Renewable Energy & Sustainability
Water splitting, Artificial Photosynthesis

“Synthesis and Application of Organic-Inorganic Nanocomposites in Artificial Photosynthesis”

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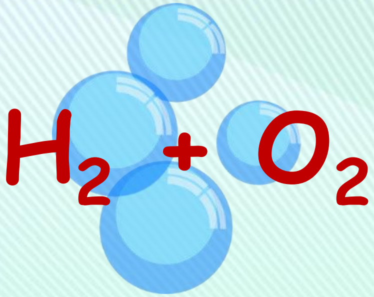
Overview

- Importance of Photosynthesis

  (Natural & Artificial)

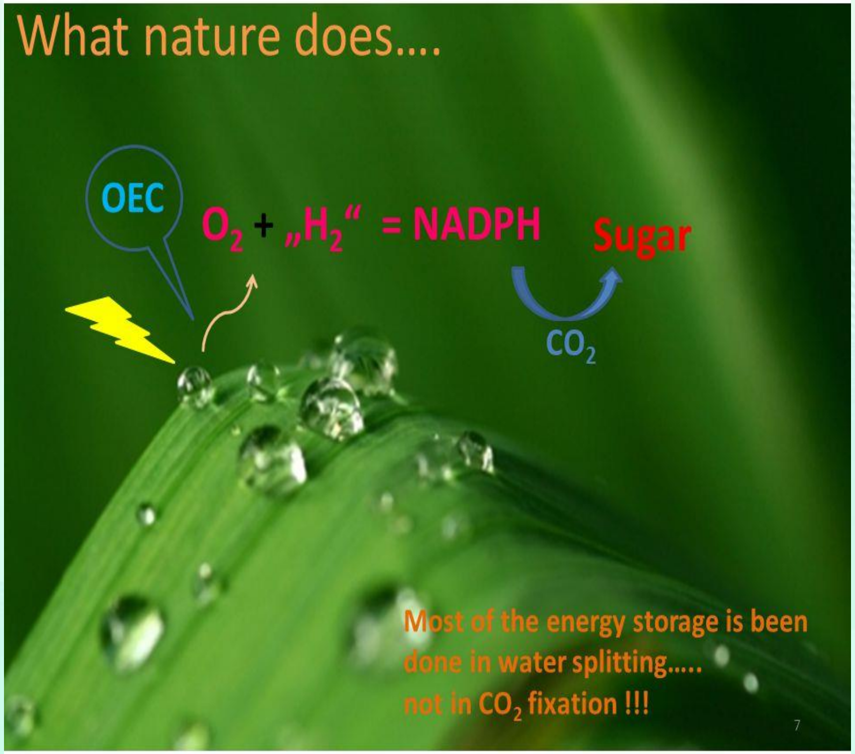
- Water Oxidation Catalysts (WOCs)
- Our project – aims
- *Mechanistic pathways for WOCs*
- Experimental work
- Results & Summary

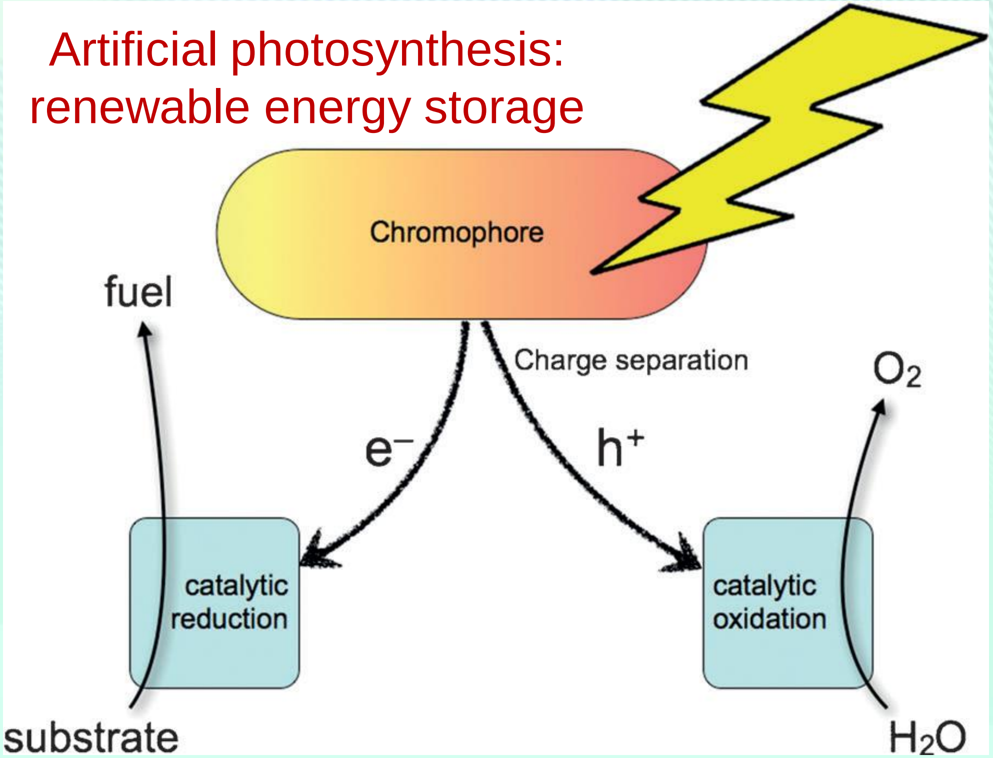


Natural & Artificial Photosynthesis

Inspired by nature

In this machinery, five major processes:
photon absorption, charge separation, electron transfer, water oxidation, and proton reduction have to be combined together to achieve high efficiency.

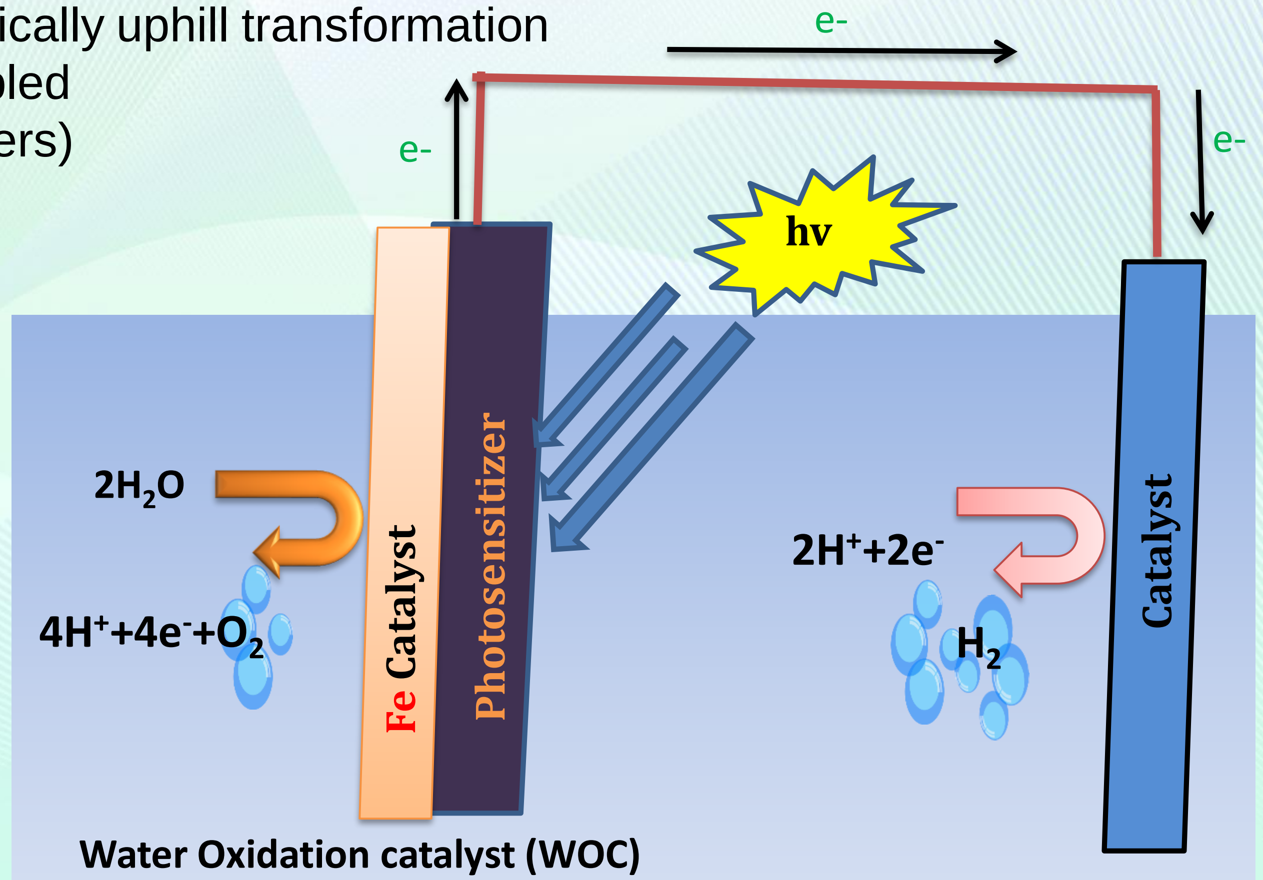




https://pubs.rsc.org/en/Content/ArticleLanding/2009/CS/B802262N#!divAbstract

Water Oxidation Catalysts

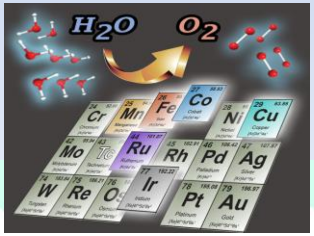
Water splitting is an energetically uphill transformation (multi-electron process coupled with a multiple proton transfers) to produce H_2



Water oxidation (Complex)
four protons and four electrons from two water molecules to produce one dioxygen molecule.

Main challenges:
find a robust, efficient, and inexpensive catalysts for Water Oxidation.

(Homogeneous or Heterogeneous)



Our Work

AIMS:

1. modify an electrode surface with catalytic units (molecules)

low-cost (Fe, simple organic heterocyclic ligands)
hydrophobic (extended aromatics)
high catalytic activity (similar to known catalysts)
avoid using additional components (Nafion)

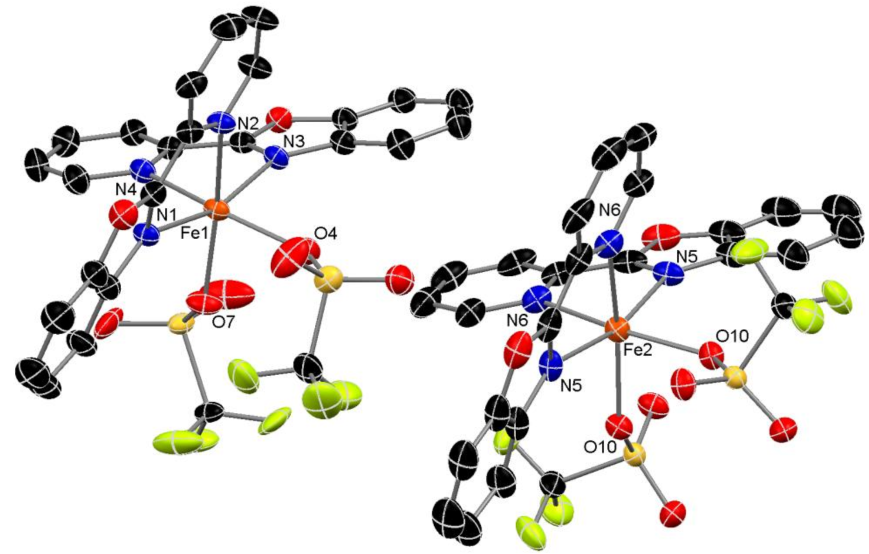
2. Compare some homolog catalysts

small structural variations (Q heteroatom)
compatible with electrochemical methods
(homogeneous and heterogeneous conditions)

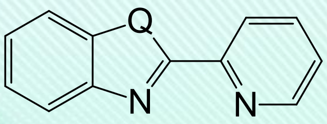
3. Understand the effect of molecular changes on the observed catalytic properties

help designing low-cost,
robust and efficient catalysts

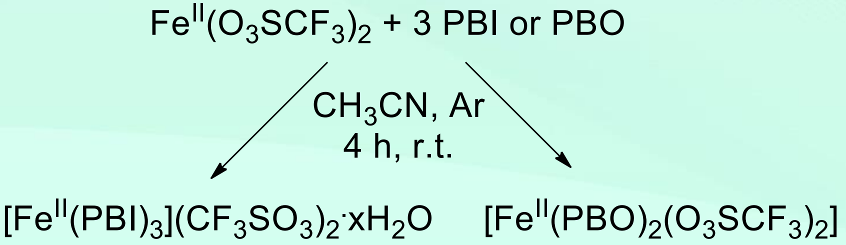
Ligands:
2-(2'-pyridyl)benzimidazole (PBI)
2-(2'-pyridyl)benzoxazole (PBO)



$[Fe(PBO)_2(O_3SCF_3)_2]$

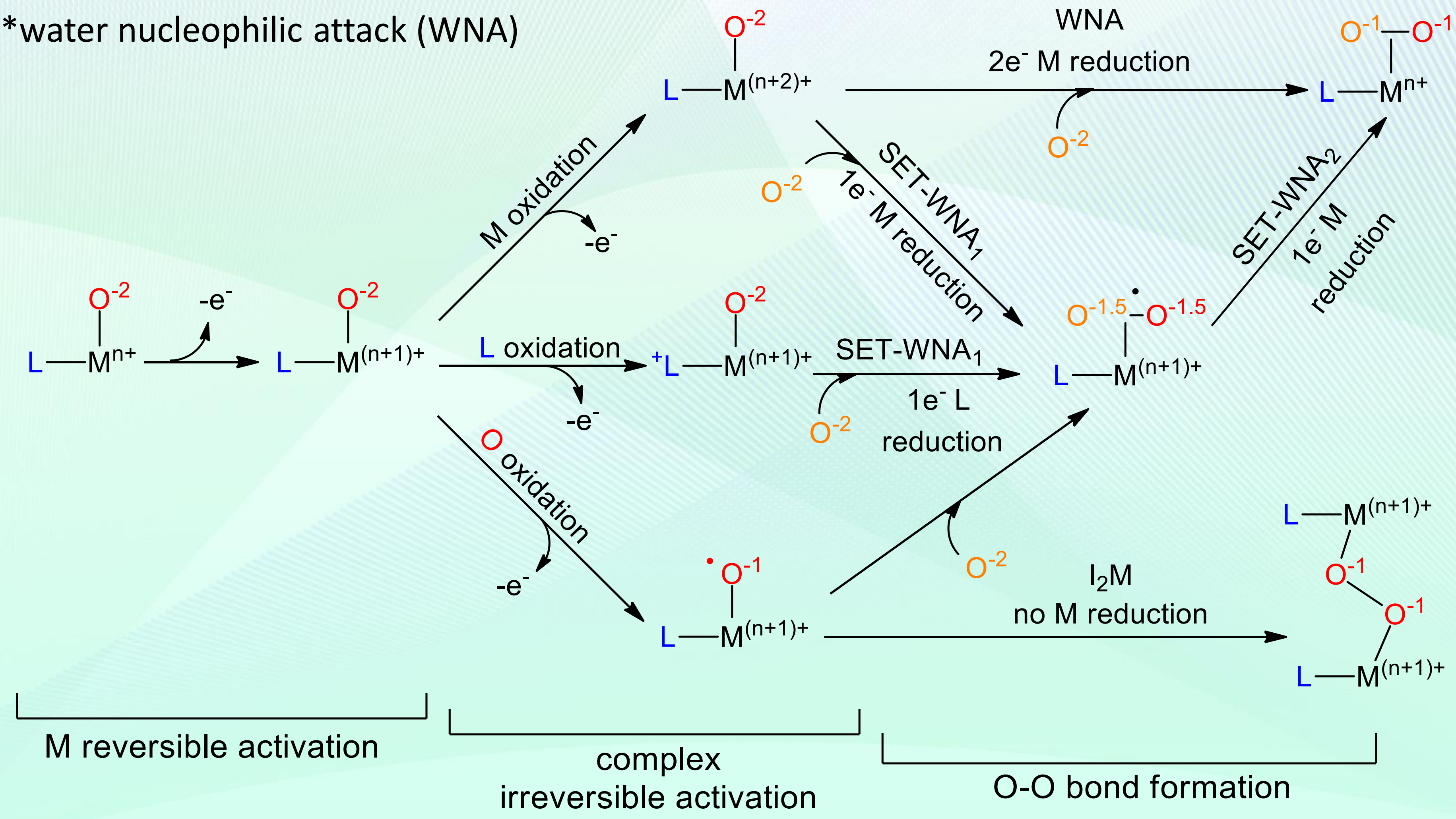


Q = NH PBI
O PBO



Mechanistic Pathways for WOCs – Initial Steps

*water nucleophilic attack (WNA)



Llobet&Maseras, *ACS Catal.* **2017**, *7*, 1712

Experimental Work Electrochemistry & Catalysis

Homogeneous

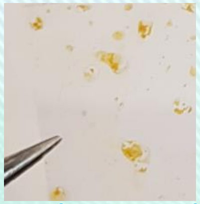
The complex is dissolved in
H_2O/acetonitrile mixtures
to examine their intrinsic molecular
catalytic capabilities

[Fe(PBO)$_2$(OTf)$_2$] and [Fe(PBI)$_3$](OTf)$_2$

Heterogeneous

dip-coating and drop-casting of
(1) the complex dissolved in methanol and
(2) dried onto Indium Tin Oxide semiconductor

ITO



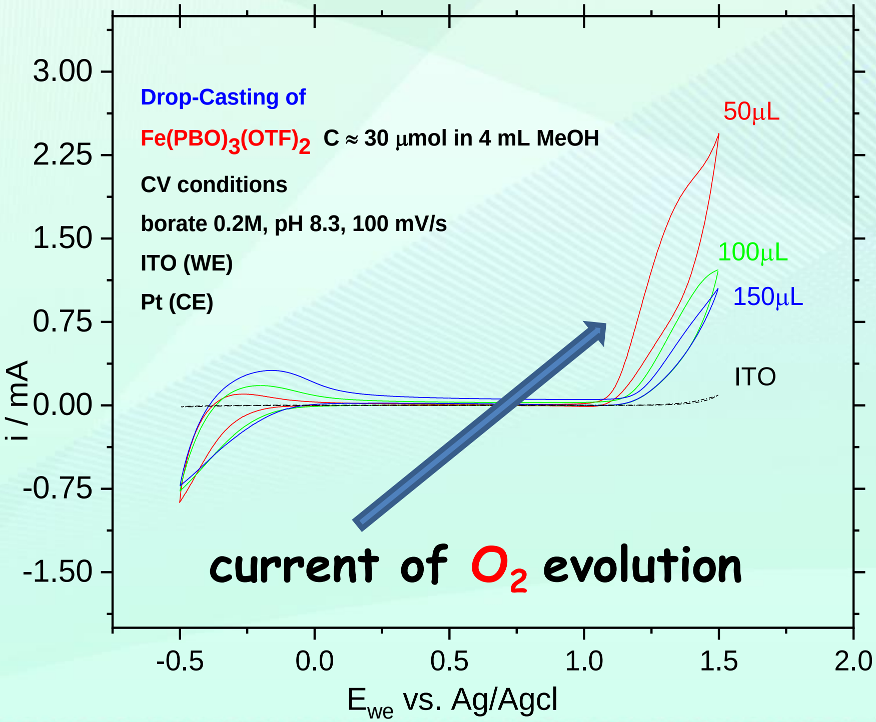
Dip-coating and drop-casting

(3) Use the complex/ITO electrode in borate buffer (pH 8.3)

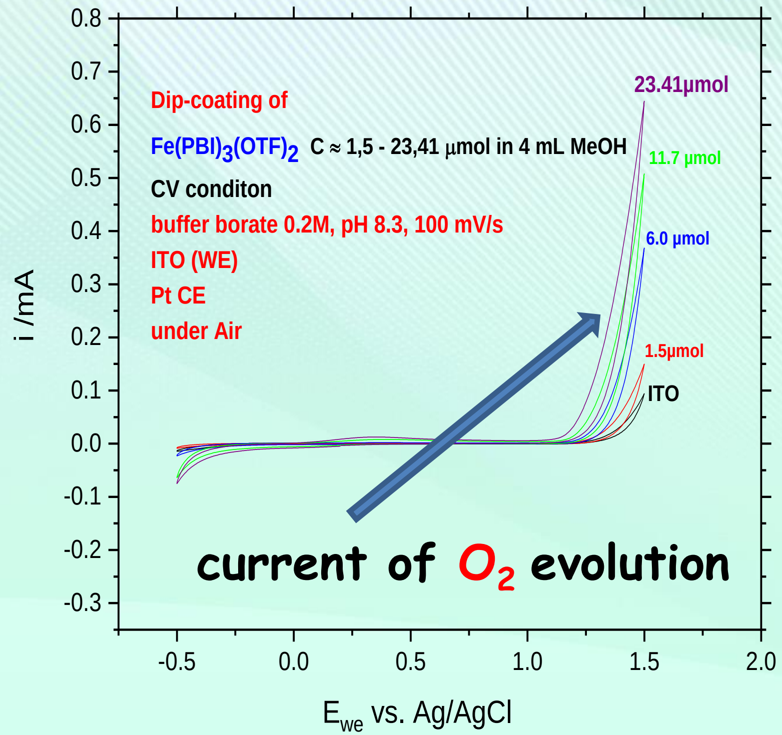
Results A

The water insoluble complexes are tested (drop-casting and dip-coating) as complex/ITO electrode in borate buffer (pH 8.3) by cyclic voltammetry (CV) as shown below:

Drop-casting $[Fe(PBO)_2(OTf)_2]$



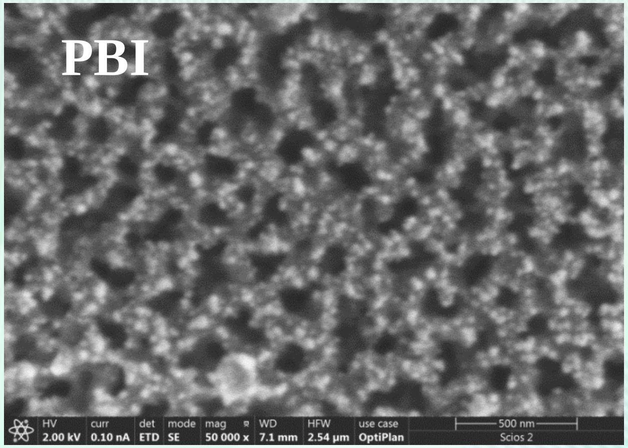
Dip-coating $[Fe(PBI)_3 (OTf)_2]$

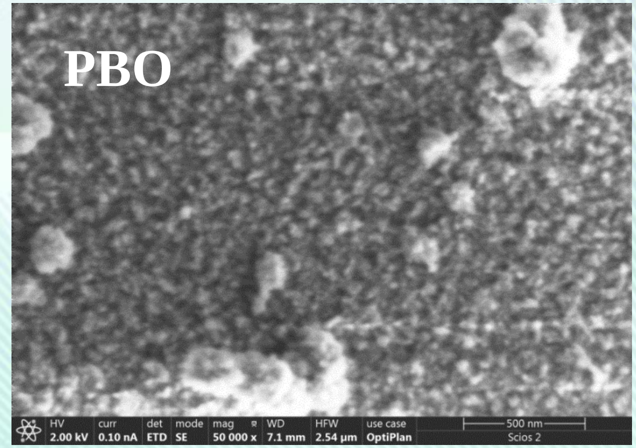


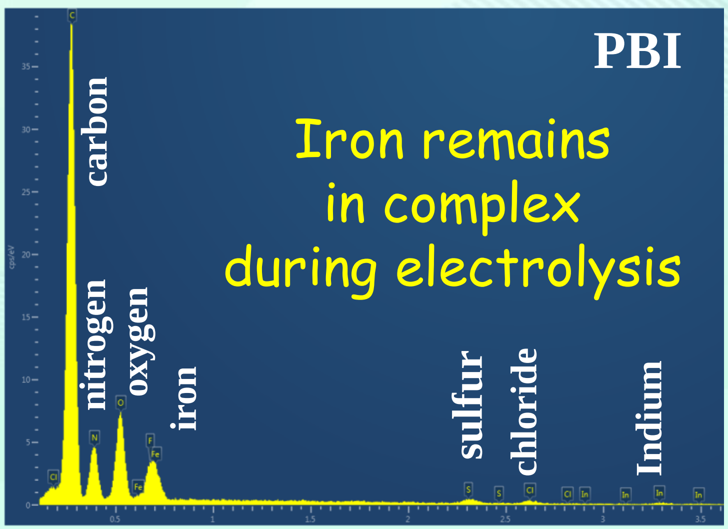
Results B

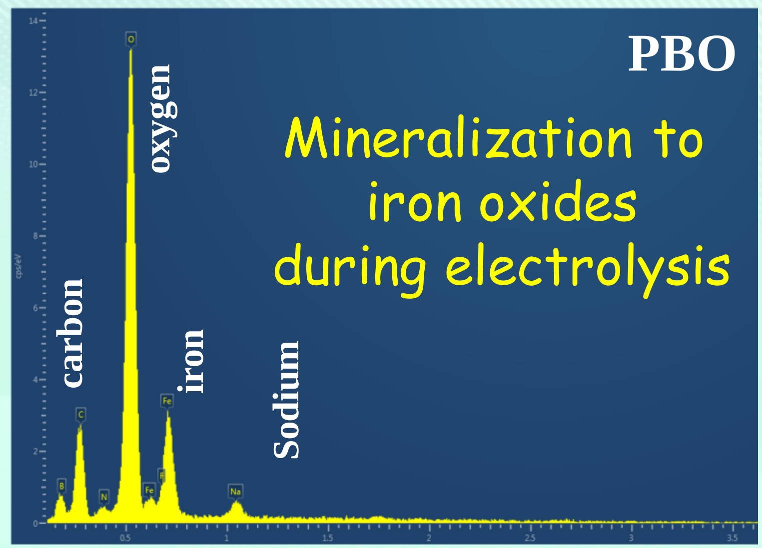
Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDX)

$[Fe(PBI)_3](OTf)_2$ And $[Fe(PBO)_2(OTf)_2]$









Summary and Future Plans

Summary

- hydrophobic properties of two complexes, high affinity for the semiconductor surface, additive-free layering onto ITO surface, the evolution of O_2 was observed in aqueous buffer
- use of the semiconductor ITO surface clearly showed the *operando* stability of $[Fe(PBI)_3](OTf)_2$ and the degradation of $[Fe(PBO)_2(OTf)_2]$.

Future plan

the evolution of O_2 for long periods by **Gas chromatography** (GC).

Mechanistic experiments (kinetics)

Poster presentation (submitted to **(E-MRS)** Spring meeting in Nice, 27-31 May 2019)
Writing manuscript to a peer reviewed journal.

Thank You

For your attention