Óbuda University, Doctoral School on Material Science and Technology

"Synthesis and Application of Organic-Inorganic Nanocomposites in Artificial Photosynthesis"

7th semester

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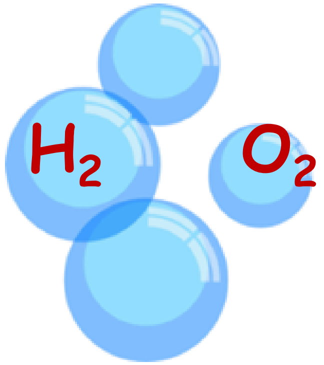
CENTRE FOR ENERGY RESEARCH
HUNGARIAN ACADEMY OF SCIENCES

Outline

- ***Introduction*:**
  - Solar to Fuels (STF), H_2 Fuel.
  - Photosynthesis: Natural & **Artificial Photosynthesis** (AP)
  - Water splitting: Oxygen Evolution Reaction (OER) & Hydrogen Evolution Reaction (HER)



- *Objectives*

$$2H_2O \xrightarrow{\textbf{WOC}} 4H^+ + \mathbf{O_2} + 4e^-$$

  - Find a Robust, Efficient, Cheap catalysts for Water Oxidation (WO)

- Publications

- Thesis points

Solar to Chemical Energy (Fuel) H_2

Global Energy

- Coal,
- Oil products, Natural gas

Provided

- Carbon-based energy
- CO_2 emission

Environm

- Air pollution
- Green house

Fossil Fuels being depleted, effect climate, CO_2

Renewable Resources Available, Ex: Wind, Hydro. Power, Solar…etc

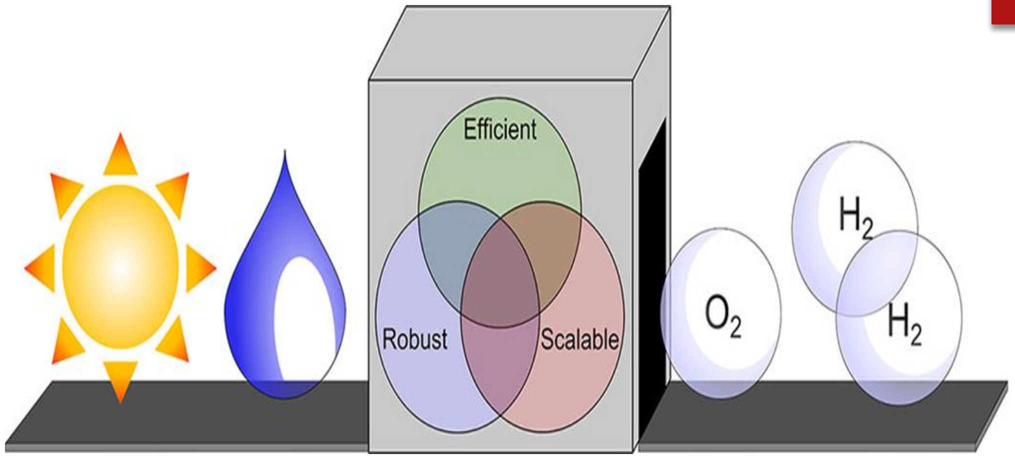
Solar cells only generating during day.

Hydrogen by Photoelectrochemical cells (PEC)

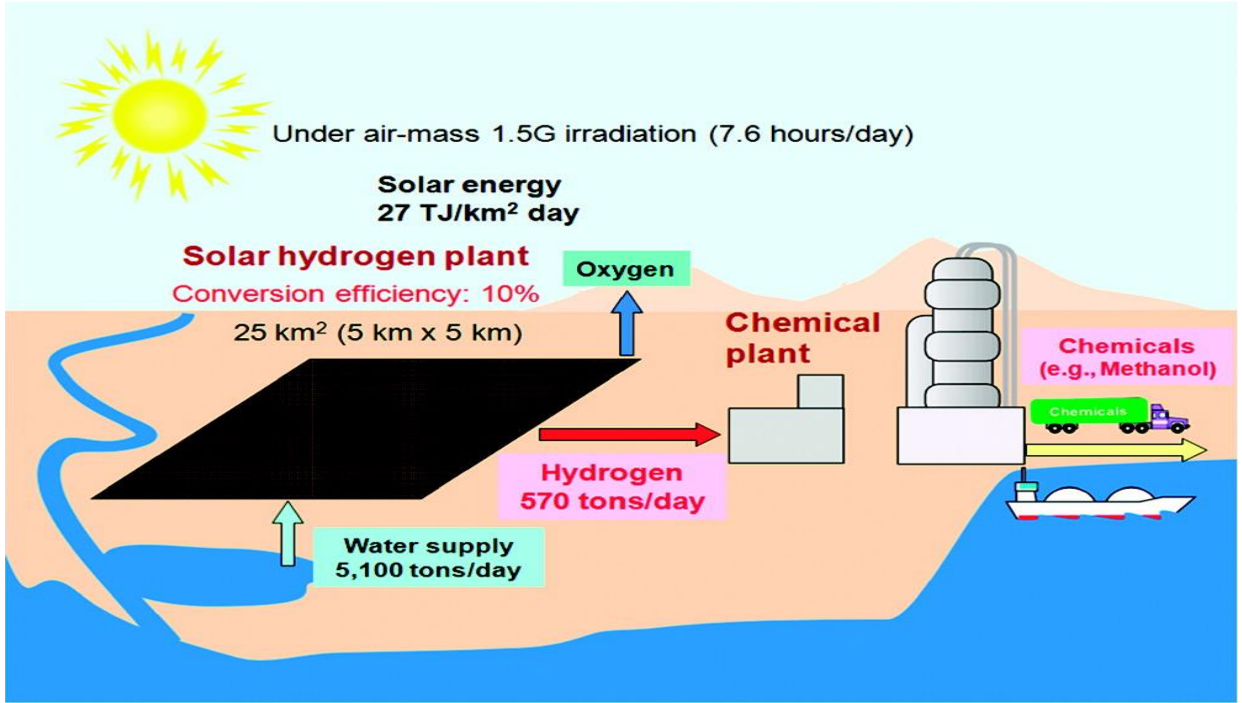
Solar to Chemical Energy-Fuel (STF)

How can achieve STF by water splitting?

- In an artificial photosynthetic system, essential devise an efficient process,
- need to be made from cheap and abundant materials.



Scheme shows the possible large-scale H_2 production via solar water splitting.

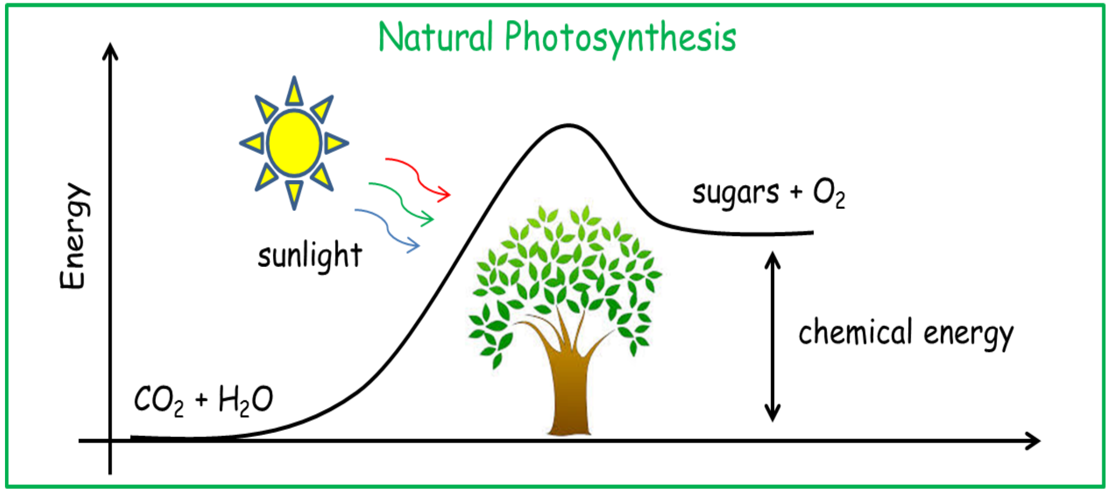


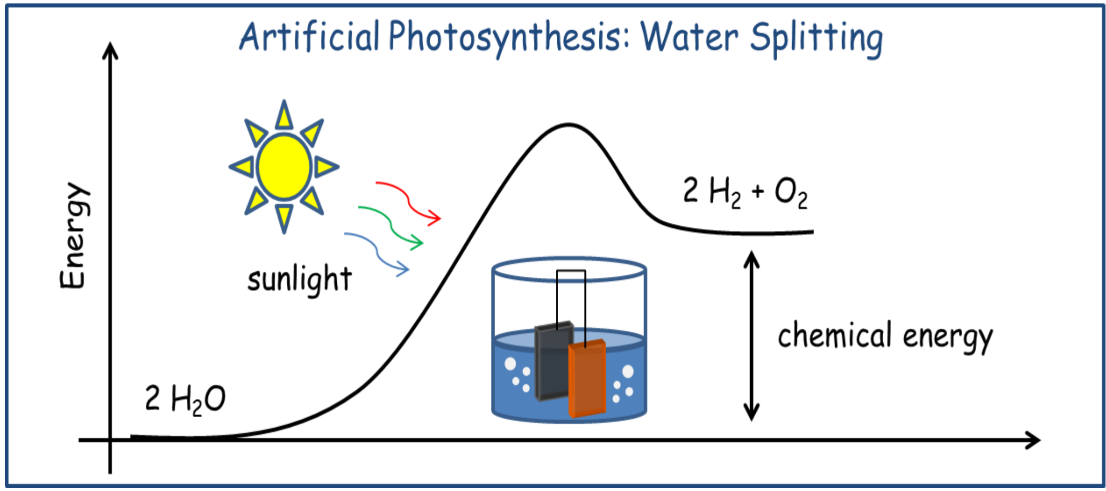
J. Phys. Chem. Lett. 2010, 1, 18, 2655-2661, *Chem. Mater.* 2014, 26, 1, 407-414

Photosynthesis:
Natural vs Artificial

- Photosynthesis has produced most of the energy that sustains life on our planet

- The artificial photosynthesis aims to mimic the natural process
- Conversion of sunlight into H_2 and O_2 by solar-driven water splitting





Nathan S. Lewis Science 2016;351:aad1920

Artificial photosynthesis

In this machinery

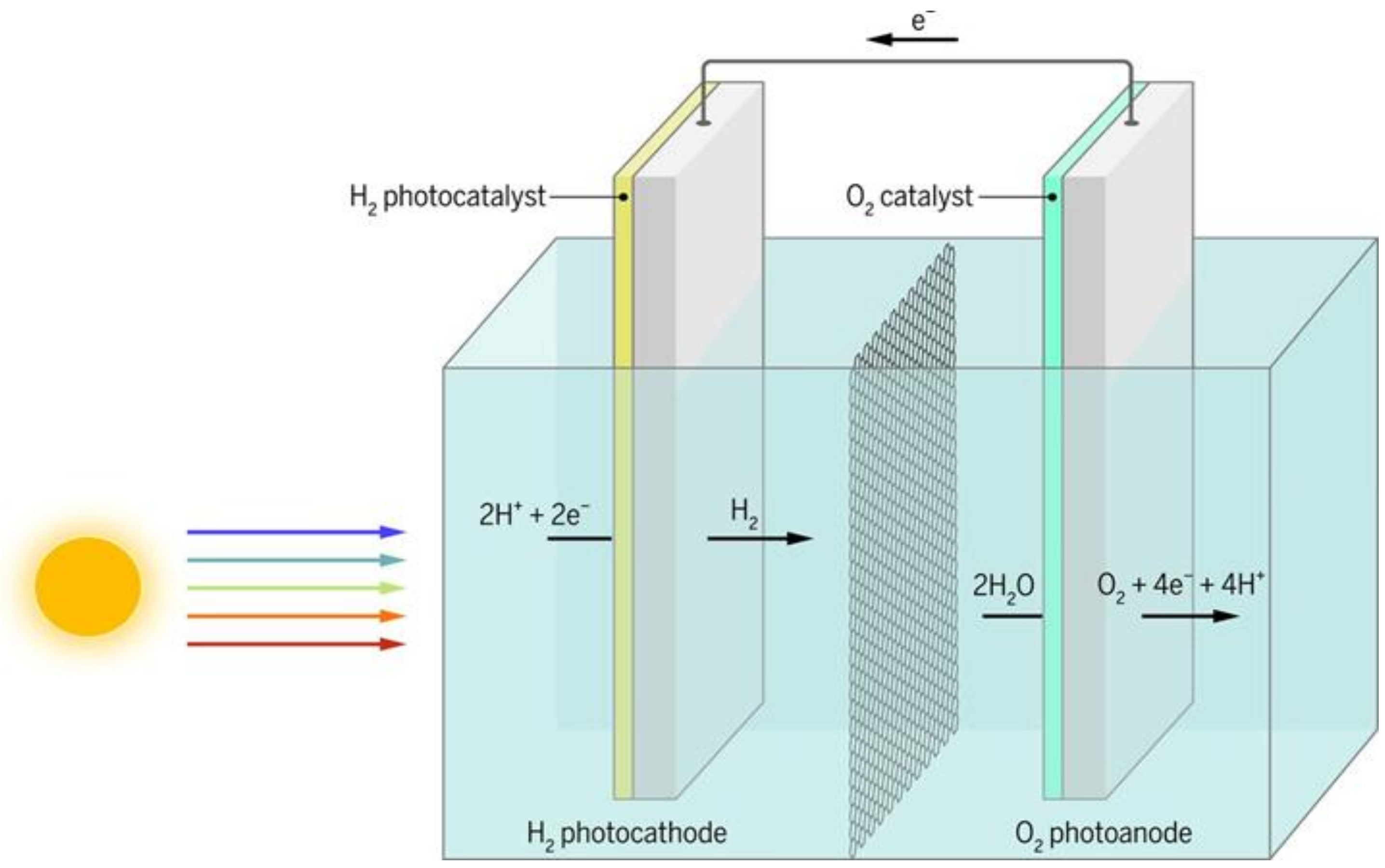
five major processes:
photon absorption,
charge separation,
electron transfer,
water oxidation, and
proton reduction, must be combined to achieve high efficiency.

Water oxidation (WO)

the bottleneck in the field of electrochemical

Electrochemical Water splitting

$$2H_2O\ (l) \rightarrow 2H_2\ (g) + O_2\ (g)$$



$$2H_2O \xrightarrow{WOC} 4H^+ + O_2 + 4e^-$$

Nathan S. Lewis Science 2016;351:

objectives

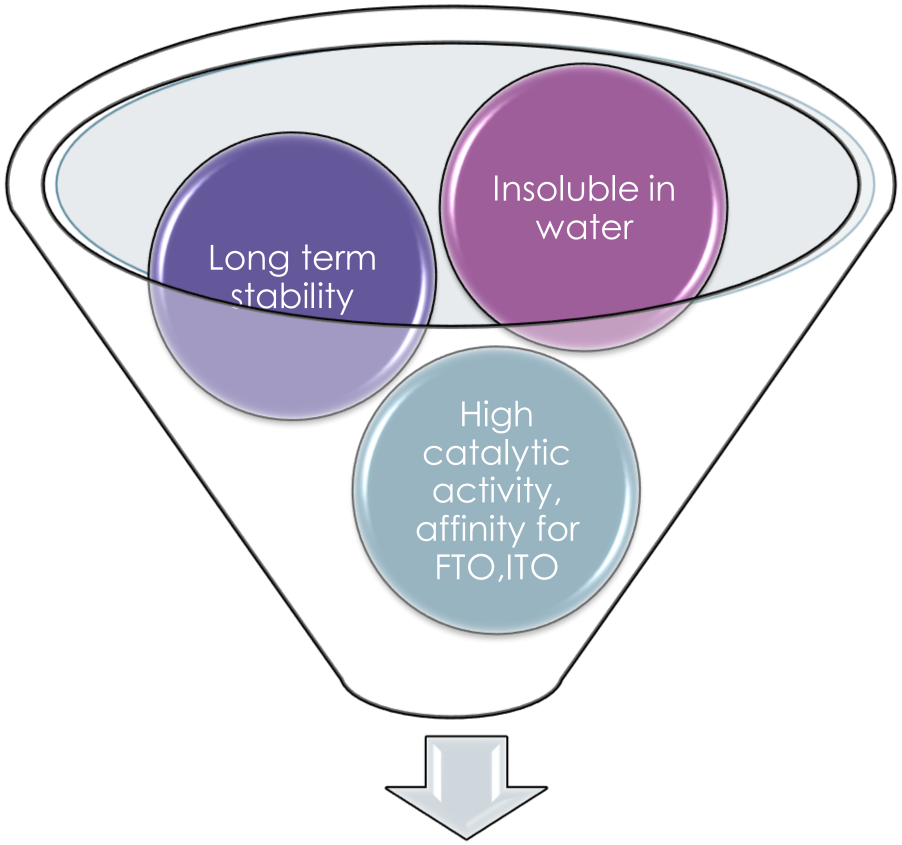
Catalysts are a very important component in efforts to design and develop efficient water splitting technologies.

Our efforts, like in many other research groups, is directed at the development of Molecular catalysts,

An **efficient** and **robust** catalyst for WO based on:

- ❑ abundant and cheap materials

the key to converting solar energy into fuels through artificial photosynthesis.



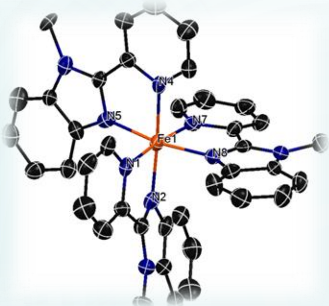
Applied in electrocatalytic Water Oxidation (WO)

1st publication Journal of Catalysis *open access* IF 7.888

Utilization of hydrophobic ligands for water-insoluble $Fe^{(II)}$ water oxidation catalysts – Immobilization and characterization

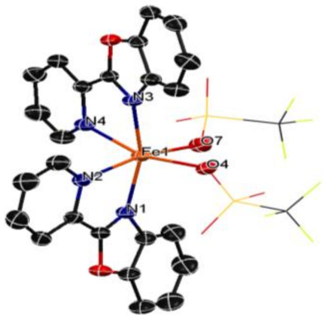
We Compared Two Fe^{II} complexes by electrochemical methods (homogeneous and heterogeneous conditions)

$Fe^{(II)}$(PBI)OTF



PBI

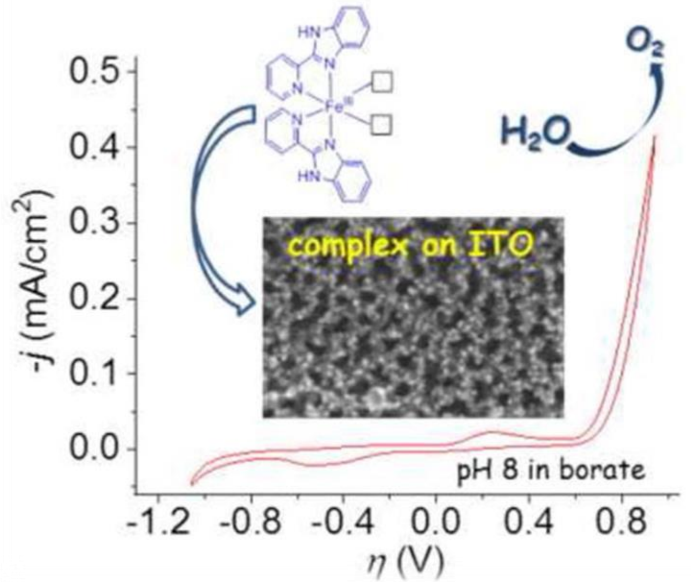
$Fe^{(II)}$(PBO)OTF



PBO

PBI ← drop-casting on ITO → PBO

Surface deposition



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

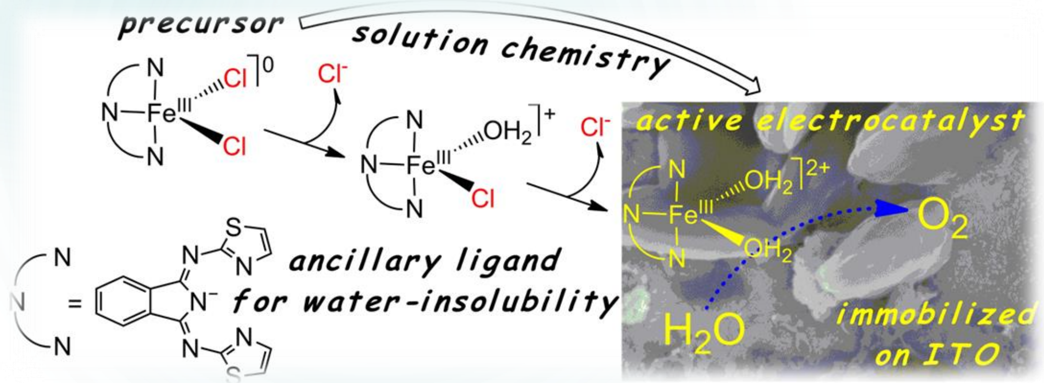
OTf = trifluoromethyl sulfonate anion

2nd publication reactions Journal open access

"An Iron(III) Complex with Pincer Ligand—Catalytic Water Oxidation through Controllable Ligand Exchange"

- *we successfully synthesized and investigated the electrochemical properties of the five-coordinate complex [$Fe^{III}Cl_2$(tia-ind)], as a potential pre-catalyst of water oxidation, in homogeneous water/acetone mixture to reveal the signatures of Cl^- to H_2O ligand exchange*

The five-coordinate complex [$Fe^{III}Cl_2$(tia-ind)]



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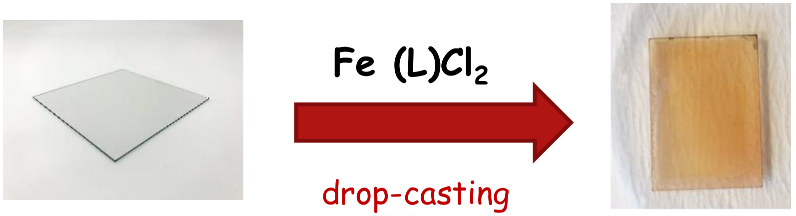
L, tia-ind = 1,3-bis(2'-thiazolylimino)isoindolinate(-)

- Immobilization of the complex from methanol on indium-tin-oxide (ITO) electrode by drop-casting resulted in water oxidation catalysis in borate buffer



ITO

3rd publication

in progress

catalysts Journal open access IF 3.520

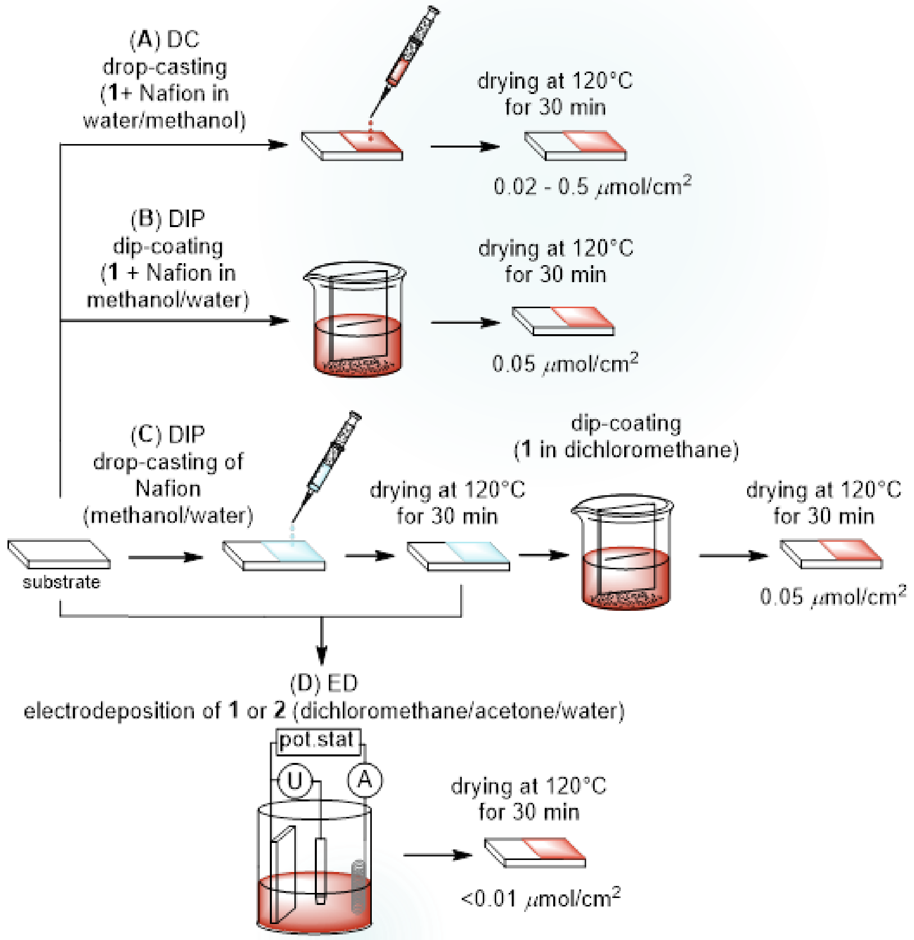
"Redox-Driven Electrodeposition of Fe-Complexes on Oxide Surfaces for Efficient OER Catalysis"

- We study the electrochemical properties of two $Fe^{(III)}$ complexes with NN'N pincer ligands in homogeneous water/Acetone/DCM mixture to reveal the signatures of Cl^- to H_2O ligand exchange

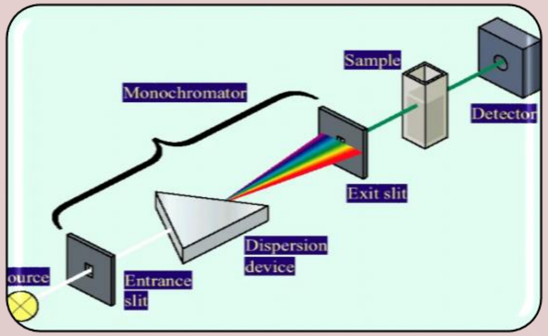
- strategies to enhance the performance of molecular catalysts: dip-coating, drop-casting, and electrodeposition, important for design for the immobilized catalyst exhibits much higher activity.

Electrodeposition: Simplicity, low cost, mild operating conditions, scalability.

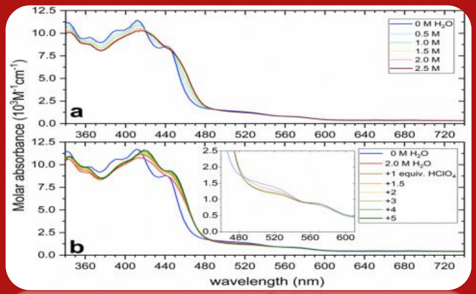
- two $Fe^{(III)}$ complexes that prepared with NN'N pincer ligands yielding by redox-driven electrodeposition (ED) of stable and active ad-layers for the electrocatalysis of the oxygen evolving reaction (OER).



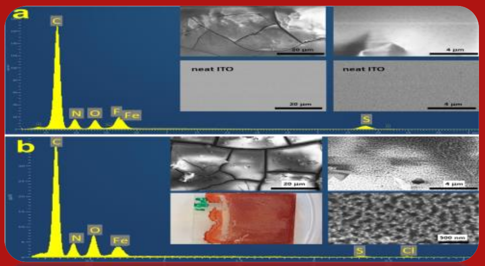
Different characteristics techniques have been used to the investigation of the complex/ITO or FTO assembly before and after catalysis that suggested that a molecular form of catalyst is responsible for water oxidation.



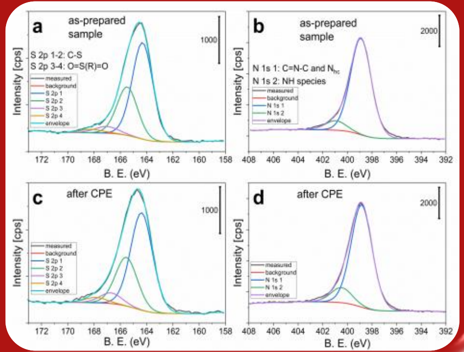
Uv-vis spectrophotometer



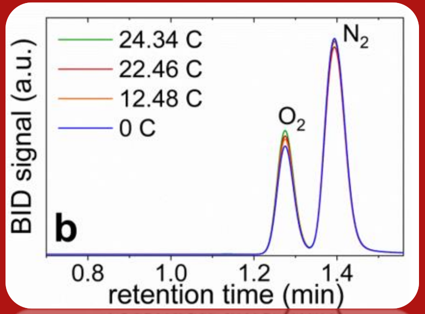
SEM & EDX



Xray photoelectron spectroscopy (XPS)



Gas Chromatography (GC) to detect Oxygen evolution



thesis points based on publications

1st & 2nd publications

- The water-insolubility of the complexes seems to be a viable strategy for the design of new molecular catalyst/(photo)anode hybrids. Hydrophobic ligands can aid the immobilization of the molecular architecture of catalysts designed to fabricate hybrid (photo)electrodes may have two-way effect, i.e., control of the complex stability in the course of catalysis and its strong attachment to the surface by secondary interactions.

1st & 2nd publications

- Ligand exchange reaction allows for the active form of the molecular catalyst methanol that promotes ligand exchange the selection of the solvent for drop-casting is of key importance to gain an active heterogenized WOC.

1st publication

- The non-coordinated heteroatoms in a heterocyclic ligand can induce fundamental changes in the redox behavior both in the homogeneous water/acetonitrile phase and when the complexes are deposited to the electrode and tested as water oxidation catalysts. The heteroatom should be sufficiently electron donating in order to support the high oxidation state intermediates occurring in the course of catalysis, otherwise the molecular units become prone to oxidative degradation and mineralization.

thesis points.....

1st & 2nd publications

- No anchoring additive is needed, hybrid systems that are efficient in water oxidation electrocatalysis can be fabricated by the scalable and simple drop-casting method.

2nd publication

- NN'N pincer ligands seem to play a role in generating the proposed active form in WNA, $[Fe^{IV}(O)(H_2O)(tia\text{-}BAI\bullet)]^{2+}$ and it also possesses available sites for proton channeling in the course of further reaction steps.

3rd publication

- The surface modification by Electrodeposition (ED) compared to other methods to fabricate ad-layers, including dip-coating, drop-casting is considered material saving and provides more efficient OER catalysis.

Thank you!