Óbuda University, Doctoral School on Material Science and Technology

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

8th semester

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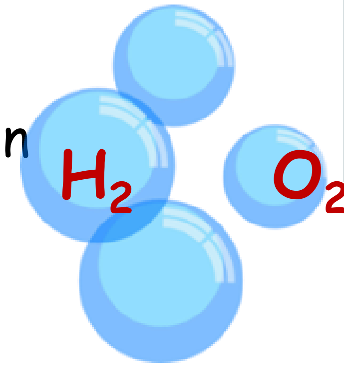
CENTRE FOR ENERGY RESEARCH
HUNGARIAN ACADEMY OF SCIENCES

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

- 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
- CO2 emission

Environ

- Air pollution
- Green house

Fossil Fuels being depleted, effect climate, CO_2

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

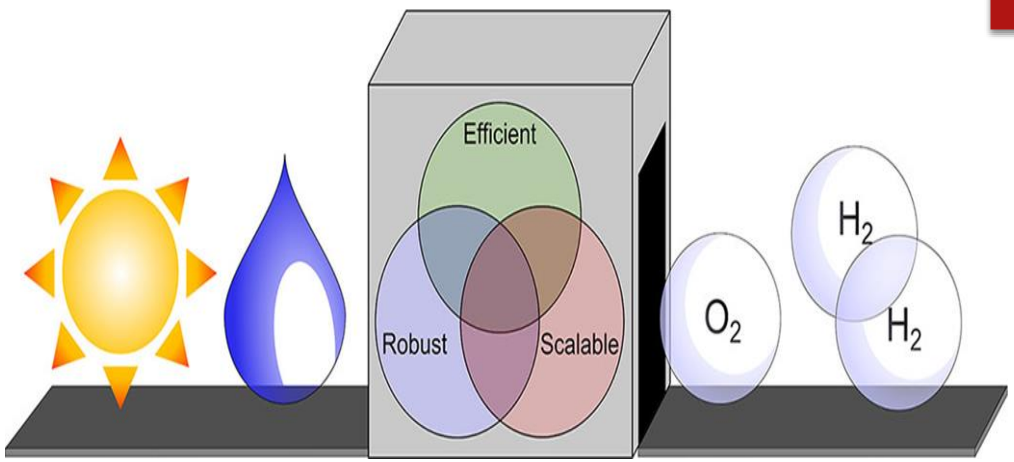
Solar cells only generating during day.

Hydrogen by Photoelectrochemical cells (PEC)

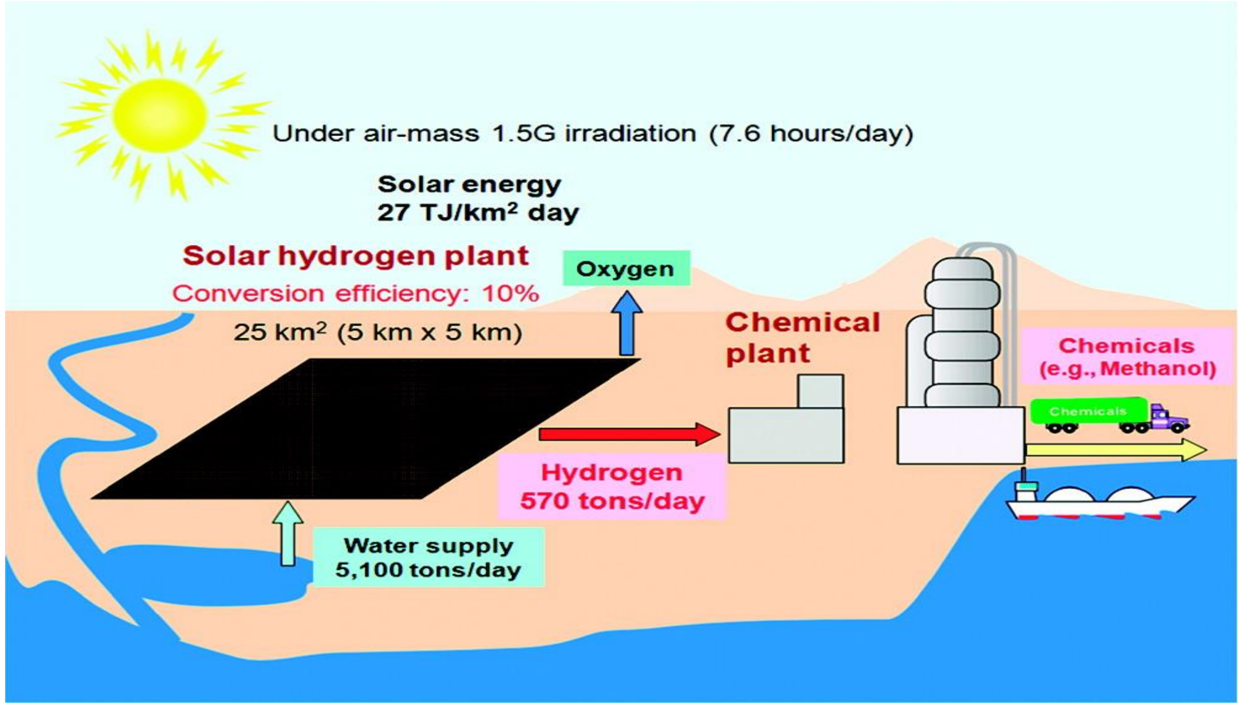
Solar to Chemical Energy-Fuel (STF)

How can achieve STF by water splitting?

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



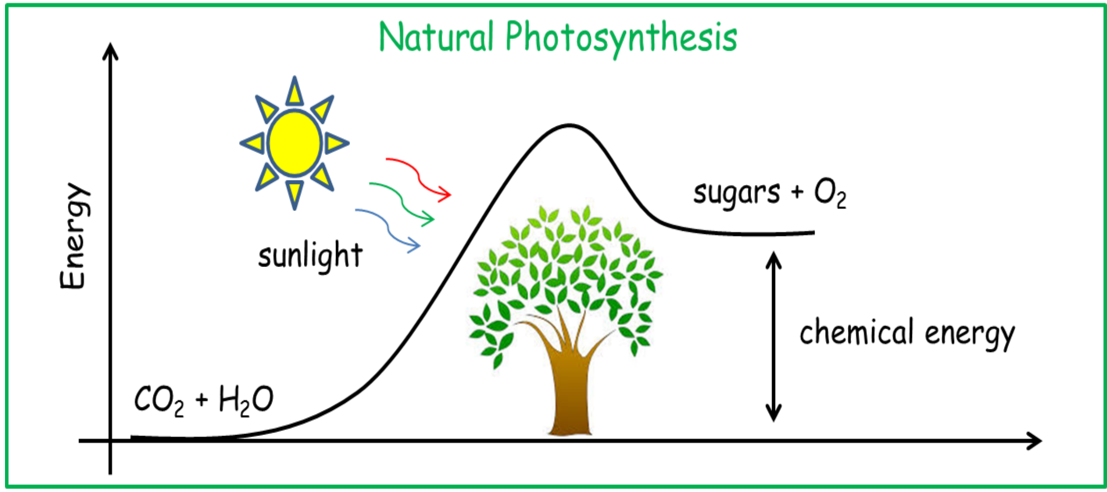
Scheme shows the possible large-scale H_2 production via solar water splitting.



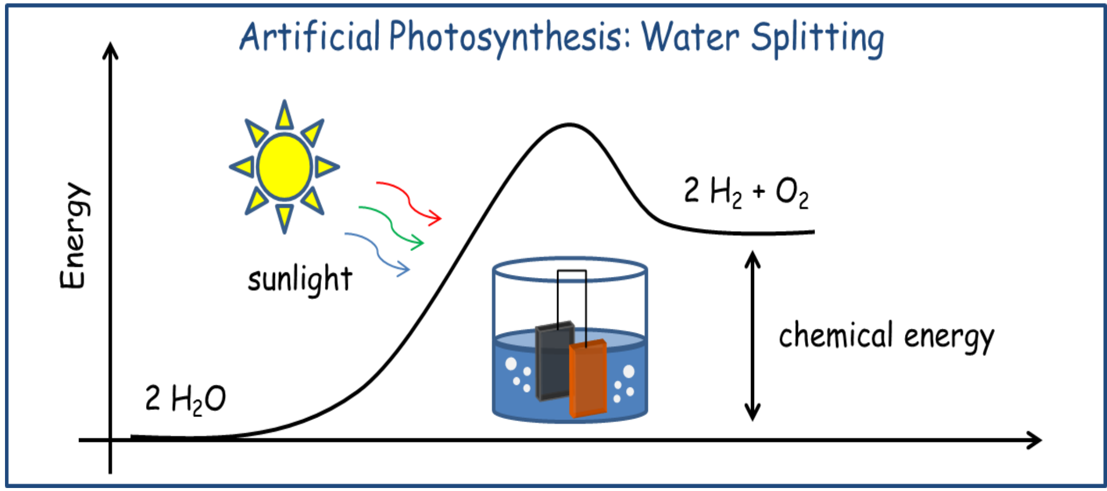
J. Phys. Chem. Lett. 2010, 1, 18, 2655–2661, *Chem. Mater.* 2014, 26, 1, 407–414

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

Electrochemical Water splitting

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

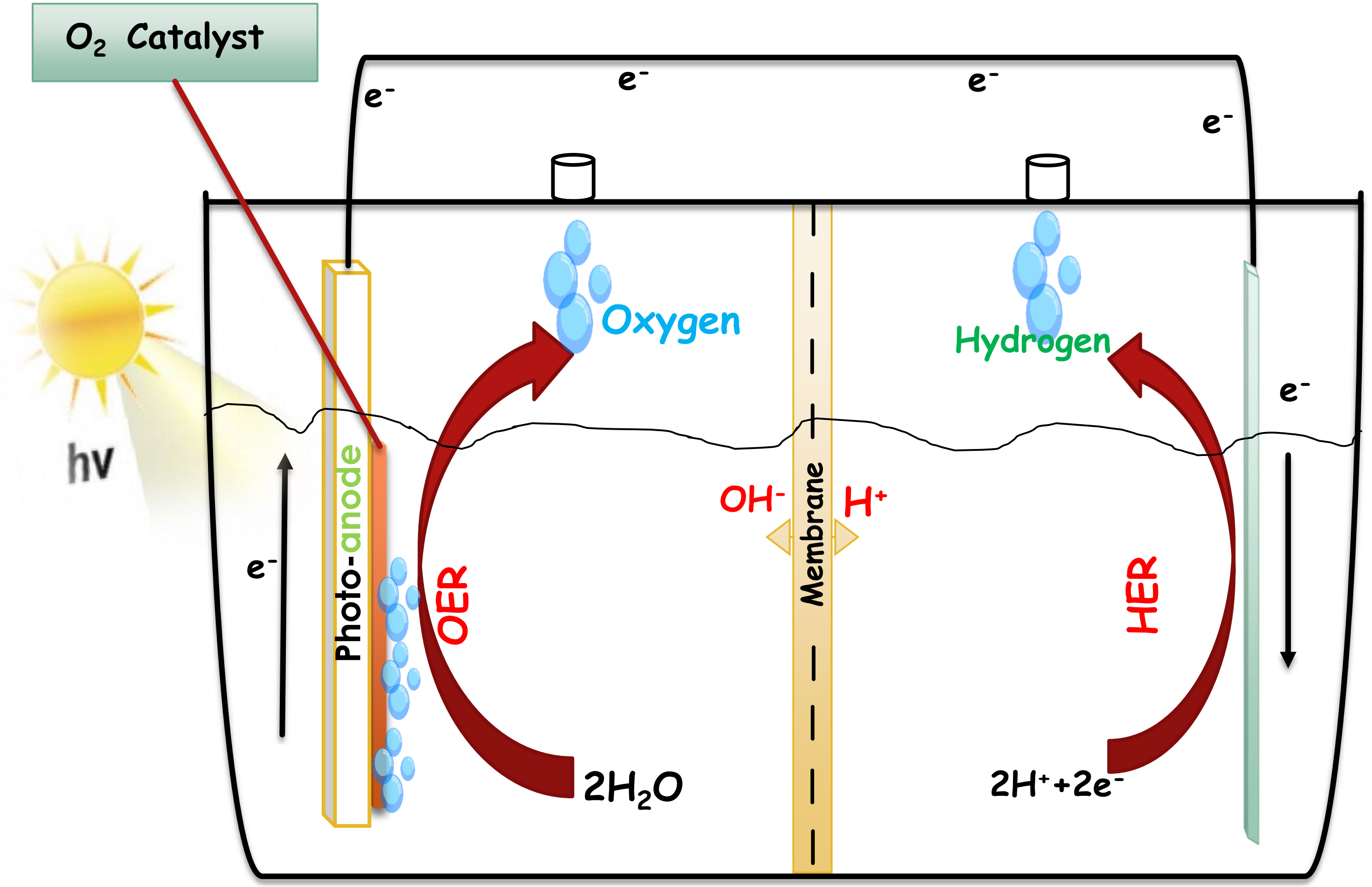


Figure: An illustration of a type of PEC device

objectives

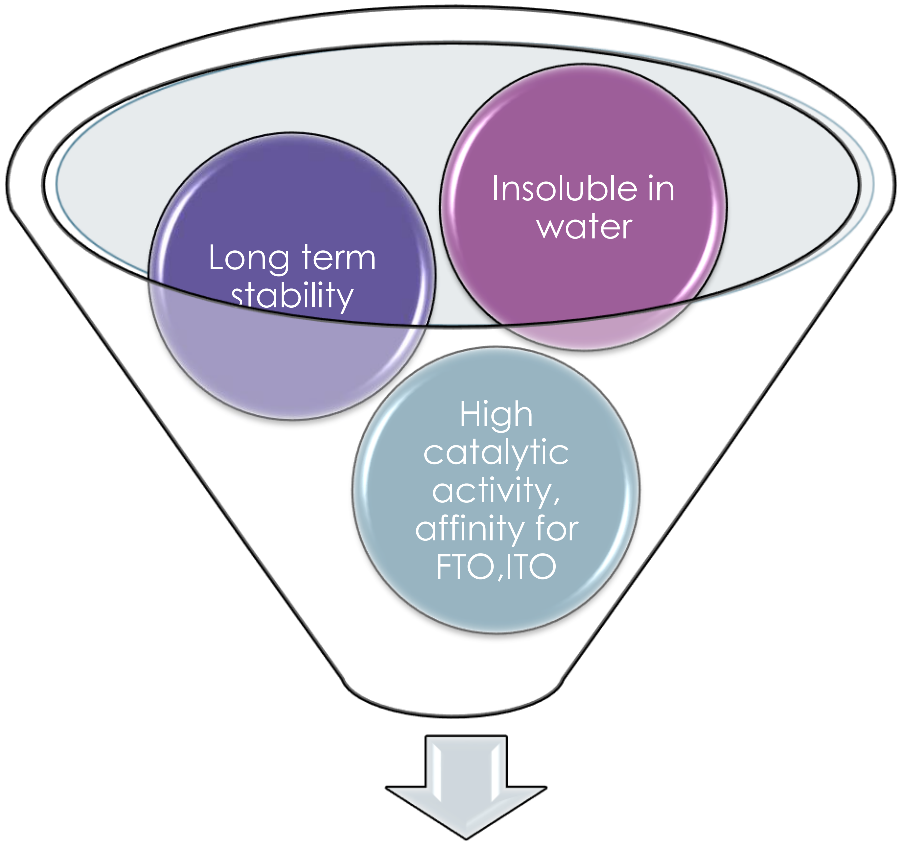
Catalysts are a very important component in efforts to design and develop efficient water splitting technologies.

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.



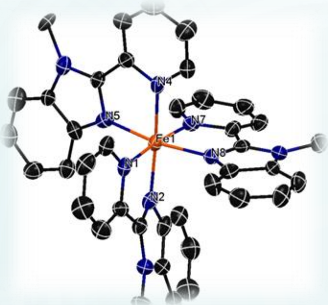
Applied in electrocatalytic
Water Oxidation (WO)

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

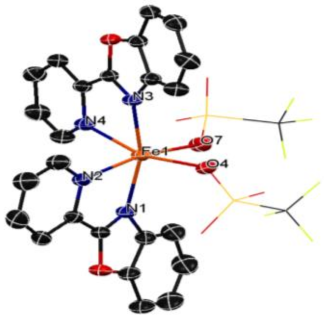
We Compared Two Fe^{II} complexes by electrochemical methods (homogeneous and heterogeneous conditions)

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

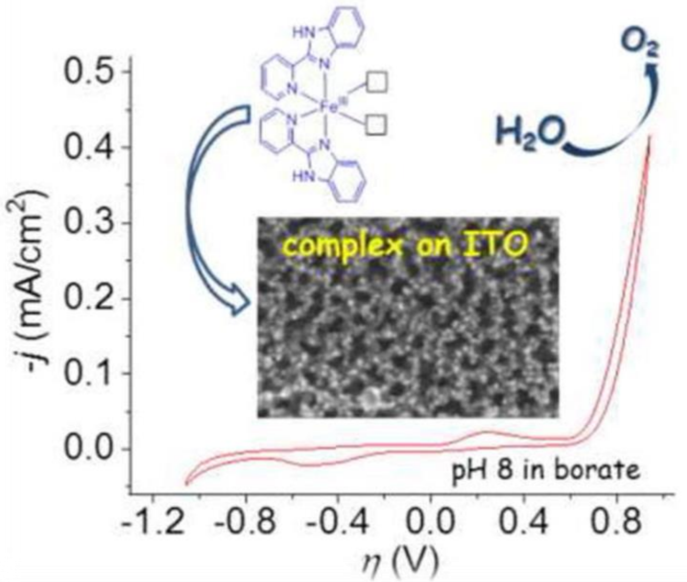


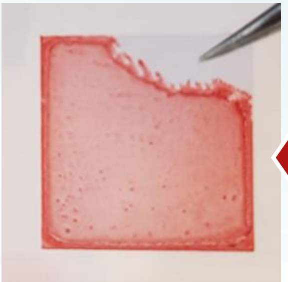
PBI

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



PBO





PBI ← drop-casting on ITO → PBO

Surface deposition

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

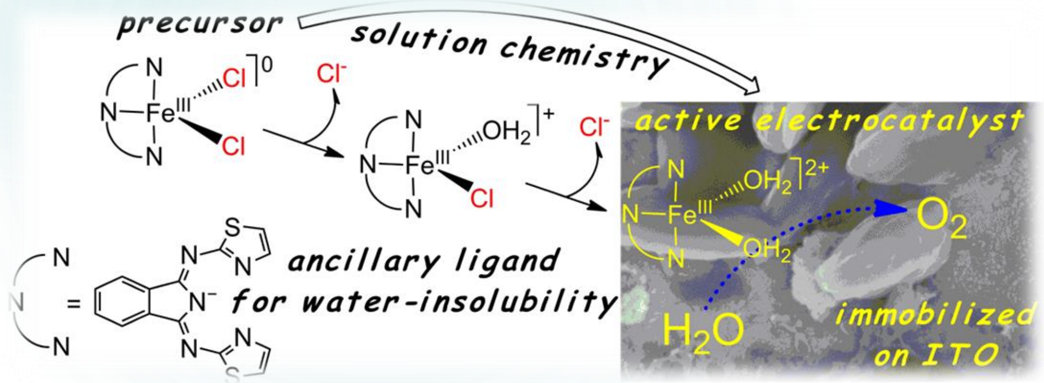
OTf = trifluoromethyl sulfonate anion

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*

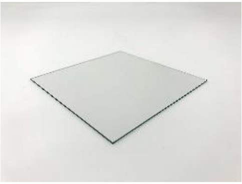
The five-coordinate complex [$Fe^{III}Cl_2$(tia-ind)]



TON > 193

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

Fe (L)Cl_2

drop-casting

^{3rd} publication

catalysts Journal open access IF 3.520

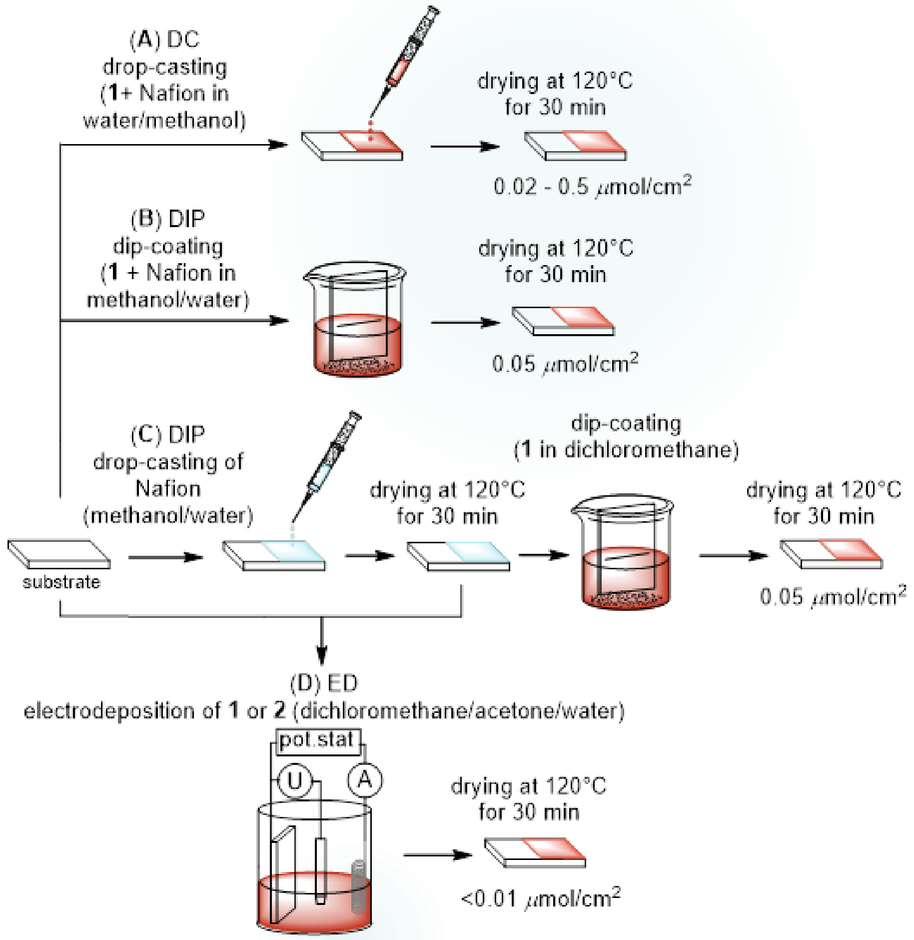
"Redox-Driven Electrodeposition of Fe-Complexes on Oxide Surfaces for Efficient OER Catalysis"

- 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.

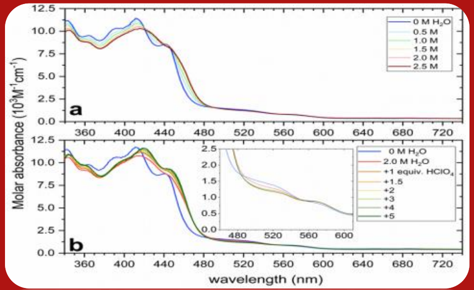
Electrodeposition: Simplicity, low cost, mild operating conditions, scalability

- 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).

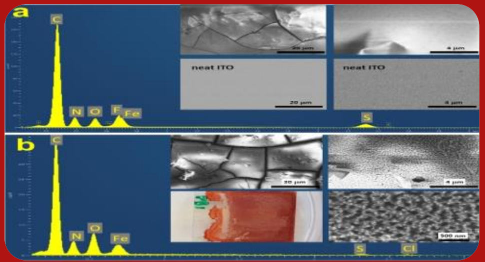


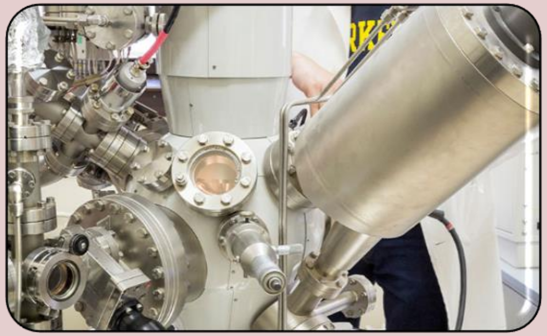
Different characteristics techniques have been used to The investigation of the complex/ITO or FTO assembly before and after catalysis that suggested that a molecular form of catalyst is responsible for water oxidation.

Uv-vis spectrophometer

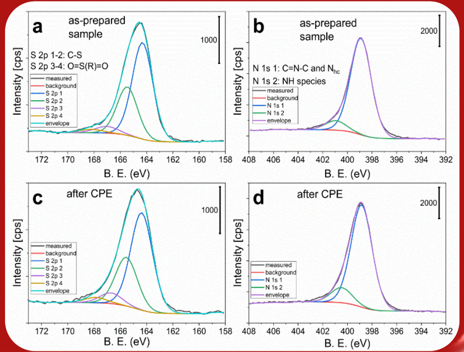


SEM & EDX

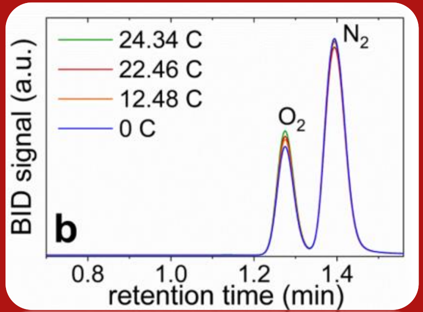




Xray photoelectron spectroscopy (XPS)



Gas Chromatography (GC) to detect Oxygen evolution



thesis points based on 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).

- 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.

- 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.

- 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.

- 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!