Laccase-Catalyzed Bioelectrochemical Oxidation of Water Assisted with Visible Light

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Water Splitting

• Goal: obtain H₂ and O₂ from H₂O through a sustainable synthesis route.
• High energy demanding process.
• Appropriate catalysts are key to the process.

\[ 2 \cdot \text{H}_2\text{O} \xrightarrow{E} 2 \cdot \text{H}_2 + \text{O}_2 \]
Electrochemical Water Splitting

• Goal: obtain H₂ and O₂ from H₂O 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?
• O₂ evolution is not a naturally-occurring reaction except for photosynthetic routes (PSI, PSII).
Bioelectrochemical $O_2$ Evolution

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

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


Photolytic Water Splitting

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

$$H_2O \rightarrow H_2 + 1/2 O_2$$

$\text{h} \cdot v \geq 3.2 \text{ eV}$

![Spectral Irradiance (W/m²/nm) vs. Wavelength (nm)]

- Sunlight at Top of the Atmosphere
- 5250°C Blackbody Spectrum
- Radiation at Sea Level
- Absorption Bands
Photolytic Water Splitting

• Other photocatalysts can harvest visible light and their conduction band allows $H_2$ evolution, although may need a cocatalyst.

• $\text{In}_2\text{S}_3$ has the physical properties to allow water split

\[
\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2
\]

\[
h \cdot \nu \geq 2 \text{ eV}
\]
In$_2$S$_3$ 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.
\[ \text{In}_2\text{S}_3 \text{ as co-catalyst for H}_2 \text{ production} \]

- \( \text{H}_2 \) photo-generation test with \( \text{In}_2\text{S}_3 + \text{NiFeSe Hase} \)
- The Hase included surface aminoacid mutations: cysteine residues substituted others close to the distal \( \text{Fe}_4\text{S}_4 \) cluster.
- Aqueous sulfide solution pH=7, tungsten lamp, mass spec. \( \text{H}_2 \) detection

C. Tapia et al., ACS Catalysis 6 (2016) 5691
In$_2$S$_3$ as co-catalyst for H$_2$ production

- Photocatalytic production of H$_2$ and In$_2$S$_3$ particles just after they are mixed together.
  - Illuminating on the mixture yielded H$_2$ 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 $\text{H}_2$ production

- $\text{In}_2\text{S}_3$ is a suitable material for $\text{H}_2$ production in combination with hydrogenase.
- If the sacrificial agent is substituted by an electrode, aiming a photobioelectrocatalytic process, $\text{H}_2$ is not produced: a p-type semiconductor is needed.
Photobiocatalytic $\text{O}_2$ production

- In$_2$S$_3$ was deposited on an FTO electrode and electrochemically modified with aminoaryldiazonium salt.
- *Trametes hirsuta* laccase was covalently bonded to the In$_2$S$_3$ surface.
- $\text{O}_2$ production was evaluated upon illumination and simultaneous application of an oxidative potential.

Cyclic Voltammetry Results

Photoelectrochemical operation of FTO + In$_2$S$_3$ + ThLc laccase

Cyclic voltammograms at 20 mV/s

(a) In dark  (b) with light

1- bare FTO
2- FTO + In$_2$S$_3$
3- FTO + In$_2$S$_3$ + phys. ads. ThLc

High current, with generation of O$_2$, only with In$_2$S$_3$ + light + bound ThLc

1- FTO + aminoph.-bound ThLc
2- FTO + In$_2$S$_3$ + aminoph.
3- FTO + In$_2$S$_3$ + aminoph.-bound ThLc

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

The irradiated electrode modified with In$_2$S$_3$ 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 of FTO at increasing V vs. SHE: evaluate response from O₂ sensor

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

Chronoamperometry of FTO at increasing V vs. SHE: evaluate response from O₂ sensor

C. Tapia et al., ACS Catalysis 7 (2017) 4881-4889.
Chronoamperometry at 1 V vs. SHE: contribution of $\text{In}_2\text{S}_3$

Chronoamperometry at 1 V vs. SHE: contribution of $\text{In}_2\text{S}_3$ + ThLc laccase

<table>
<thead>
<tr>
<th>$E$ (SHE) / V</th>
<th>Charge (mC)</th>
<th>$\text{O}_2$ (nmol)</th>
<th>Faradaic yield (%)</th>
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<tbody>
<tr>
<td>0.7</td>
<td>0.3 ± 0.1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.8</td>
<td>0.7 ± 0.1</td>
<td>0.5 ± 0.1</td>
<td>30 ± 5</td>
</tr>
<tr>
<td>0.9</td>
<td>0.6 ± 0.2</td>
<td>0.44 ± 0.03</td>
<td>30 ± 10</td>
</tr>
<tr>
<td>1.0</td>
<td>0.8 ± 0.2</td>
<td>0.93 ± 0.04</td>
<td>45 ± 5</td>
</tr>
</tbody>
</table>

C. Tapia et al., ACS Catalysis 7 (2017) 4881-4889.
Light effect on ThLc

ThLc immobilized on FTO or FTO-In$_2$S$_3$ electrodes keeps its natural activity.

After irradiating either FTO-ThLc or FTO-In$_2$S$_3$-ThLc electrodes.

Inactivation took place under applied +0.8V potential, also with no applied potential.
Xe Light affects severely to ThLc.

We used light filters to remove UV

O$_2$ production detected only when $\lambda \geq 400$ nm was irradiated.

In any case ThLc survived longer than 5 min
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!