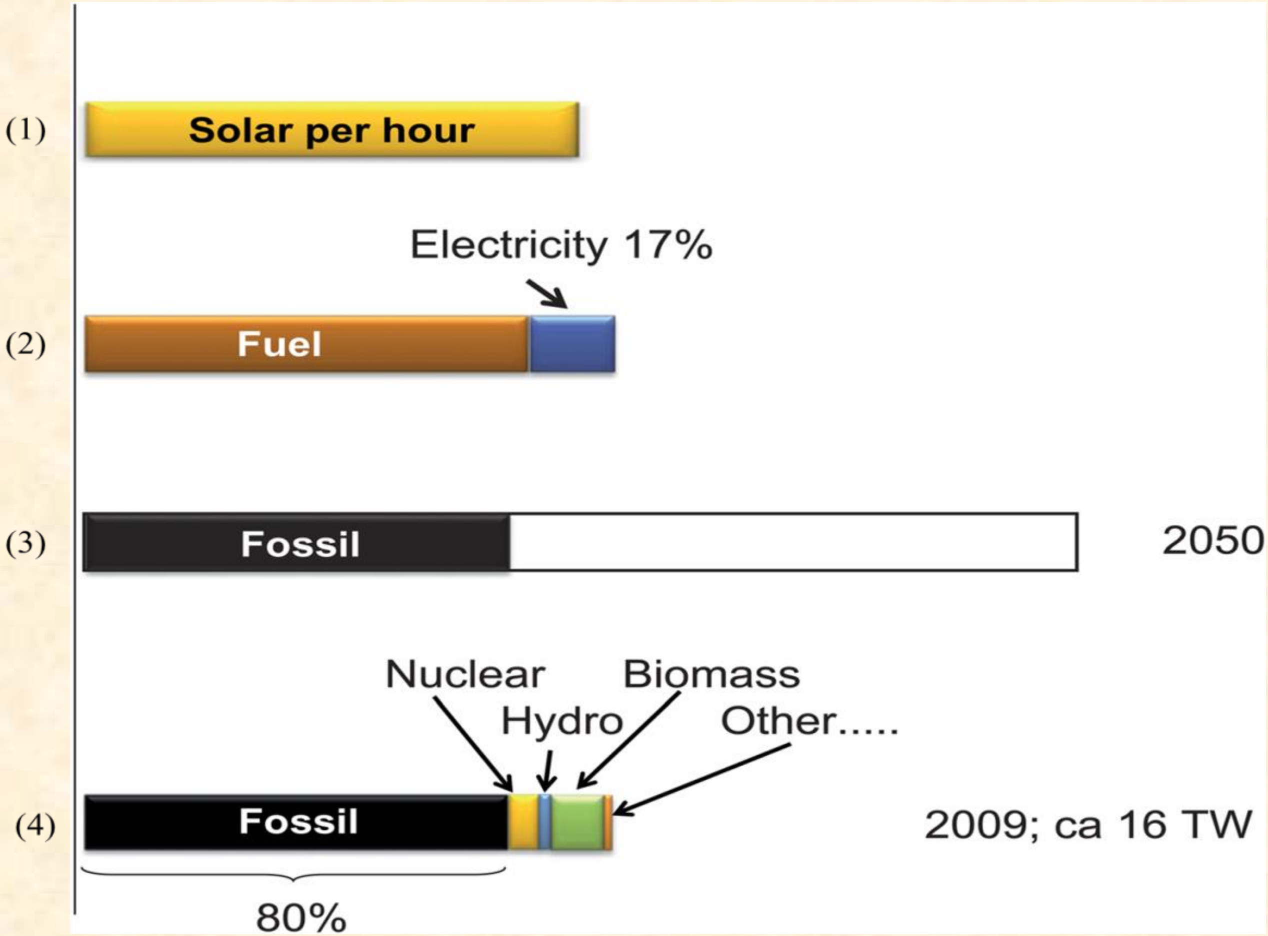

بسم الله الرحمن الرحیم

Nano Mn-Ca oxide surrounded by polypeptides as a biomimetic catalyst for water-splitting systems

Introduction

Total amount of energy used in the world



S. Styring, Faraday discussions, 155 (2012) 357-376

Fossil Fuel

Energy Crisis

Climate Change

CO_2 Production

Global Warming

Hydrogen Fuel

Significant Properties of Hydrogen:

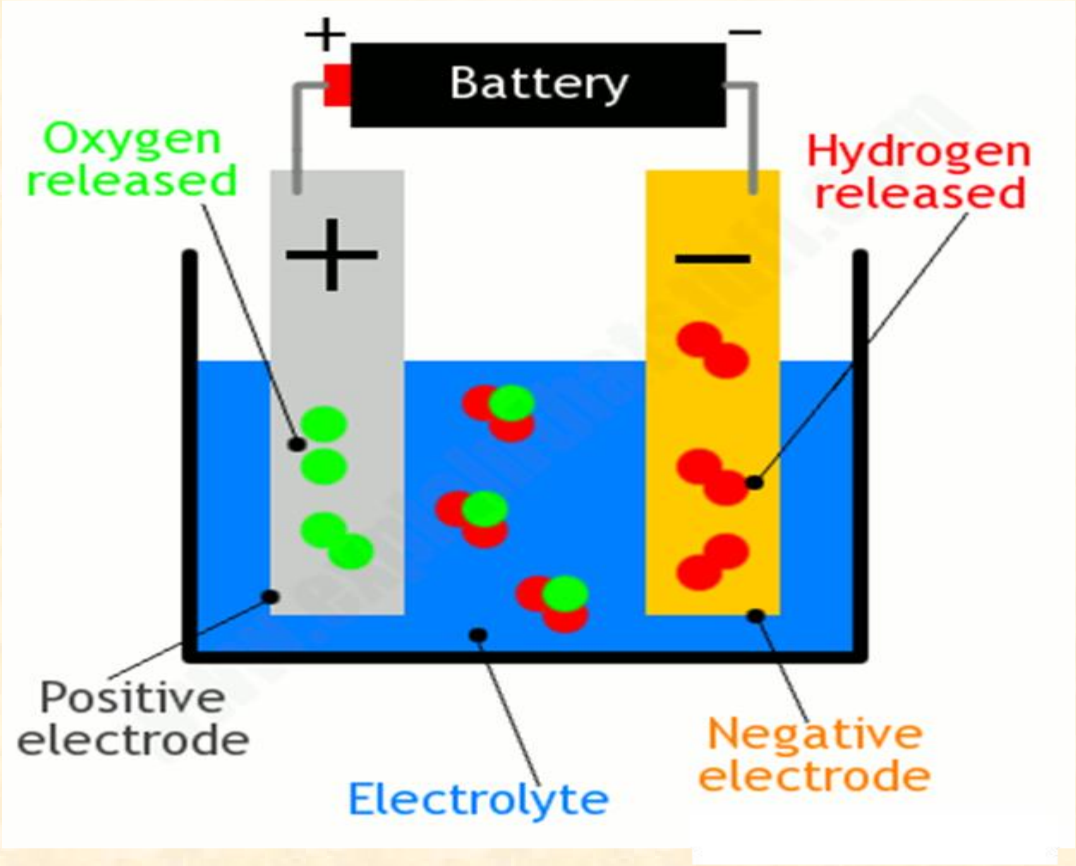
Transportable
High efficient
Safe

Hydrogen Production:

Catalytic conversion of light hydrocarbons
Thermal decomposition of water
Photo decomposition of water
Water electrolysis

A. Ursu´a et.al, Proceedings of the IEEE, 100 (2012) 410-426

Water electrolysis



$$O_2 + 4e^- + 4H^+ \leftrightarrow 2H_2O \qquad E_{anodic} = 1.23\ V - 0.059\ (pH)\ V\ (NHE)$$

$$4e^- + 4H^+ \leftrightarrow 2H_2 \qquad E_{cathodic} = 0\ V - 0.059\ (pH)\ V\ (NHE)$$

D. Nocera et.al, Progress in Inorganic Chemistry, 57 (2012) 505-560

Water electrolysis

Electrochemistry

It is caused first by the resistance of several cell elements to the electrons flow. They are also consequence of the opposition to the ions flow.

Concentration overvoltage, is caused by mass transport processes (convection and diffusion).

1.23 V

$$V_{\mathrm{cell}} = V_{\mathrm{rev}} + V_{\mathrm{ohm}} + V_{\mathrm{act}} + V_{\mathrm{con}}$$

1.5-1.8 V

$$\eta_{\mathrm{a}} + |\eta_{\mathrm{c}}|$$

Decrease of anodic overvoltage:
Using Catalyst

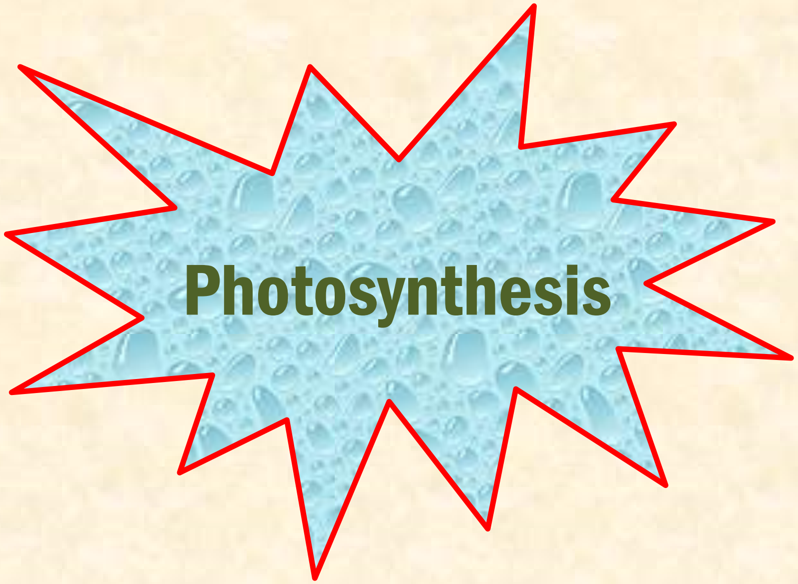
Activation overvoltage, is due to electrode kinetics. The charge transfer between the chemical species and the electrodes demands energy.

D. Nocera et.al, Progress in Inorganic Chemistry, 57 (2012) 505-560
A. Ursu´a et.al, Proceedings of the IEEE, 100 (2012) 410-426

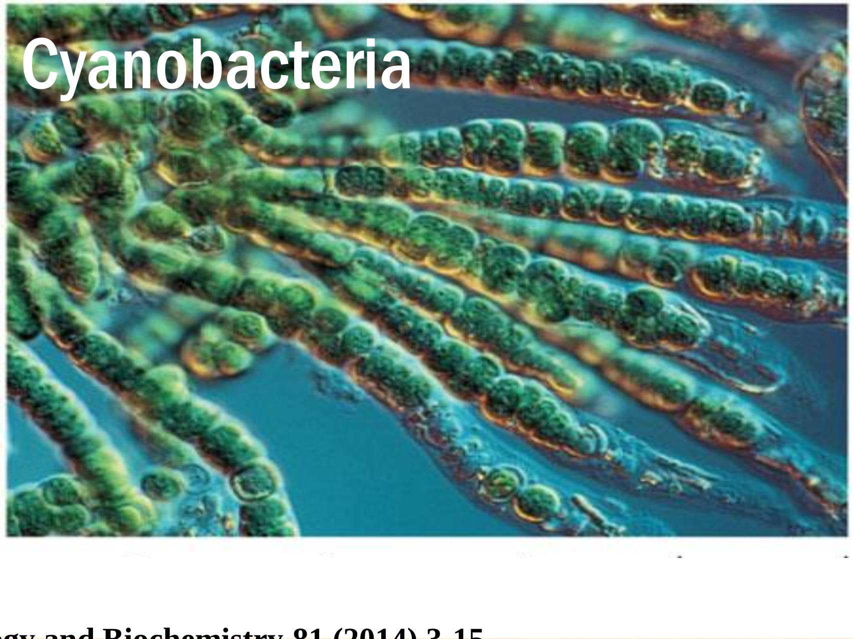
Water electrolysis
Main drawbacks

1. Need to high overvoltage for water oxidation half-reaction.

2. Interfere of other ions like chloride.

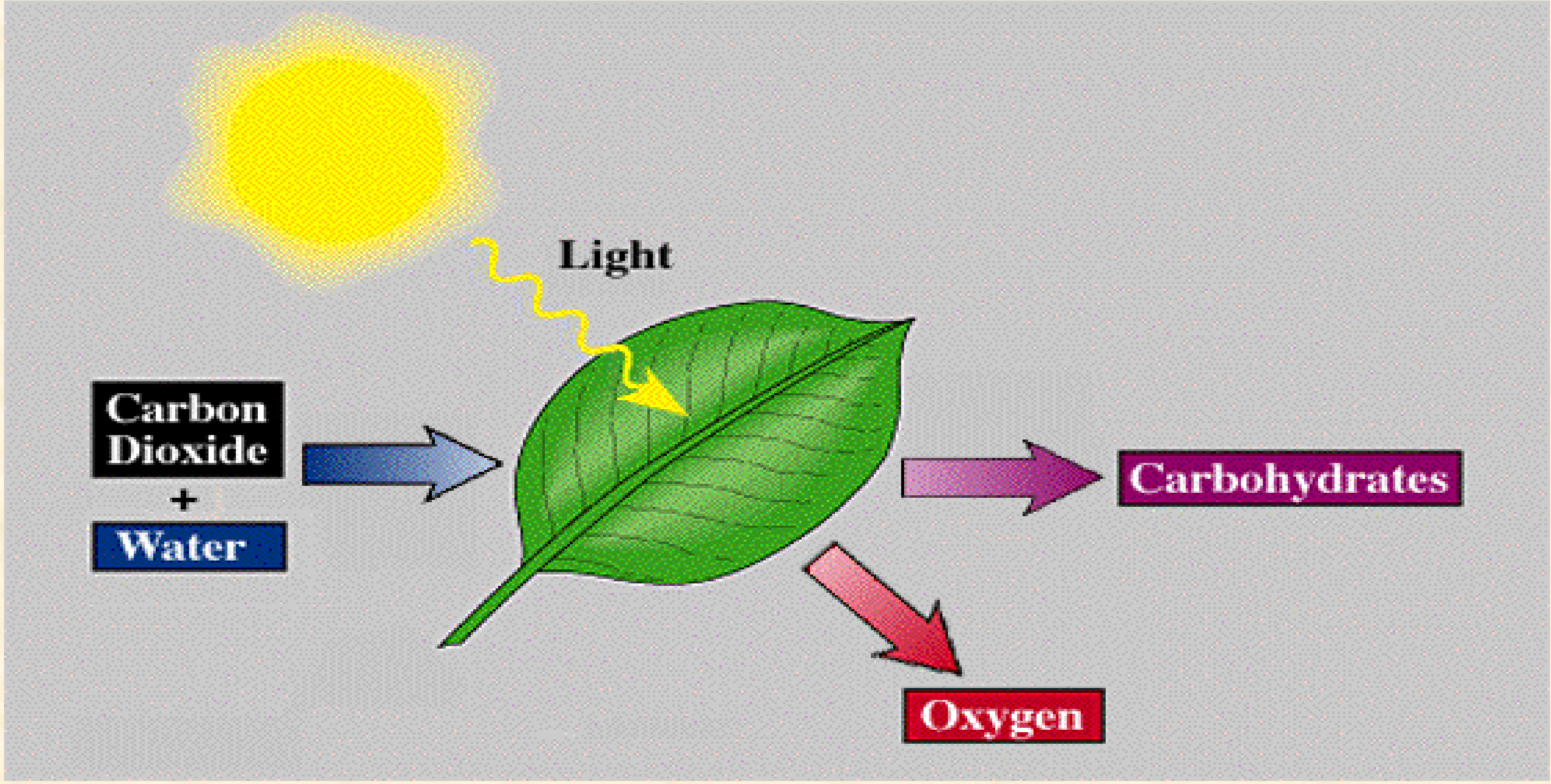


Photosynthesis



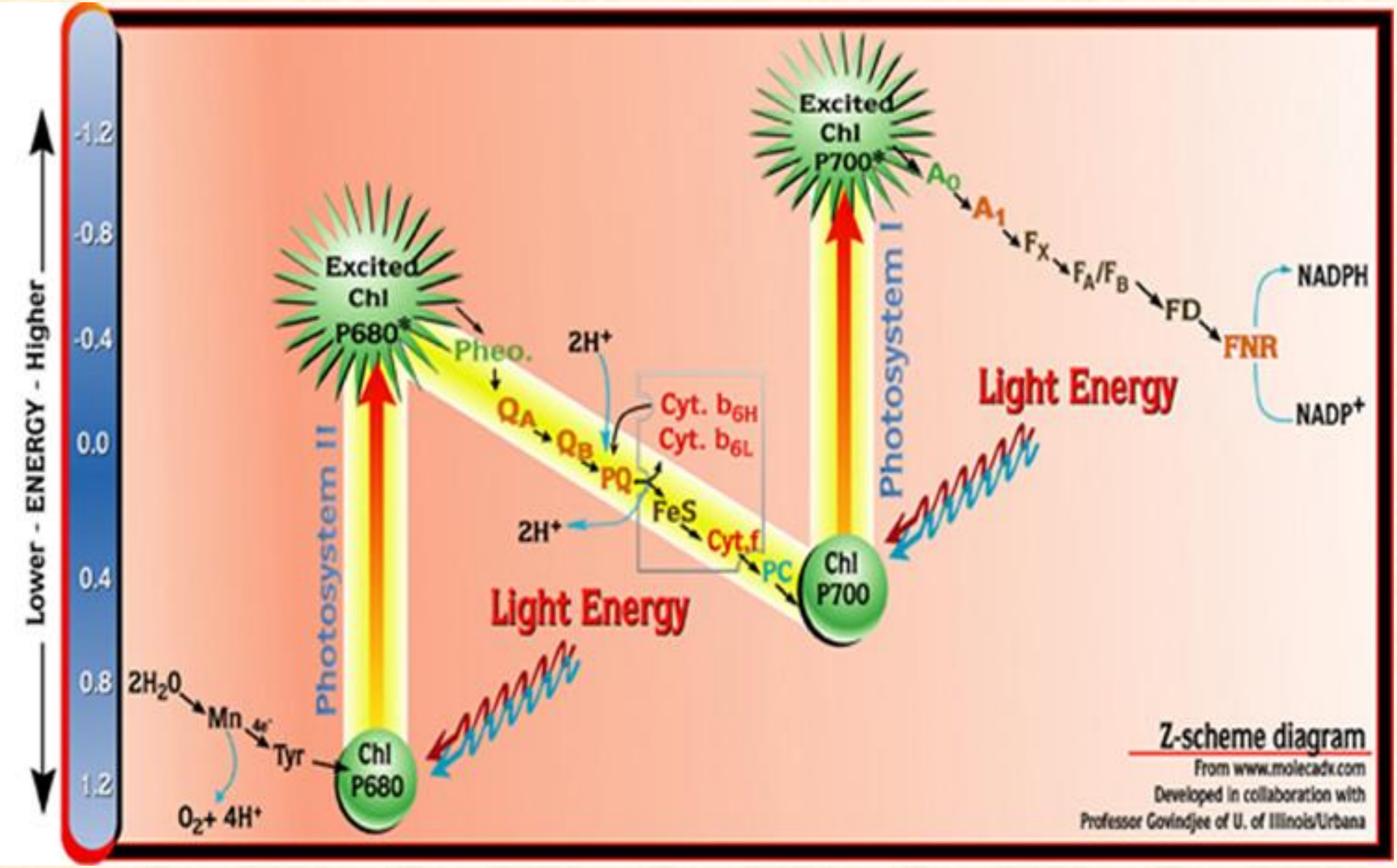
M. M. Najafpour, et al., Plant Physiology and Biochemistry 81 (2014) 3-15

Photosynthesis



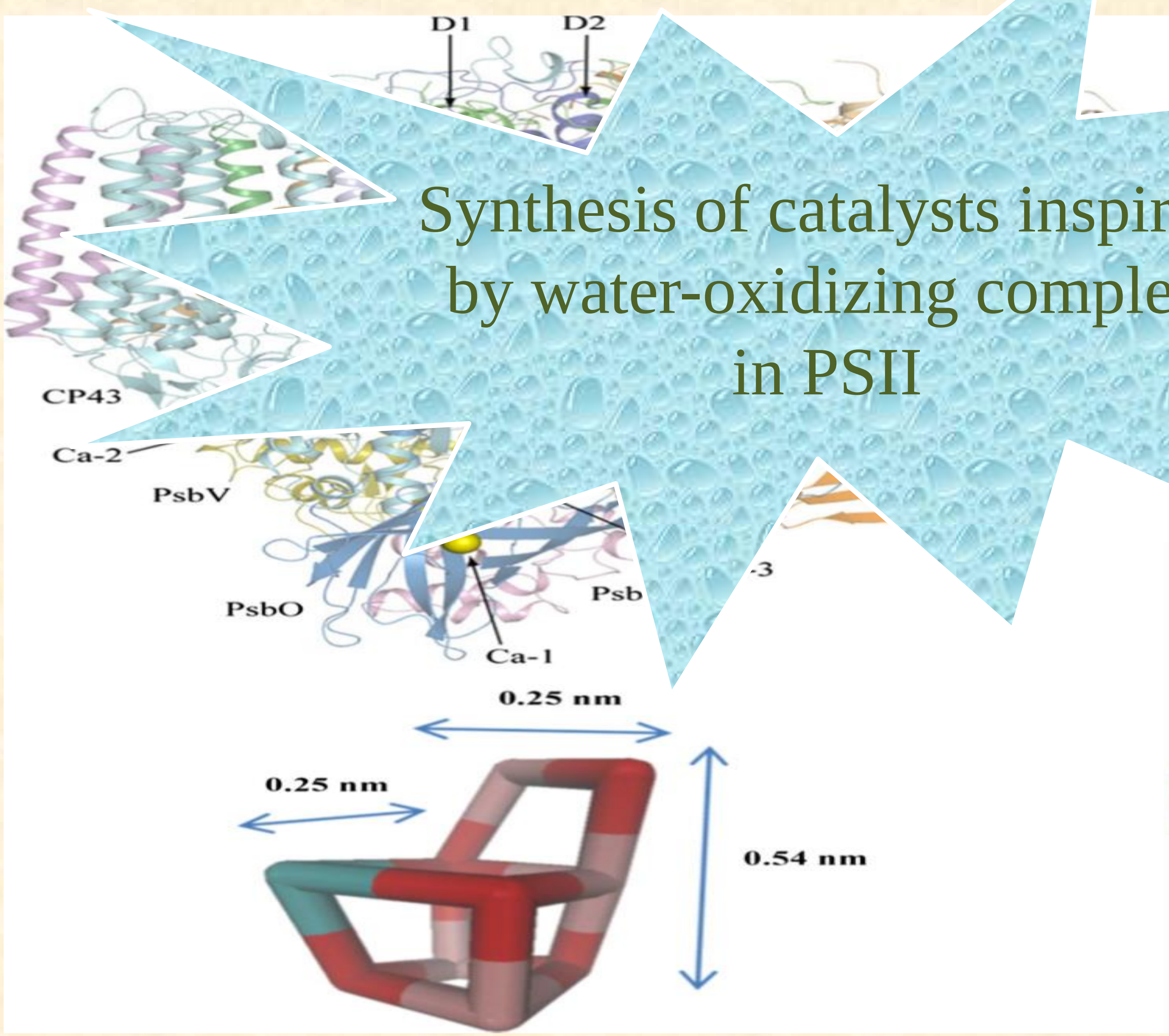
Photosynthesis

Photosystem I, II

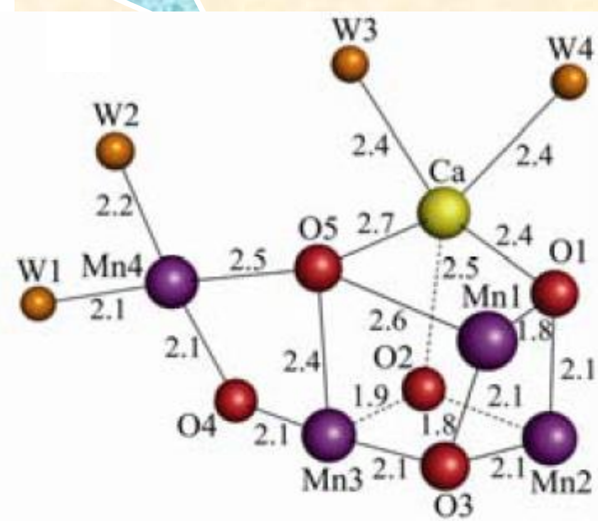


Photosystem II (PSII)

Mn_4CaO_5 Cluster



Synthesis of catalysts inspired by water-oxidizing complex in PSII



Shen et al. Nature, 473 (2011) 55-60.

Artificial water-oxidizing catalysts

Ru, Ni, Pt, Au, Ag, Pd, Re, Co, Fe, Ir, Cu,

Mn

Mn Oxide

Mn Complex

M. M. Najafpour et al. Biochimica et Biophysica Acta (BBA)Bioenergetics, 1847 (2015) 294-306

Experimental Design for Evaluating Water Oxidation Catalysts

Chemical Oxidants: Ceric ammonium nitrate, sodium periodate, Tris(bipyridine)ruthenium(II), potassium peroxymonosulfate

Photochemical water Oxidation

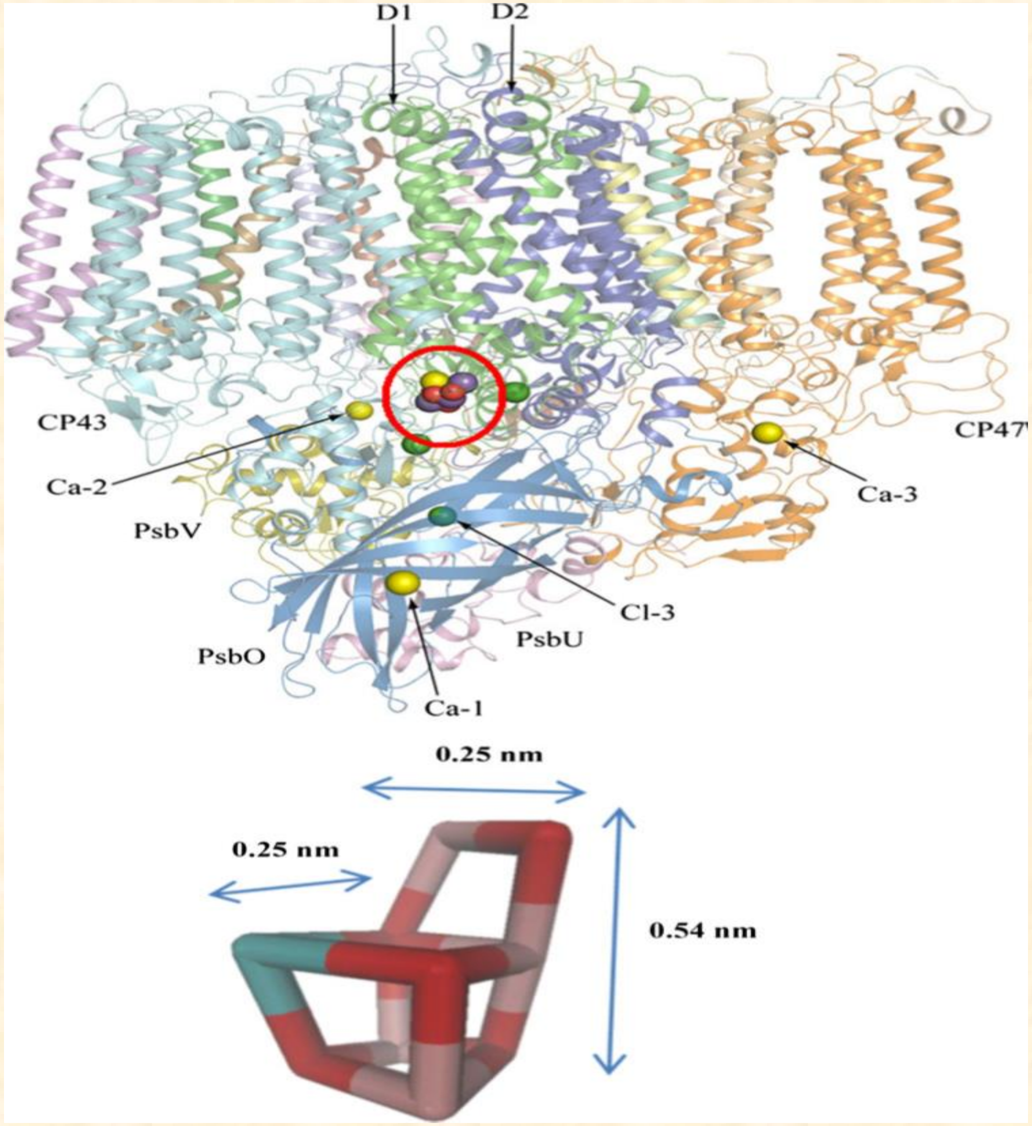
Electrochemical water Oxidation

M. D. Kärkäs et al. Chem. Rev, 114 (2014) 11863-12001

Our work


IF GLOBAL WARMING CONTINUES THEN.....
MAJOR CITIES WILL SUFFER THE FATE OF ATLANTIS
CORAL REEF WILL BE WIPED OFF VERY SOON

Photosystem II (PSII)



Roles for the residues that come in contact directly with the Mn-Ca cluster include regulation of charges and electrochemistry of the Mn-Ca cluster, and help in coordinating water molecules at appropriate metal sites and stability of the cluster.

Shen et al., Nature, 473 (2011) 55-60

Important parameters for synthesis new manganese oxide-based catalysts for water oxidation

(i) A mean oxidation state of Mn between +3 and +4.

(ii) A layered-oxide structure of low order with extensive di-μ-oxo bridge between Mn ions.

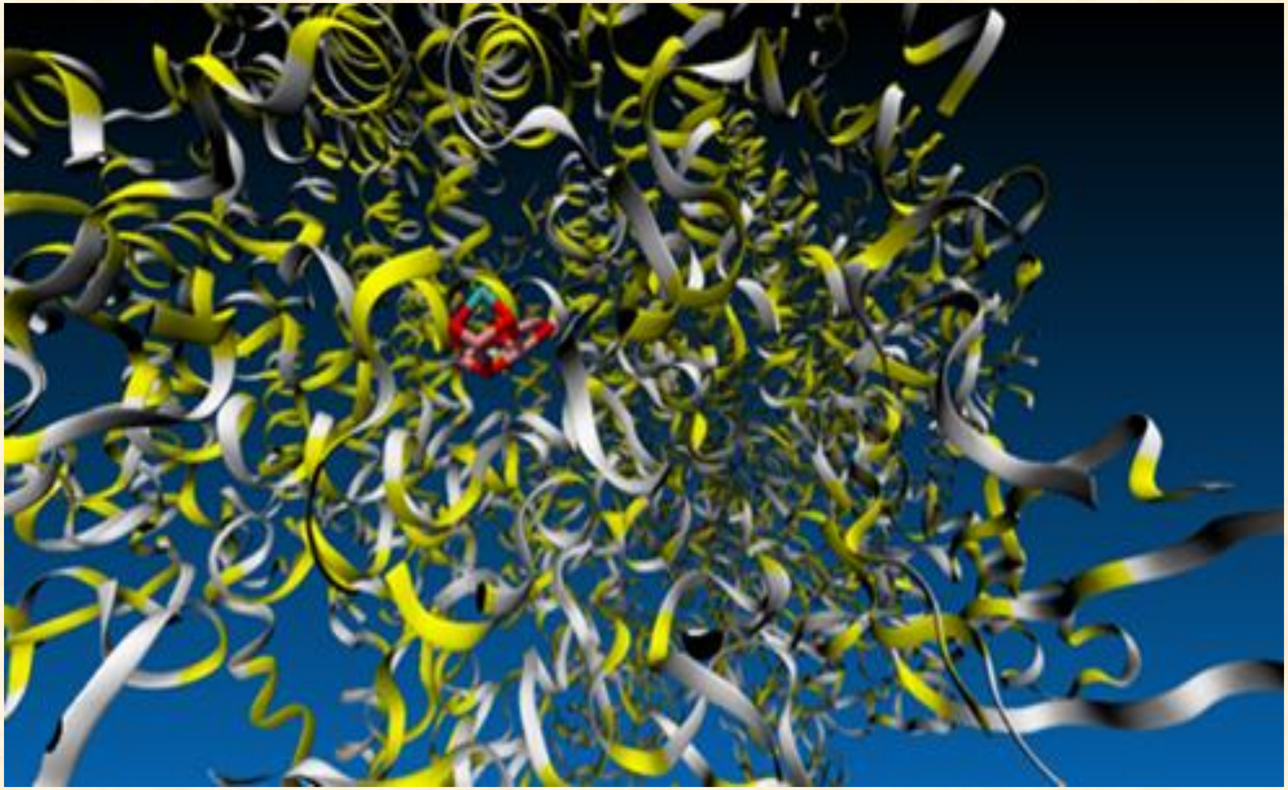
(iii) Presence of redox- inactive cations that are linked to Mn ions by μ-oxo bridges.

Mn(III,IV) >Mn(III) >Mn(IV), Mn(II) and Mn(II,III)

H. Dau et al., Energy Environ. Sci., 4 (2011) 2400-2408
H. Dau et al., Energy Environ. Sci., 5 (2012) 7081-7089
M. M. Najafpour et al., Biochimica et Biophysica Acta (BBA)Bioenergetics, 1847 (2015) 294-306

Synthesis of new manganese-based catalyst in protein environment

Direct:
Carboxylate
Imidazole



Hydrophilic (white) and hydrophobic (yellow) residues around Mn-Ca cluster.

Indirect:
D1-Asp61
D1-His33
CP43-Arg357

Role: Stability of Mn cluster, proton, water or oxygen transfer.

Layered $MnCaO_x$ surrounded by engineered poly peptide matrix

Glu-Glu-Glu-Glu-Glu-Glu-Glu-His-Val-Val-Val-Val-Val-Val-Val-Val(G_7HV_8).

- **The hydrophobic property of valine helps to peptide insolubility in water that is necessary to use the compound as heterogeneous catalyst.**
- **This bulky groups cause inhibit from leaking from the surface of oxide to solution.**
- **The protein is stable in the presence of potential needs for water oxidation.**
- **The carboxylate and imidazole groups stabilize Mn(III).**

Synthesis of MnCaOx-G_7HV_8

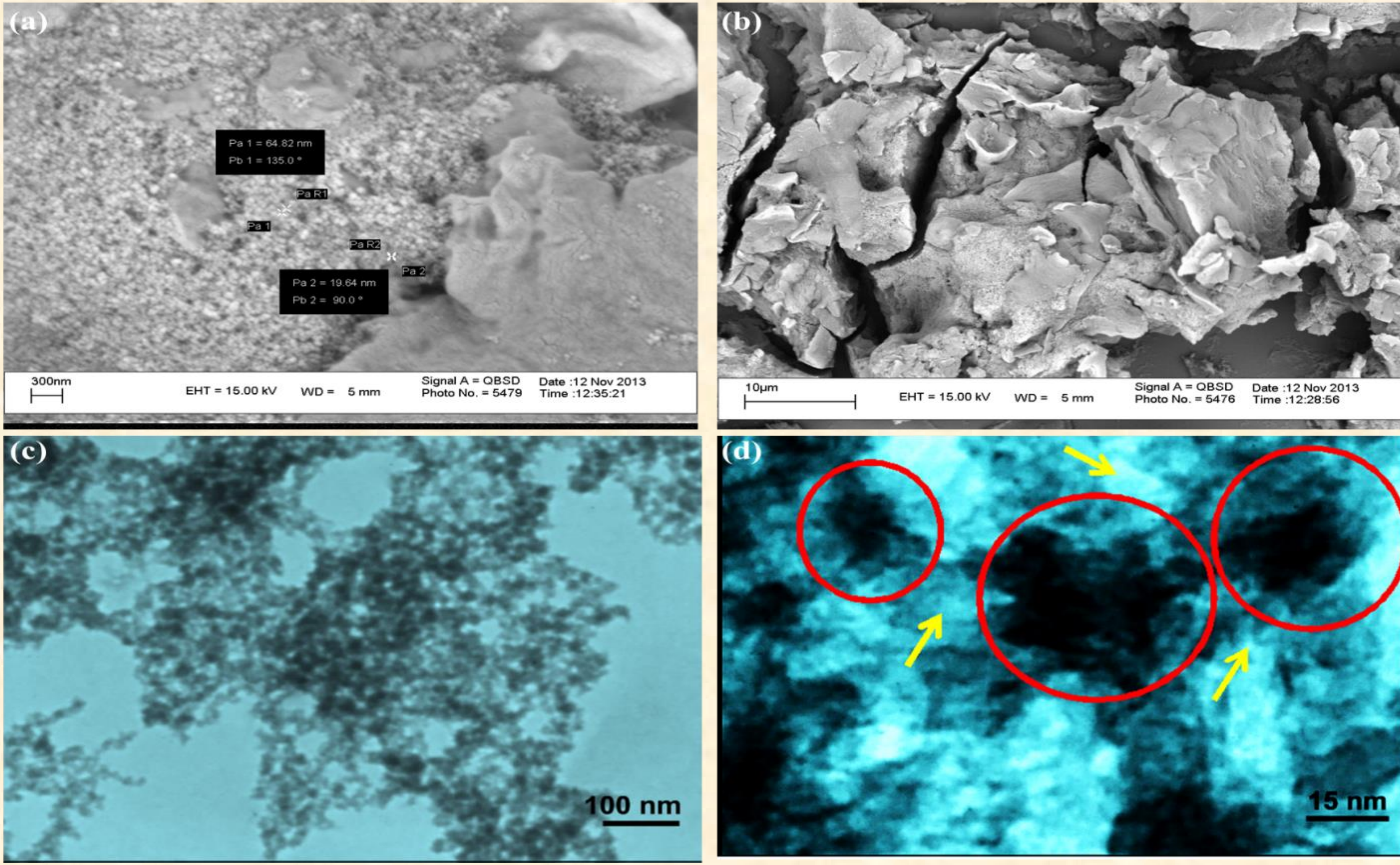
Glu-Glu-Glu-Glu-Glu-Glu-Glu-His-Val-Val-Val-Val-Val-Val-Val-Val(G_7HV_8).

To the engineered polypeptide (25 mg) in water (10 mL), $Mn(OAc)_2.4H_2O$ (6 mg) and $Ca(NO_3)_2$ (3 mg) were added and stirred for 1 h. Then, a solution of $KMnO_4$ (1.8 mg) in water (2 mL) containing $Ca(OH)_2$ (pH = 9) was added at 4 ^oC and stirred for 30 minutes.

Results

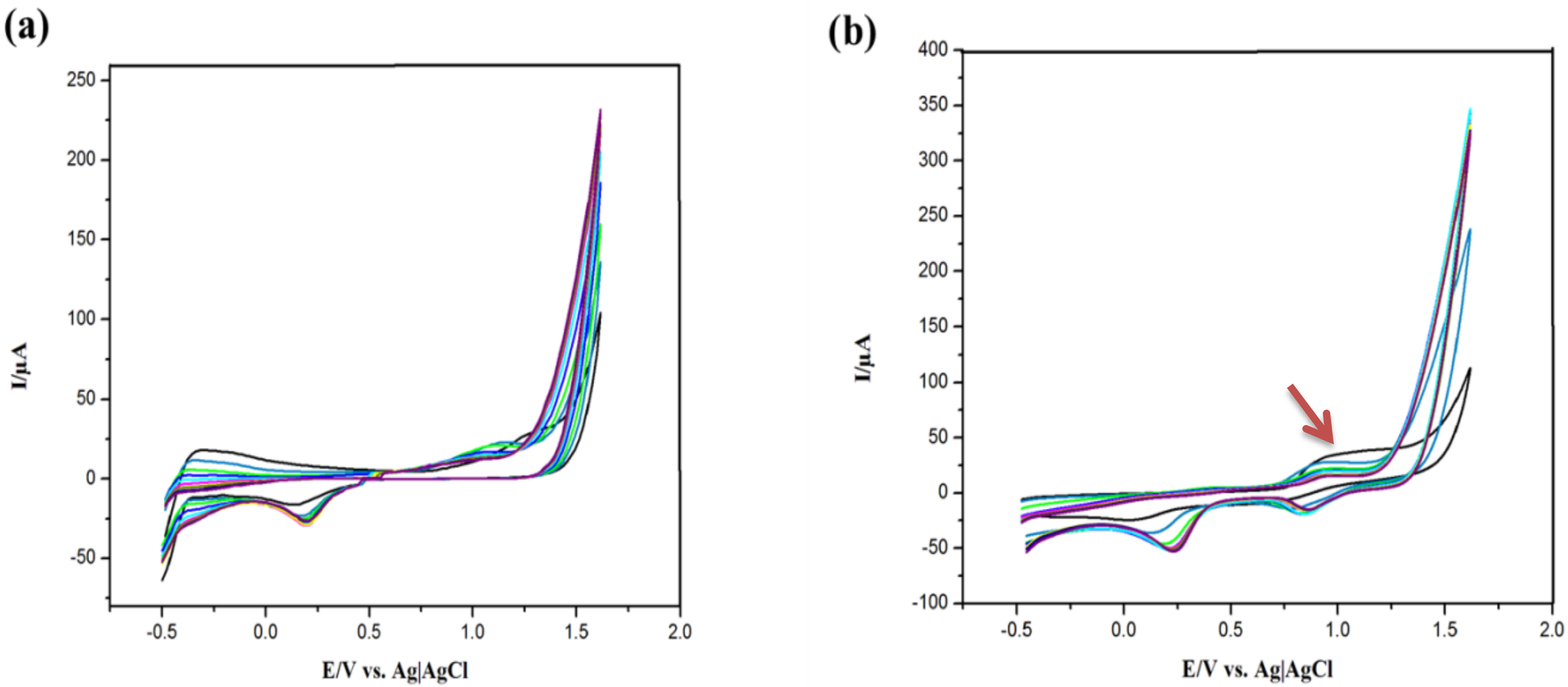
Characterization

SEM and TEM



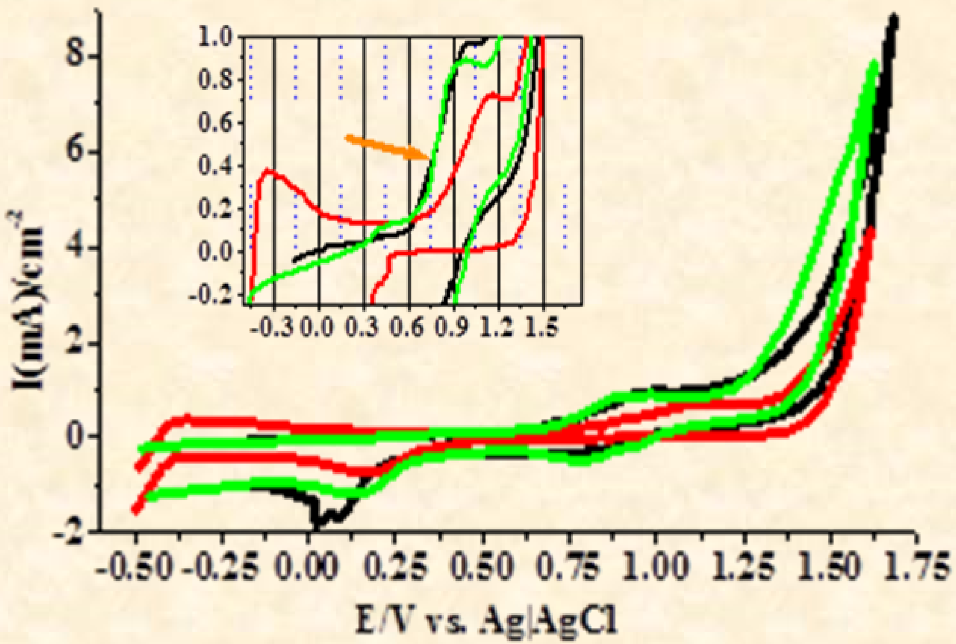
SEM (a,b) and TEM (c,d) images of MnCaOx-G_7HV_8.

Cyclic Voltammetry



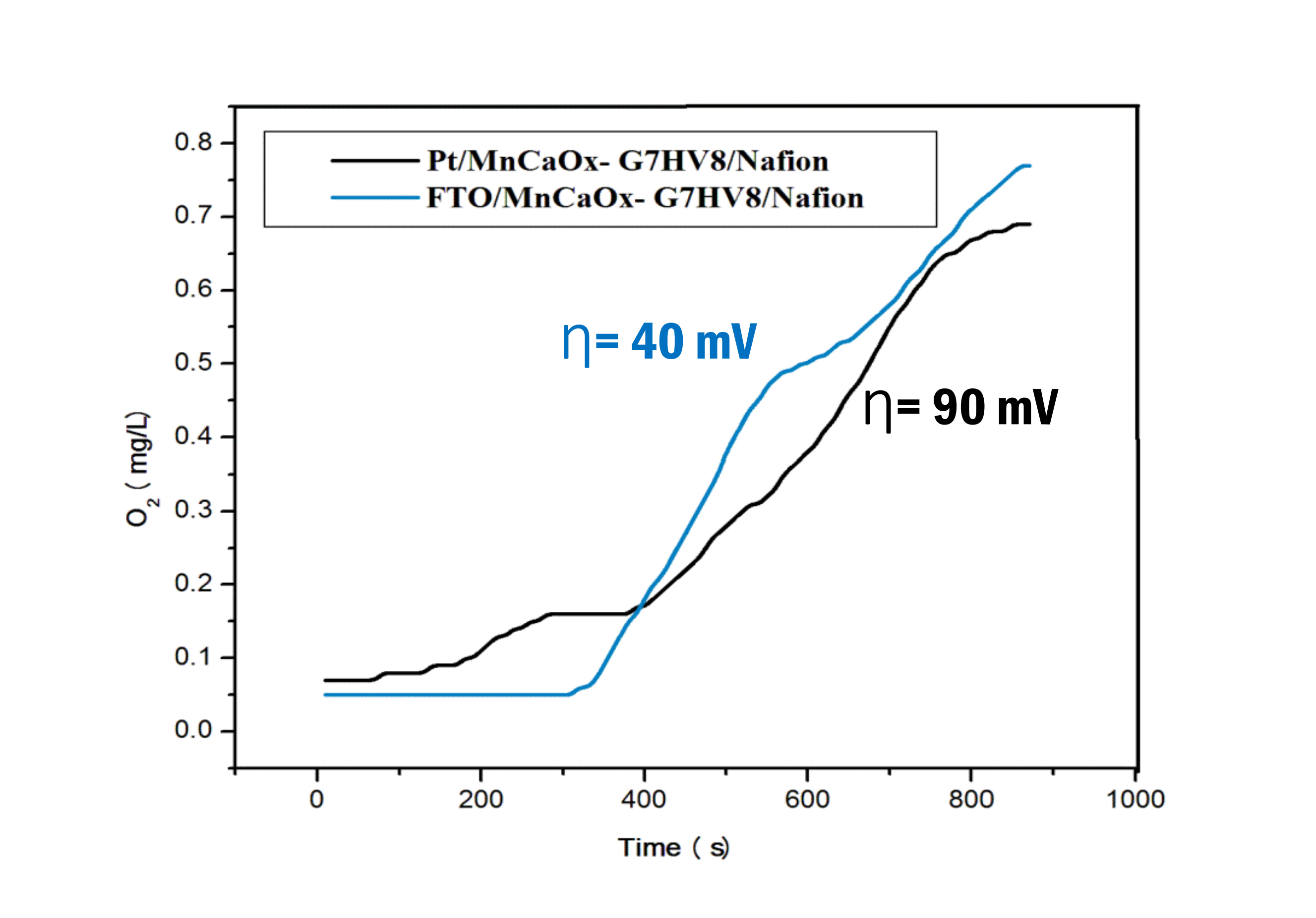
Cyclic voltammograms (CVs) of (a) Pt/G_7HV_8/Nafion , (b) Pt/$MnCaO_x$-G_7HV_8/Nafion in $LiClO_4$ solution (0.1 M), pH = 6.3 at a scan rate of 100 mV s^{-1}.

Cyclic Voltammetry



Cyclic voltammograms (CVs) of Pt/G_7HV_8/Nafion, Pt/$MnCaO_x$/Nafion, Pt/$MnCaO_x$-G_7HV_8/Nafion in $LiClO_4$ solution (0.1 M), pH = 6.3 at a scan rate of 100 mV s^{-1}. The arrow represents the oxidation of Mn(III) to Mn(IV) oxidation.

Chronoamperometry



Oxygen evolution by Pt/$MnCaO_x$–G_7HV_8/Nafion at potential of 0.75V and FTO/$MnCaO_x$–G_7HV_8/Nafion at 0.7V (vs. Ag/AgCl) in $LiClO_4$ solution (0.1 M), pH = 6.3.

Conclusion

- The layered manganese oxides are more efficient catalysts than other structures.
- Proper choice of matrix environment around manganese oxides leads to decrease required overpotential for water oxidation reaction.
- The groups which stabilize Mn(III), can reduce the potential of water oxidation.

Thank you for your attention