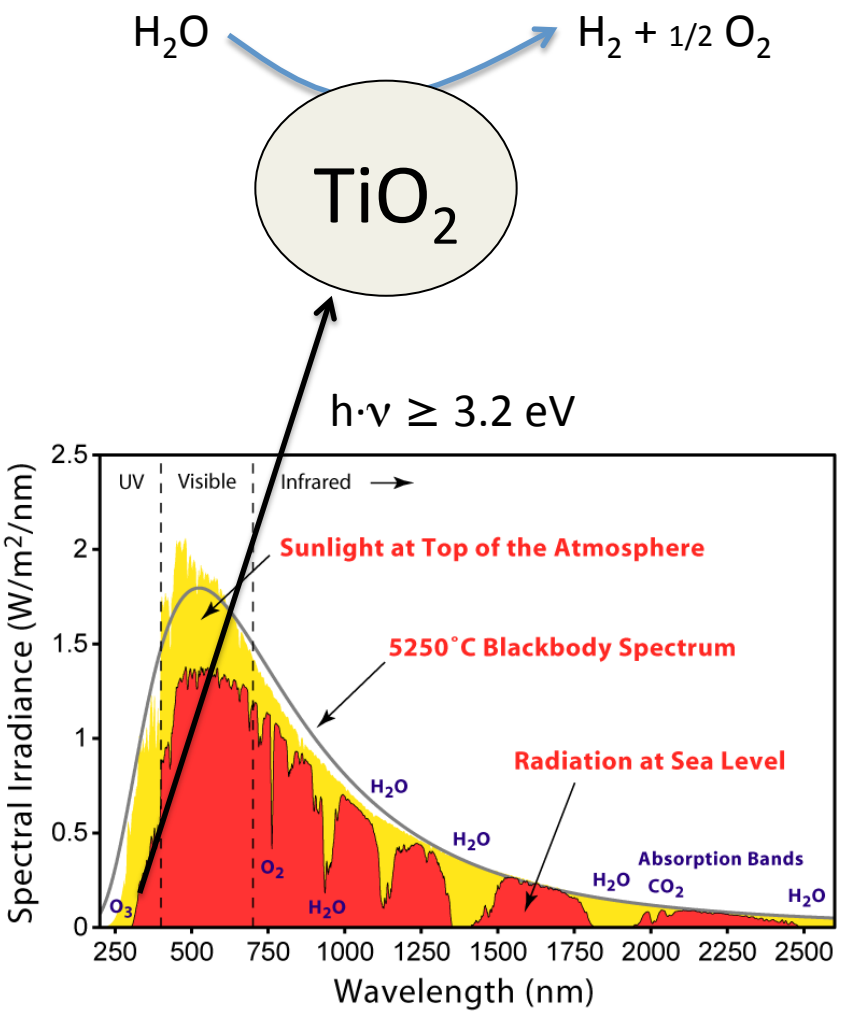
- Laccase immobilized on an electrode can be forced through an external potential to produce O_2 from water.



Pita, M. *et al*. J. Am. Chem. Soc. **2014**, 136, 5892-5895

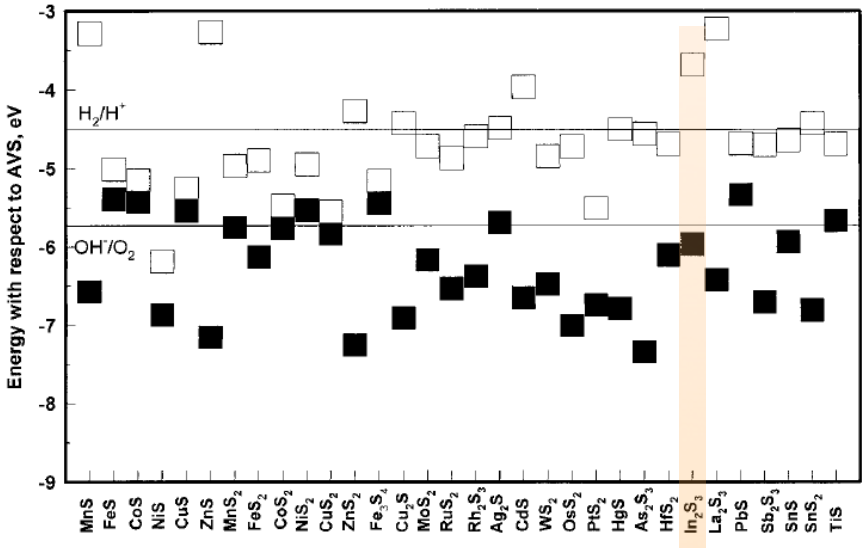
Photolytic Water Splitting

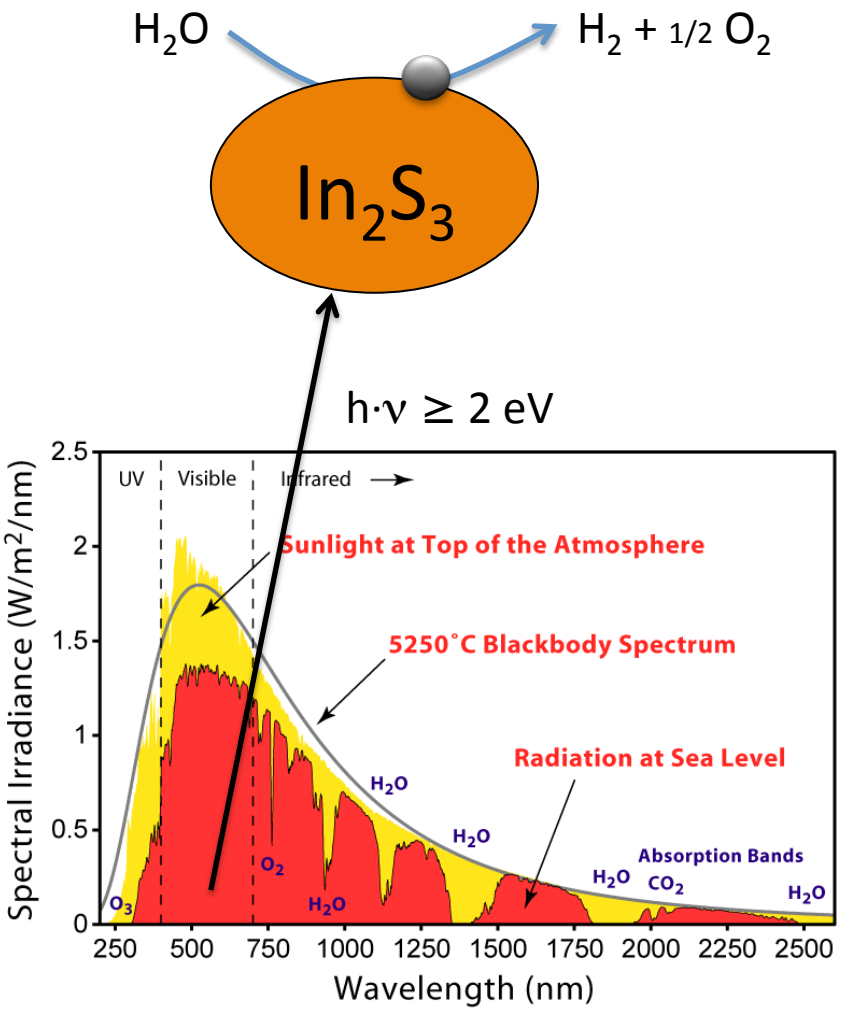
- Solar light can provide the energy if appropriate catalysts are used. First example Fujishima, Honda (1972 Nature).
- Only uses UV, disregards ≥ 95% solar spectrum.
- It can be doped, used with co-catalysts, even co-biocatalysts to ease the H_2 evolution.



Photolytic Water Splitting

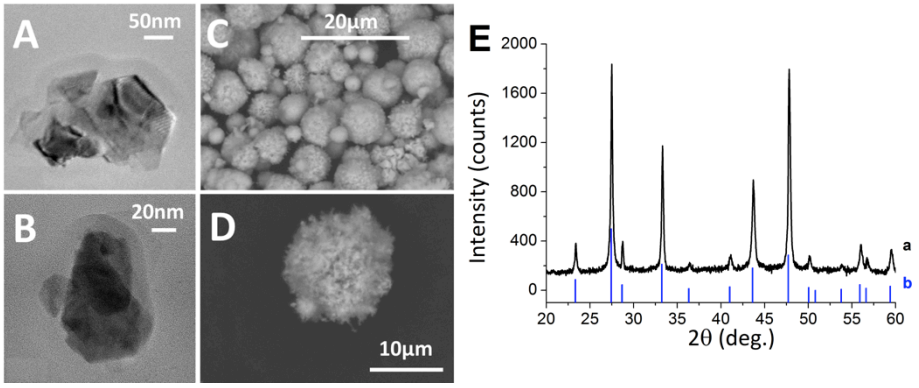
- Other photocalysts can harvest visible light and their conduction band allows H_2 evolution, although may need a cocatalyst.
- In_2S_3 has the physical properties to allow water split

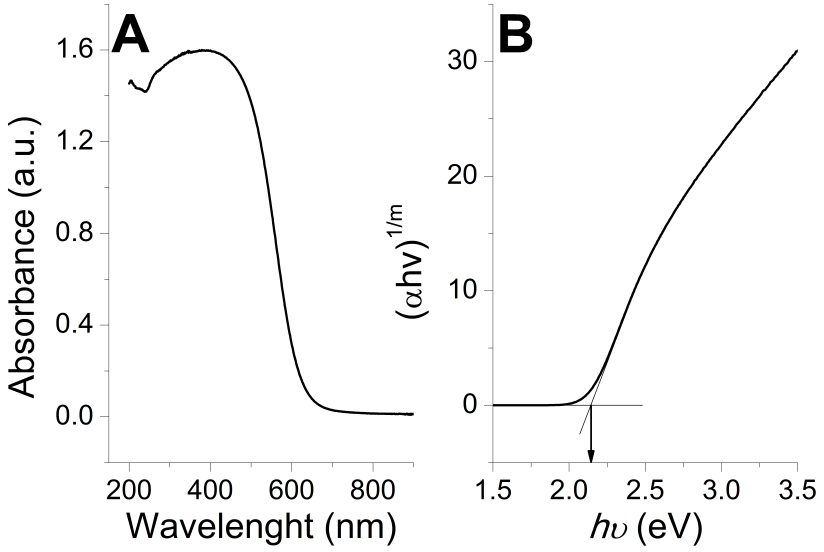




In_2S_3 Characterization

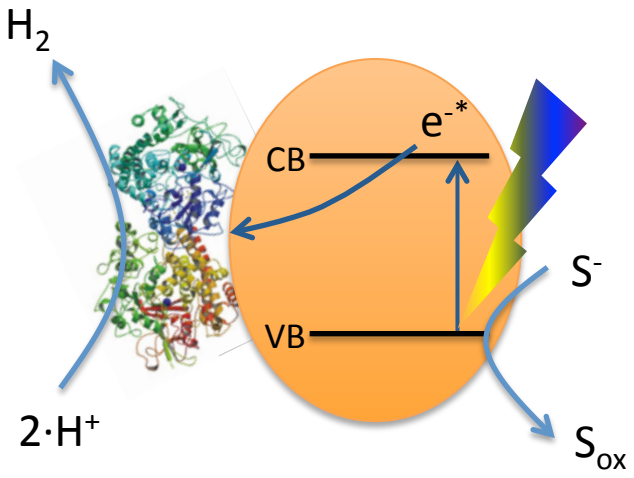
- Microparticles ranging 100 nm − 1 μm. Crystal size: 37.2 nm (XRD).
- Band gap: 2.1 eV
- n-type semiconductor
- High surface and porosity:
  - 40.6 $\pm$ 0.3 m^2/g, 0.168 cm^3/g,
  - average pore diameter: 16.5 nm.





In_2S_3 as co-catalyst for H_2 production

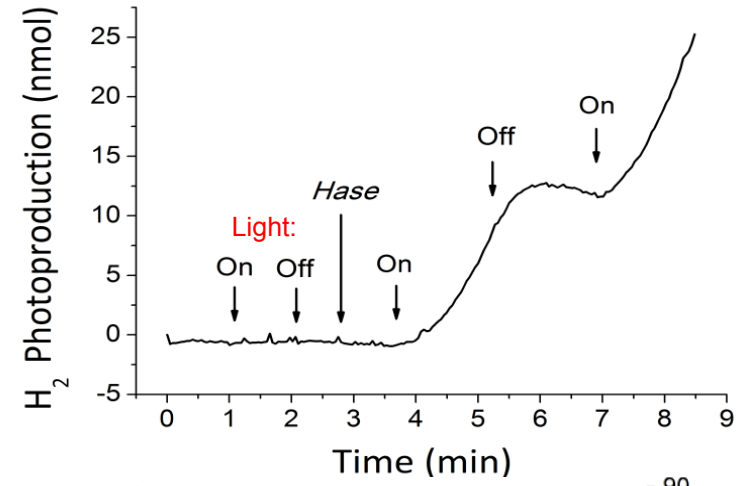
- H_2 photo-generation test with In_2S_3 + NiFeSe Hase
- The Hase included surface aminoacid mutations: cysteine residues substituted others close to the distal Fe_4S_4 cluster.
- Aqueous sulfide solution pH=7, tungsten lamp, mass spec. H_2 detection

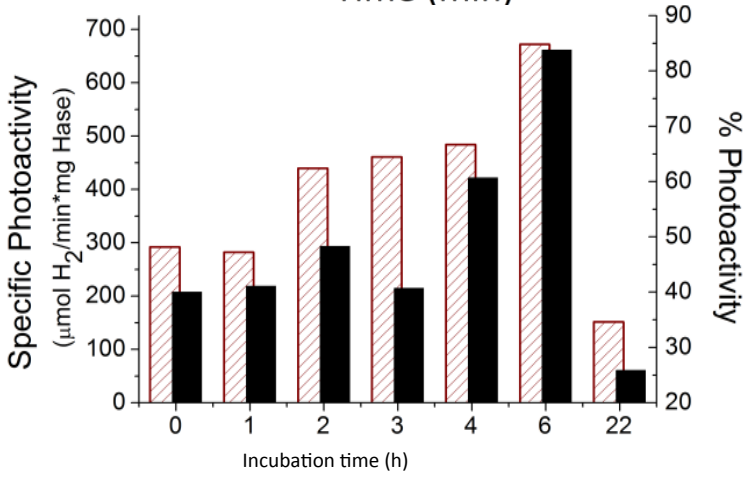


C. Tapia *et al.*, ACS Catalysis 6 (2016) 5691

In_2S_3 as co-catalyst for H_2 production

- Photocatalytic production of H_2 and In_2S_3 particles just after they are mixed together.
  - Illuminating on the mixture yielded H2 production, whereas illuminating only one of the components failed.
- Incubation time was analyzed.
- 6 hours incubation yielded the best results in both specific activity and photoactivity vs methyl viologen standard activity.
- 1 day incubation affected the interface between the catalysts-





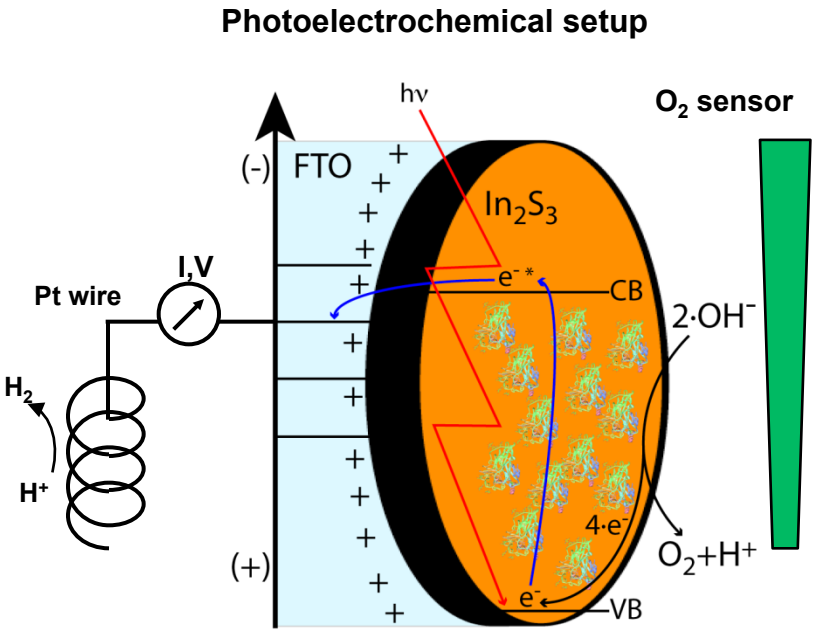
C. Tapia *et al.*, ACS Catalysis 6 (2016) 5691

Photobiocatalytic H_2 production

- In_2S_3 is a suitable material for H_2 production in combination with hydrogenase.
- If the sacrificial agent is substituted by an electrode, aiming a photobioelectrocatalytic process, H_2 is not produced: a p-type semiconductor is needed.

Photobiocatalytic O_2 production

- In_2S_3 was deposited on an FTO electrode and electrochemically modified with aminoaryldiazonium salt.
- *Trametes hirsuta* laccase was covalently bonded to the In_2S_3 surface.
- O_2 production was evaluated upon illumination and simultaneous application of an oxidative potential.

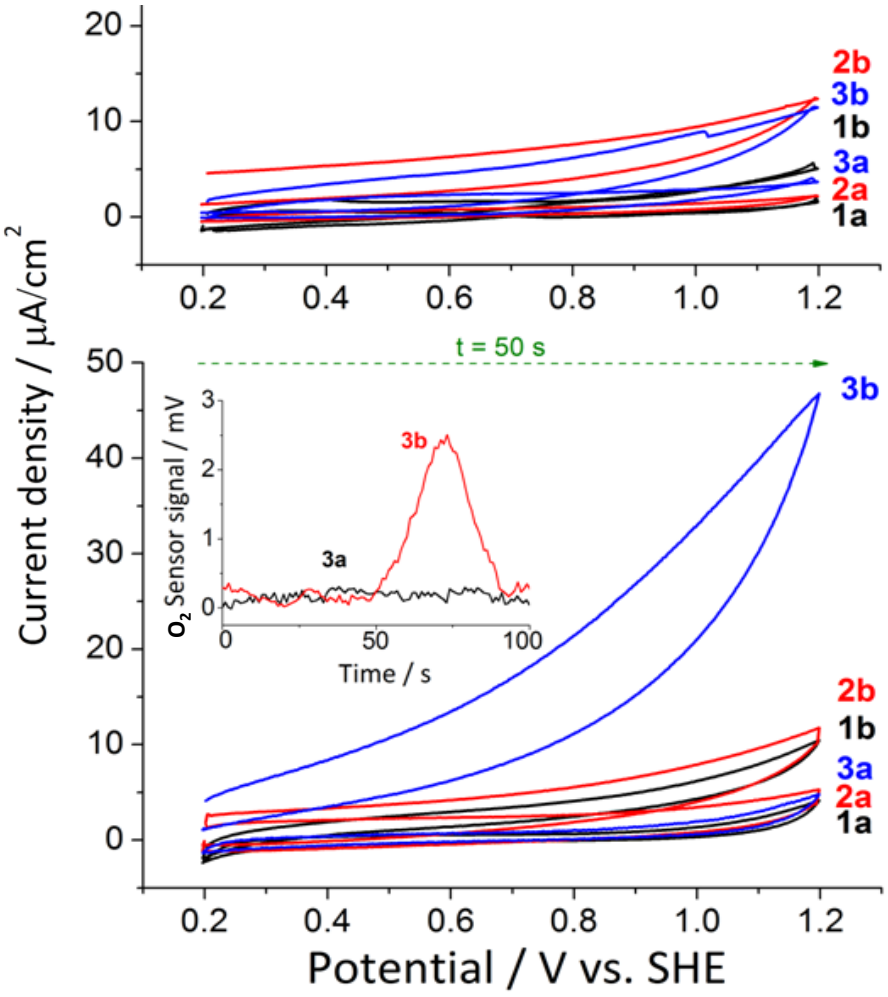


C. Tapia *et al.*, ACS Catalysis 7 (2017) *4881-4889.*

Cyclic Voltammetry Results

Photoelectrochemical operation of FTO + In_2S_3 + ThLc laccase

Cyclic voltammograms at 20 mV/s



(a) In dark (b) with light

1- bare FTO
2- FTO + In_2S_3
3- FTO + In_2S_3 + phys. ads. ThLc

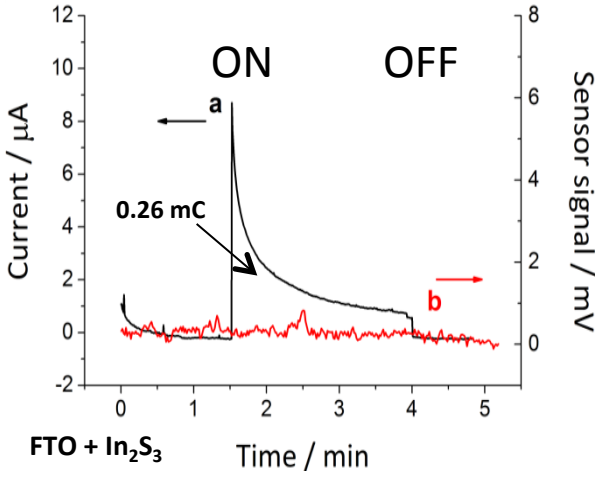
High current, with generation of O_2, only with In_2S_3 + light + bound ThLc

1- FTO + aminoph.-bound ThLc
2- FTO + In_2S_3 + aminoph.
3- FTO + In_2S_3 + aminoph.-bound ThLc

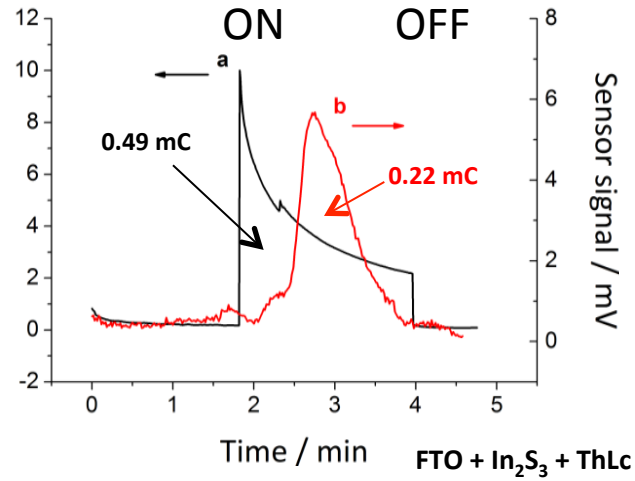
C. Tapia *et al.*, ACS Catalysis 7 (2017) *4881-4889.*

Chronoamperometry Results

Chronoamperometry at 1 V *vs.* SHE: contribution of In_2S_3



Photoelectrochemical operation of FTO + In_2S_3 + ThLc laccase



The irradiated electrode modified with In_2S_3 and laccase yields O_2 production.

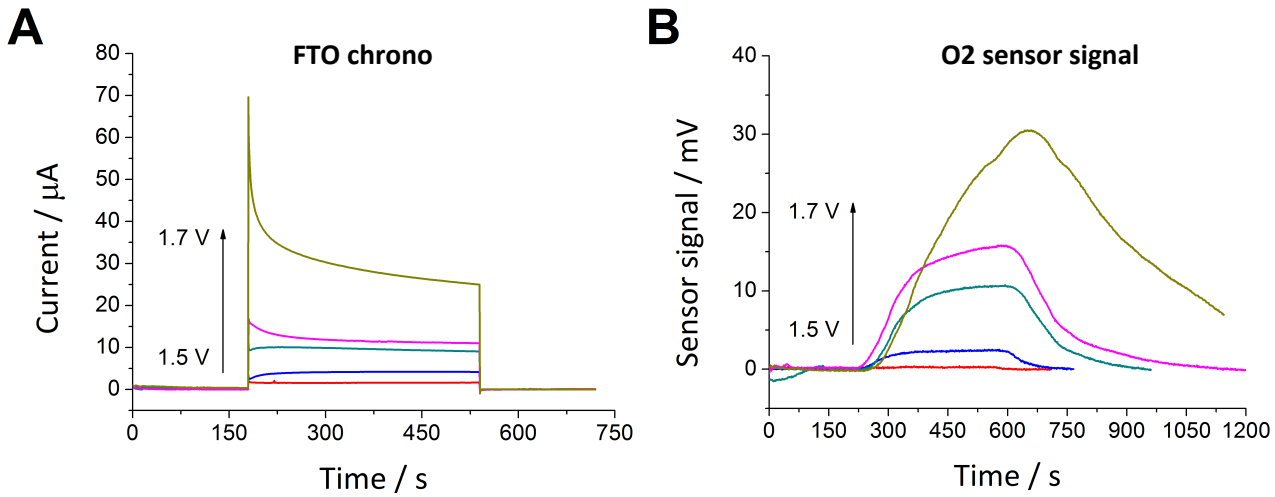
There appears a 50s delay between the current measured and the O_2 sensor signal.

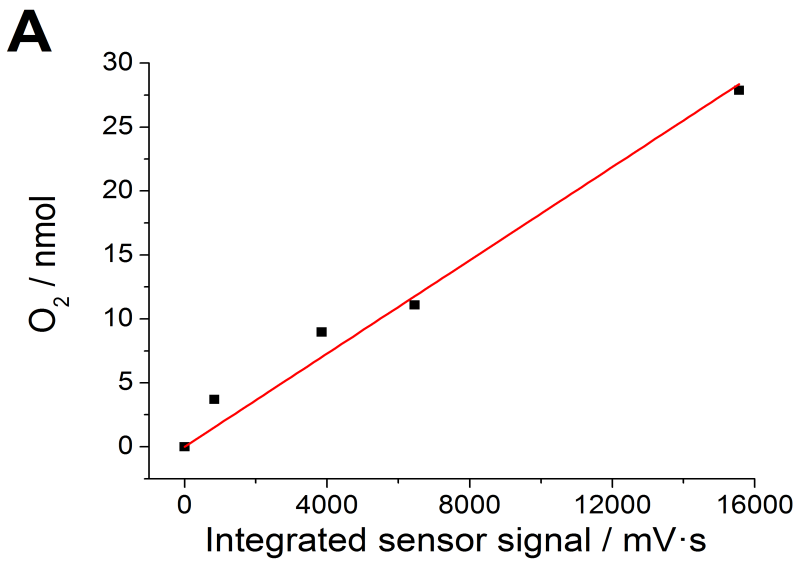
Interest in quantifying the amount of O_2 produced.

C. Tapia *et al.*, ACS Catalysis 7 (2017) *4881-4889.*

Chronoamperometry Calibration

Chronoamperometry of FTO at increasing V *vs.* SHE: evaluate response from O_2 sensor

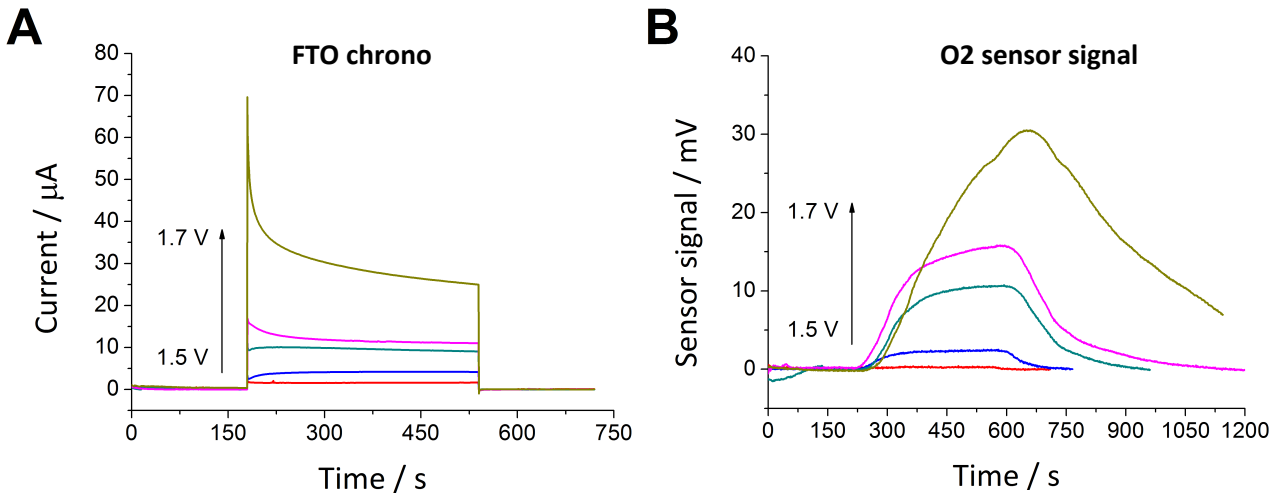


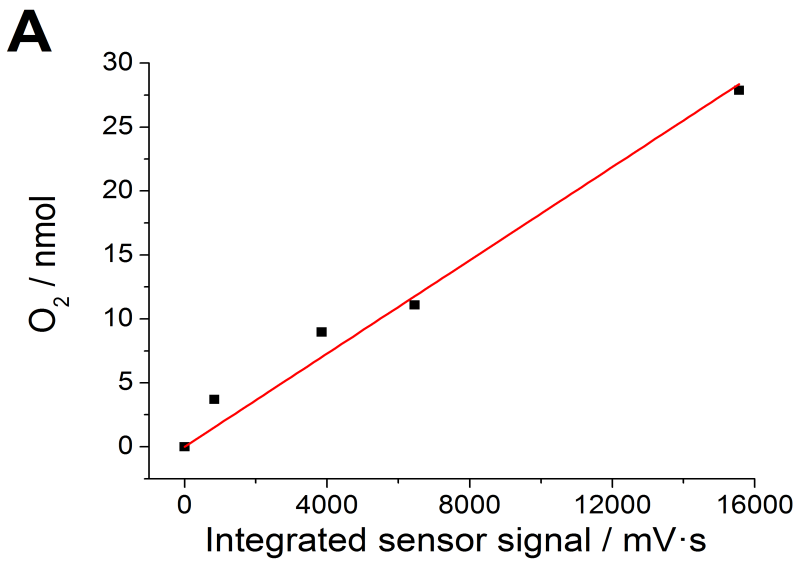


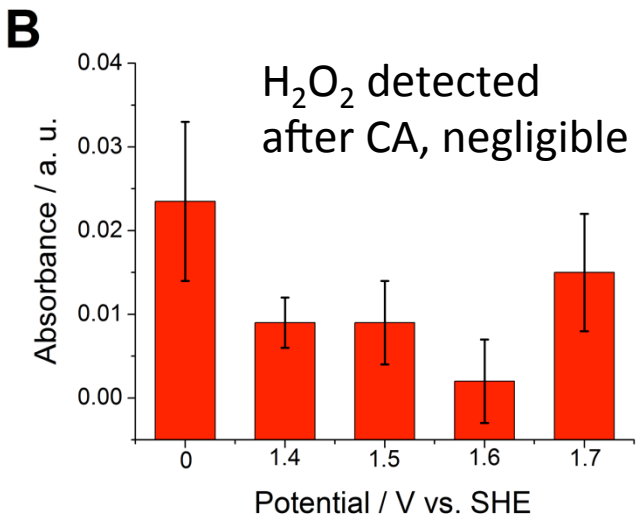
C. Tapia *et al.*, ACS Catalysis 7 (2017) *4881-4889.*

Chronoamperometry Calibration

Chronoamperometry of FTO at increasing V *vs.* SHE: evaluate response from O_2 sensor



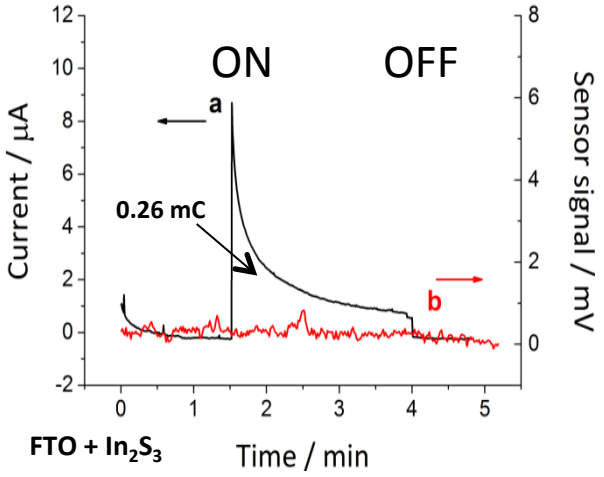




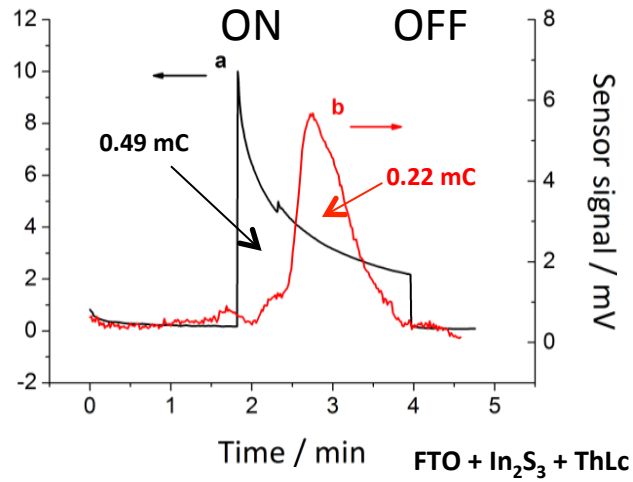
C. Tapia *et al.*, ACS Catalysis 7 (2017) *4881-4889.*

Chronoamperometry Results

Chronoamperometry at 1 V *vs.* SHE: contribution of In_2S_3



Photoelectrochemical operation of FTO + In_2S_3 + ThLc laccase



E (SHE) / V	Charge (mC)	O_2 (nmol)	Faradaic yield (%)
0.7	0.3 ± 0.1	0	0
0.8	0.7 ± 0.1	0.5 ± 0.1	30 ± 5
0.9	0.6 ± 0.2	0.44 ± 0.03	30 ± 10
1.0	0.8 ± 0.2	0.93 ± 0.04	45 ± 5

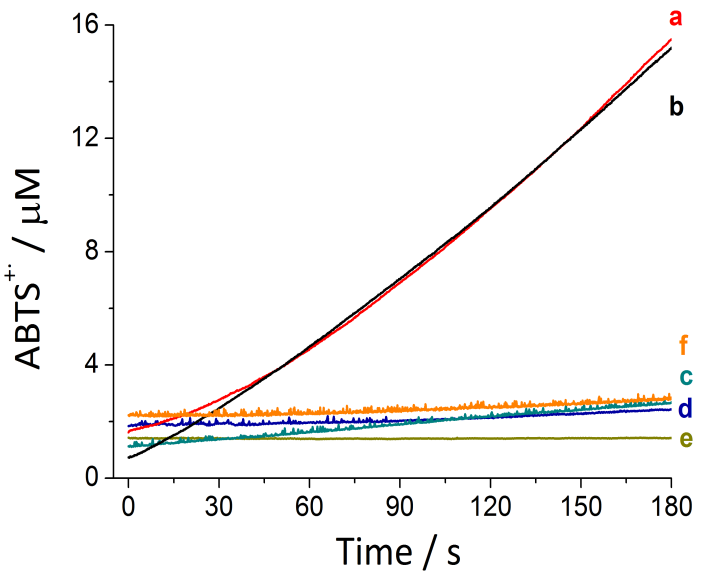
C. Tapia *et al.*, ACS Catalysis 7 (2017) *4881-4889.*

Light effect on ThLc

ThLc immobilized on FTO or FTO-In_2S_3 electrodes keeps its natural activity.

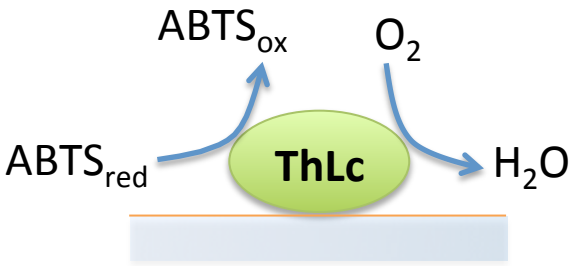
After irradiating either FTO-ThLc or FTO-In_2S_3-ThLc electrodes.

Inactivation took place under applied +0.8V potential, also with no applied potential.



Electrodes before light

Electrodes after light



C. Tapia *et al.*, ACS Catalysis 7 (2017) *4881-4889.*

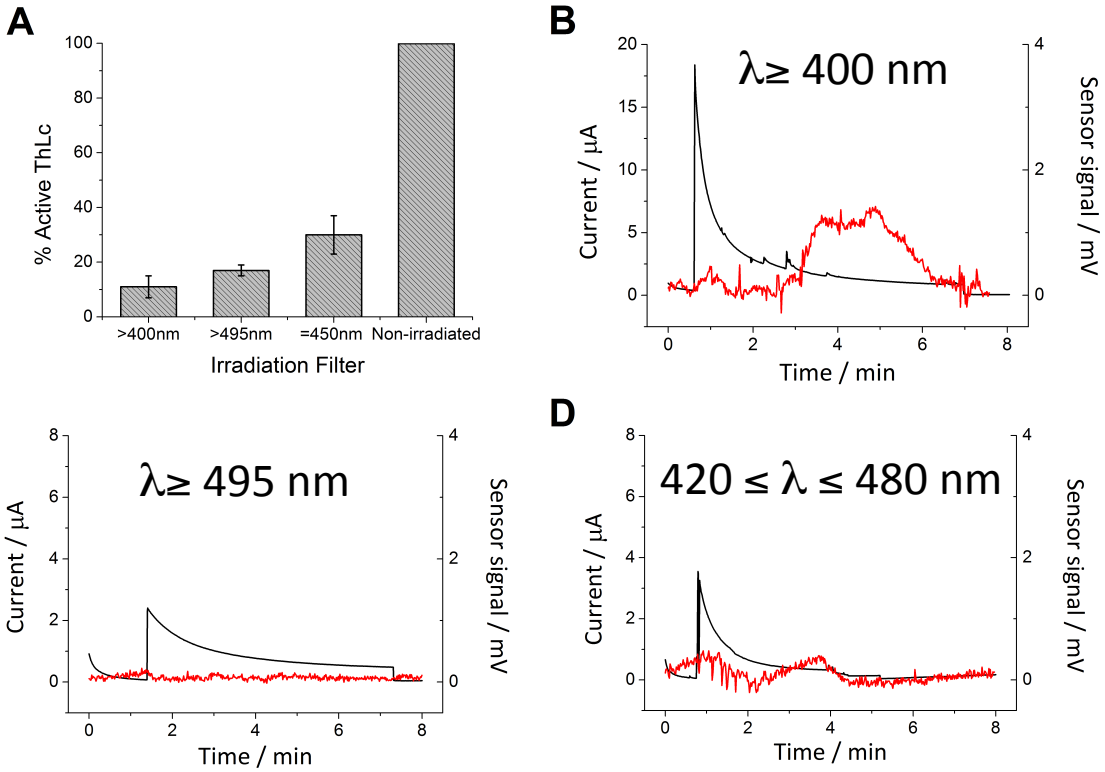
Light filter effect

Xe Light affects severely to ThLc.

We used light filters to remove UV

O_2 production detected only when λ≥ 400 nm was irradiated.

In any case ThLc survived longer than 5 min



C. Tapia *et al.*, ACS Catalysis 7 (2017) *4881-4889.*

Future Work

- Test alternative semiconductors absorbing in VIS range: SnS_2, CuO…
- Protect laccase from light inactivation.
- Increase effective area (nanoparticles).
- Assemble a full water splitting cell able of photobioproducing H_2 and O_2.

Thank you!