The 3rd. TRI-NATIONAL WORKSHOP ON STANDARDS FOR NANOTECHNOLOGIES

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Construction of Functional Electrodes by means of Nanosized Oxide Semiconductors for Photovoltaics and Photoelectrocatalysis Applications

c i d e t e q

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Motivation

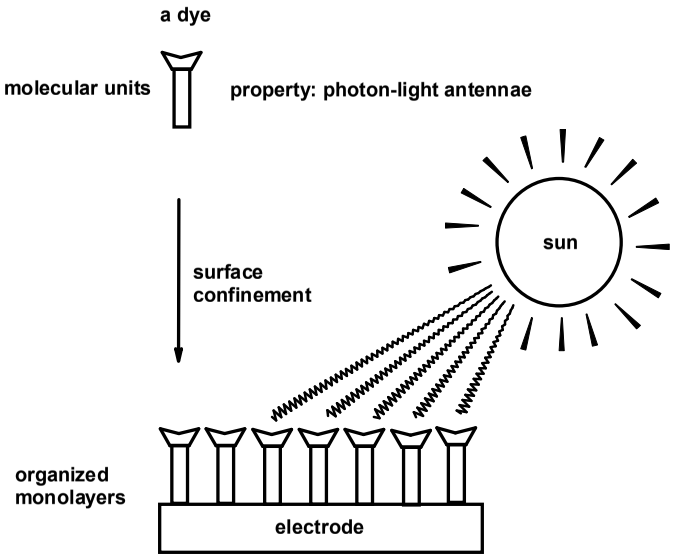
To share how some nanomaterials have been used for assembling functional electrodes looking for applications in photovoltaics and photoelectrocatalysis.

To promote the nanotechnology development in Mexico and to remark the need of new centers of research dedicated to the synthesis and commercialization of nanometric materials.

What´s the key?

The Sistemic Concept in Chemistry

...the operation of a system can be designed intentionally if the physical chemical properties of the most simple units are known...

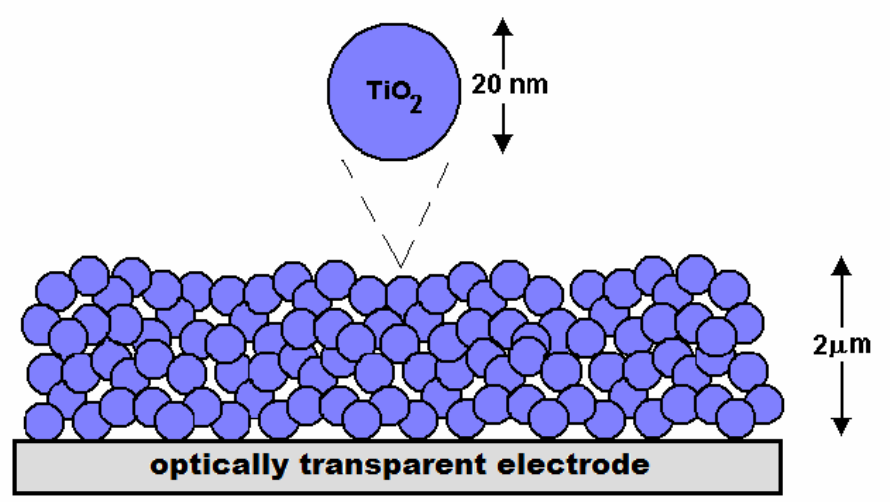


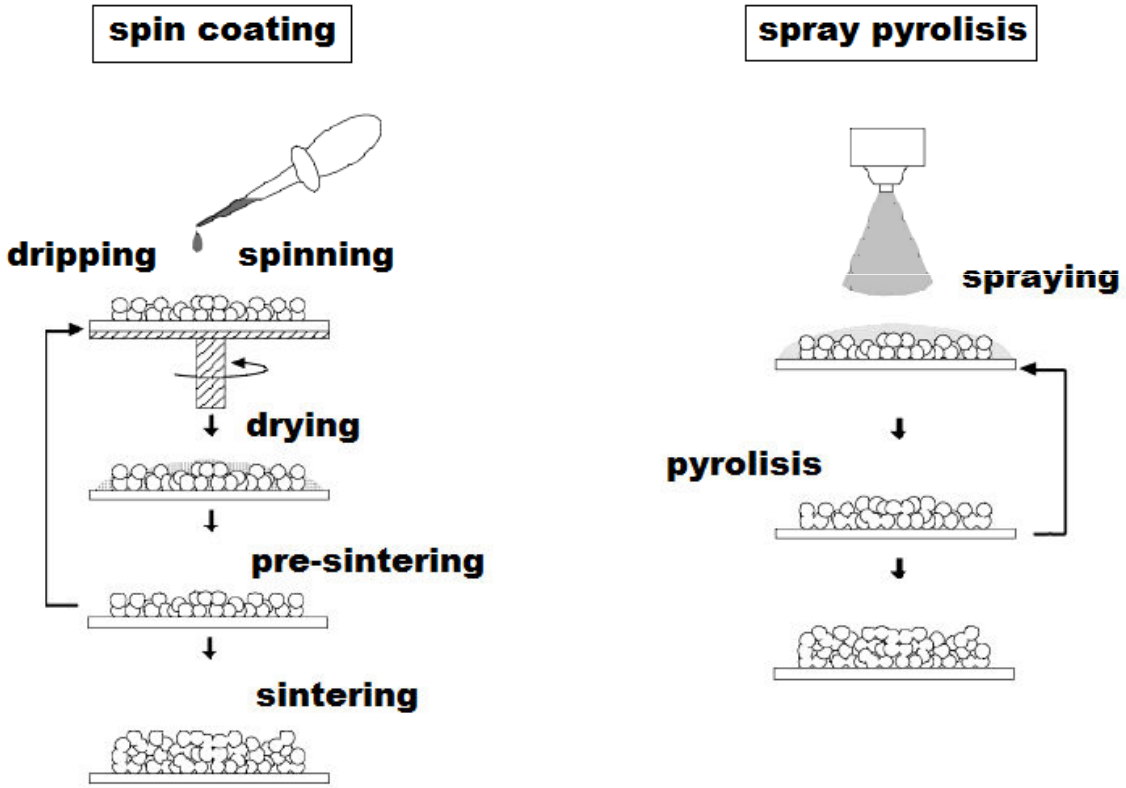
Function 1: surface for sunlight harvesting

Function 2: environmental photoelectrocatalysis

Creating semiconductor electrodes having large areas

Construction of Nanoporous TiO_2 Electrodos by means of Electrophoretic Deposition (EPD)



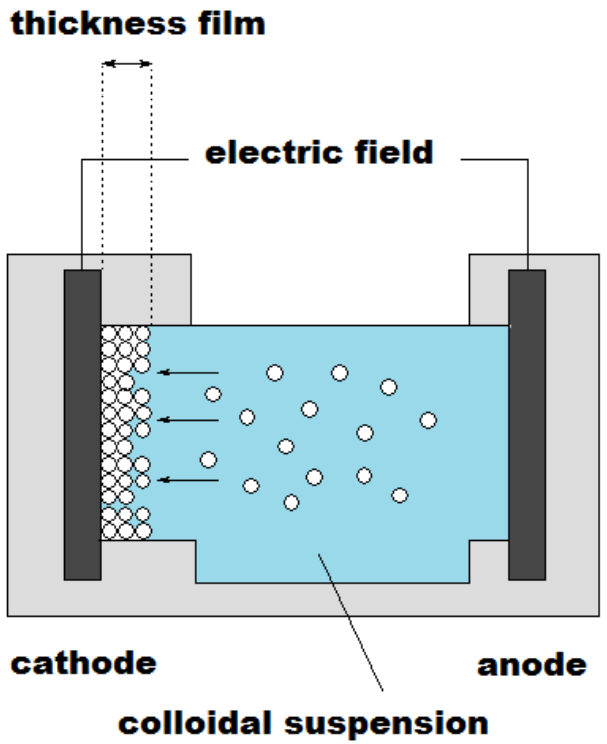


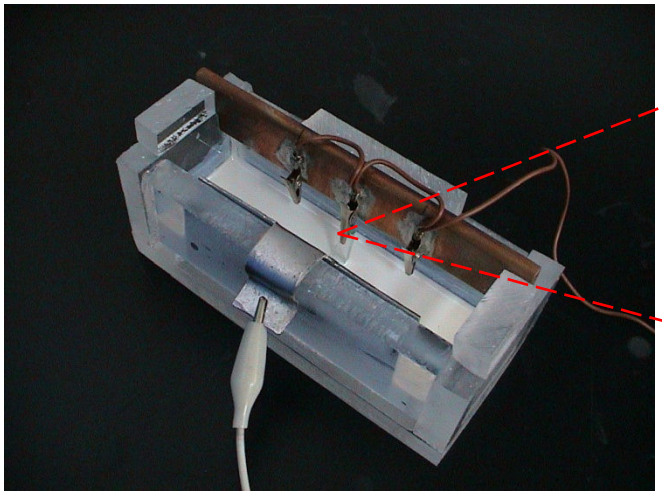
Problem: Too thin films for applications in photovoltaics and photoelectrocatalysis, which need large surface areas.

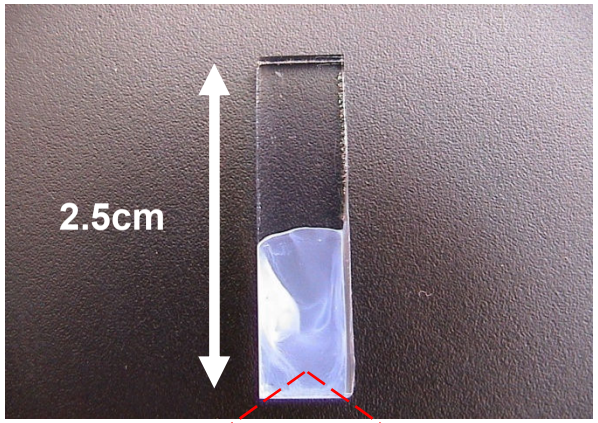
Solution

Promoting the migration of colloidal semiconductor nanoparticles under the effect of an electric field.

electrophoretic deposition (EPD)





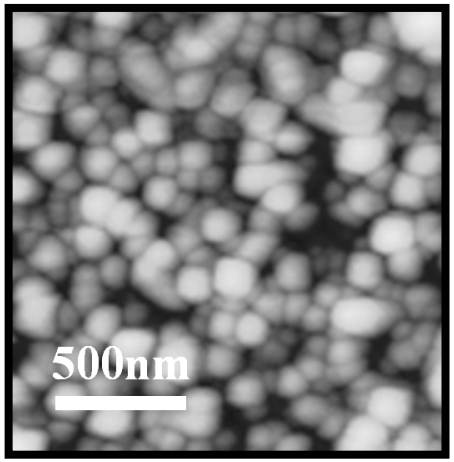


EPD Setup

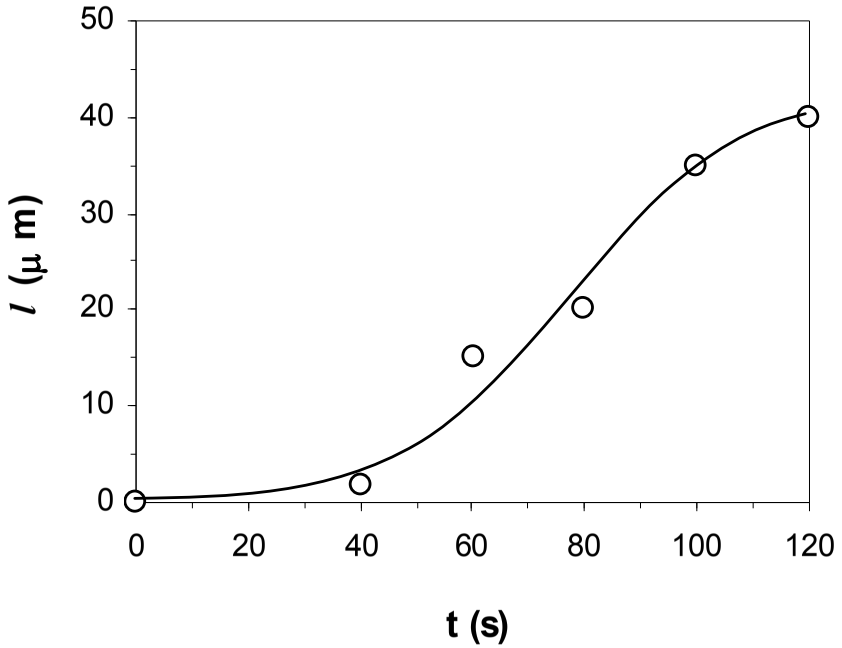
TiO_2 P25 Degussa (75% anatasa, 25% rutilo, 20nm)

After sintering

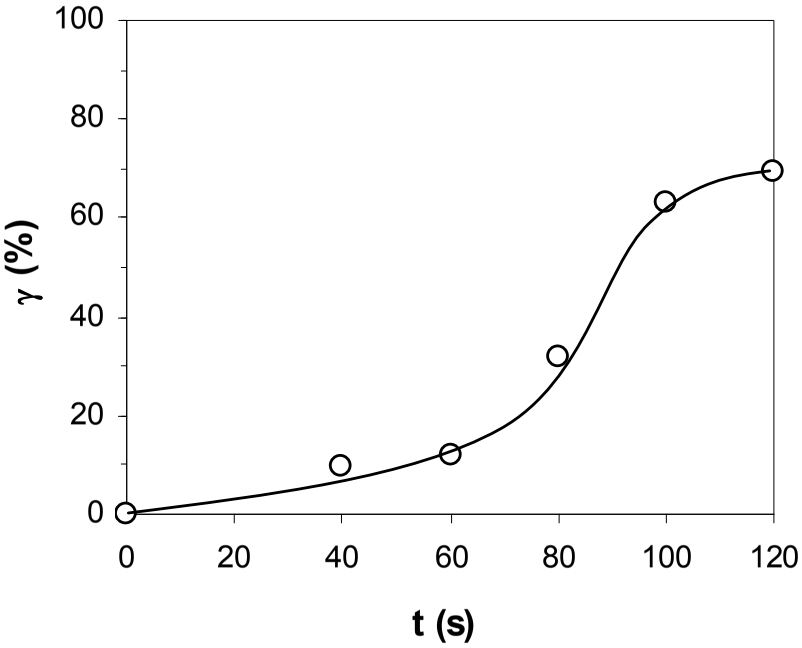
Furnace at 450 °C for 30min



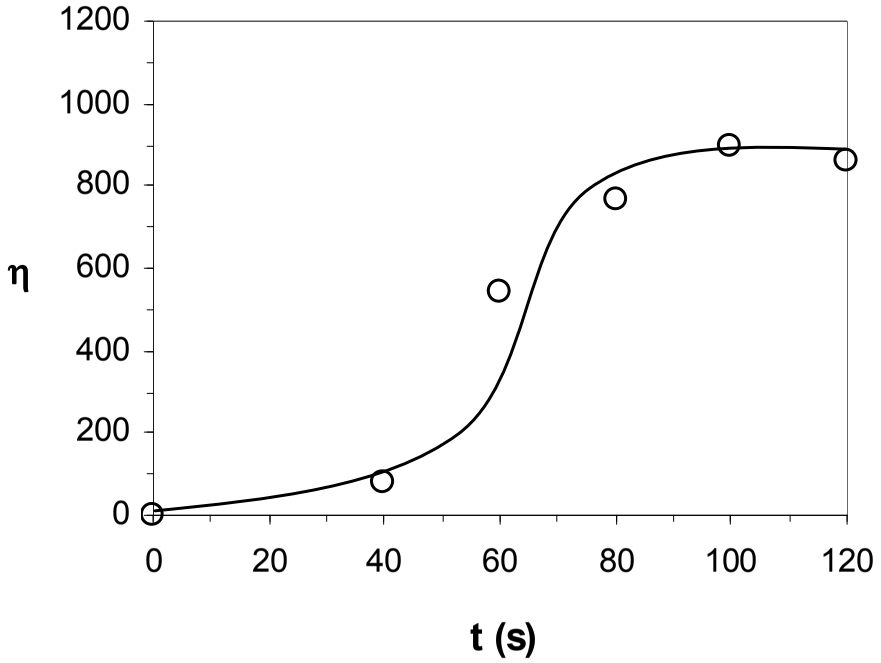
thickness



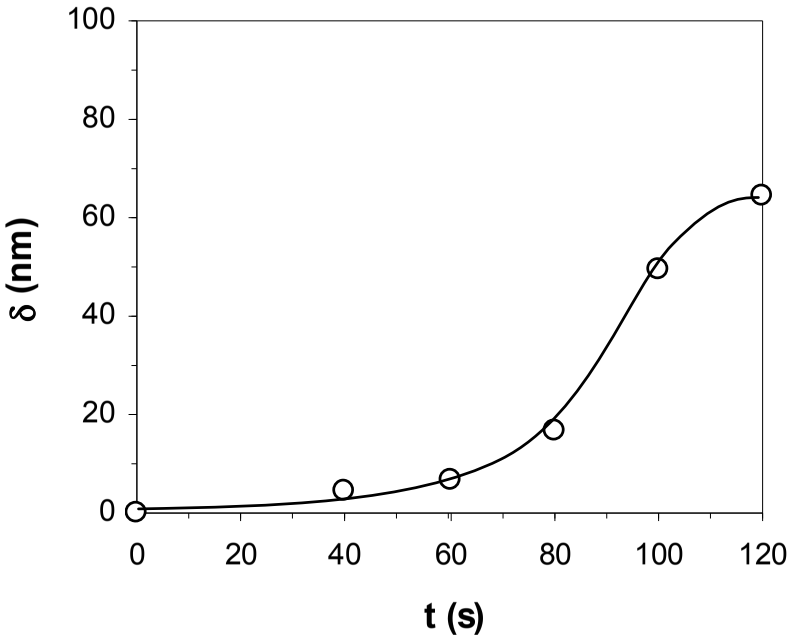
porosity



roughness factor

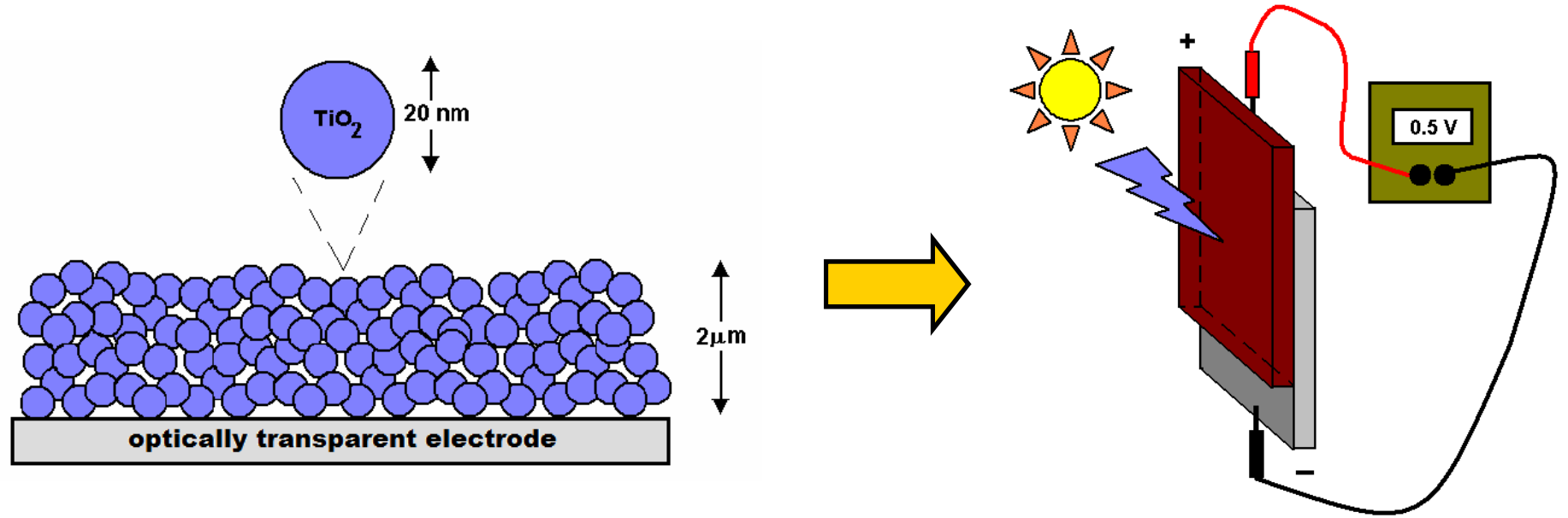


pore diameter

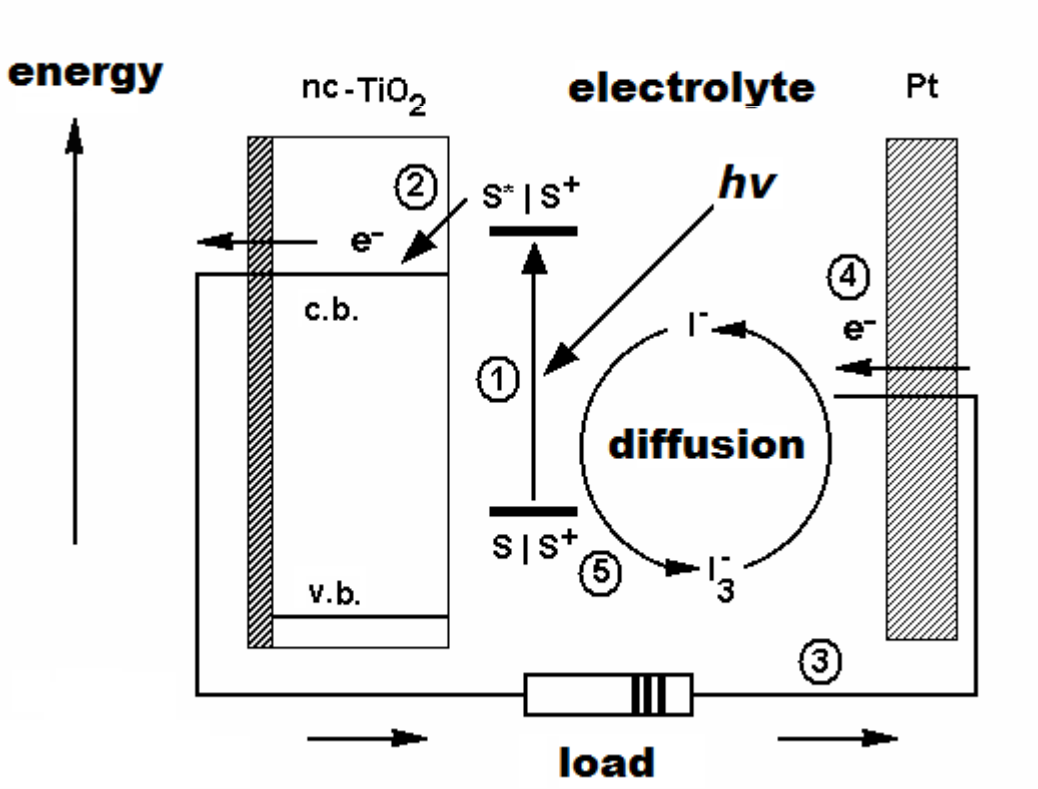


Photovoltaics

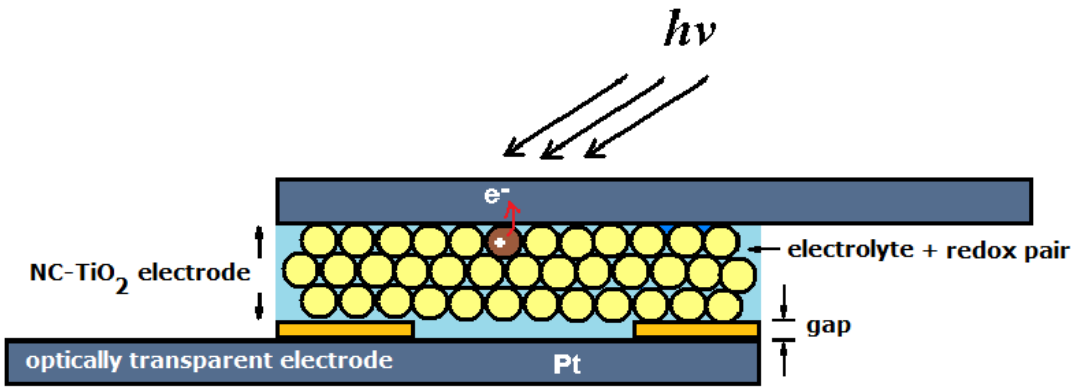
Construction of Efficient Dye-Sensitized Solar Cells (DSSC)



How works a DSSC ?



Assembling DSSC



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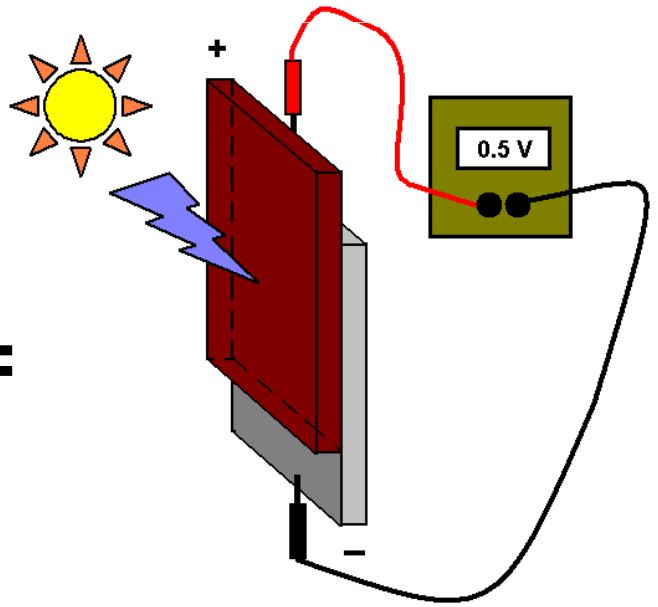
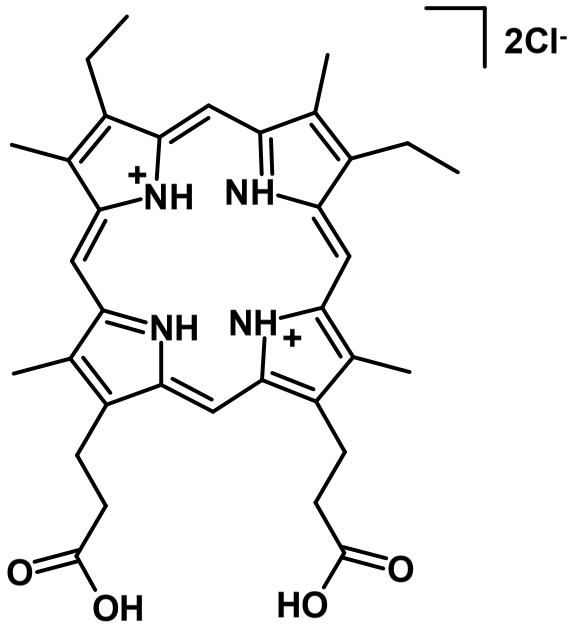


Porphyrins as TiO_2 sensitizers

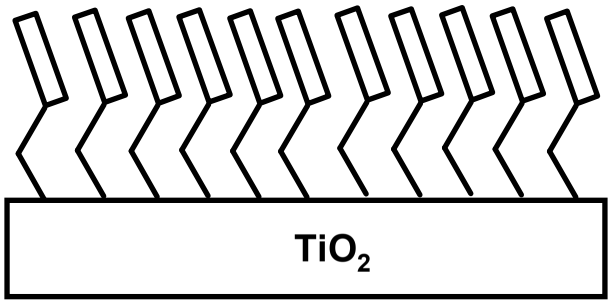


meso-porphyrin IX hydrochloride (PIX)

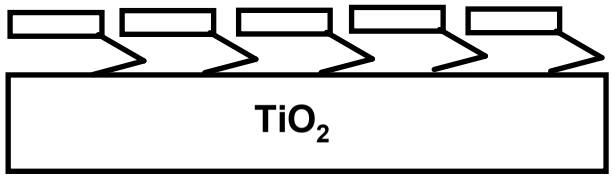
Perpendicular vs. Parallel Orientation

What's the best orientation for photovoltaics?

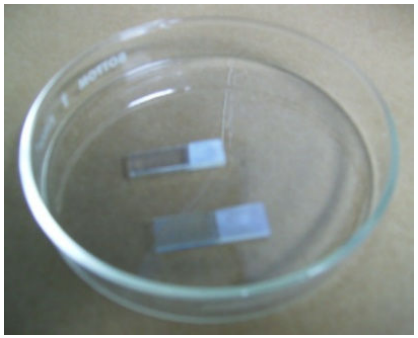
A



B

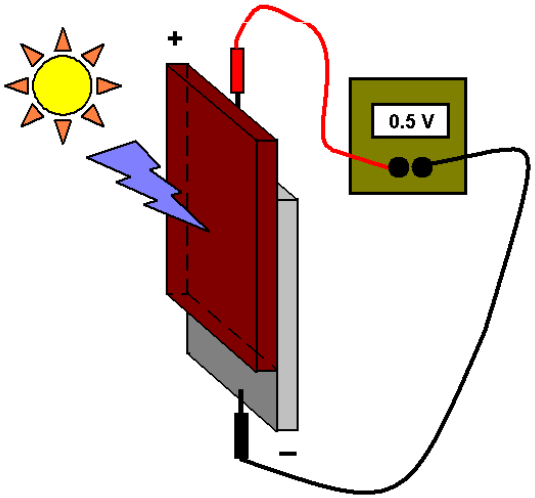


Direct Adsorption Deposition = Parallel Orientation



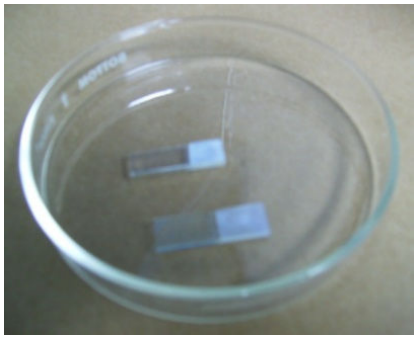
NC-TiO_2 electrodes previously prepared by EPD

Immersion of NC-TiO_2 electrode in EtOH+PIX solutions for 24h

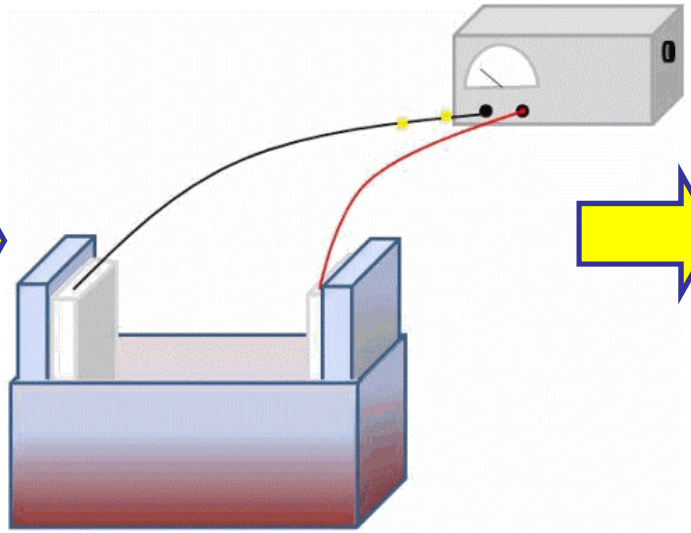


DSSC

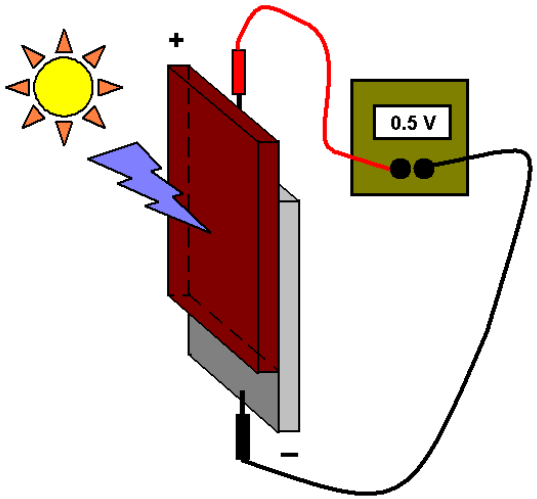
Electrophoretic Deposition = Perpendicular Orientation



NC-TiO_2 electrodes previously prepared by EPD

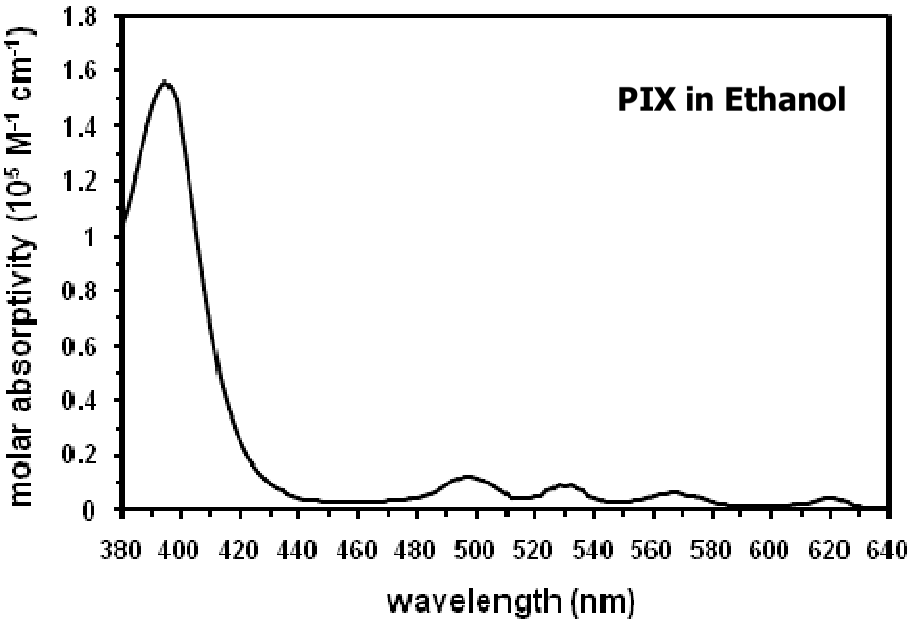


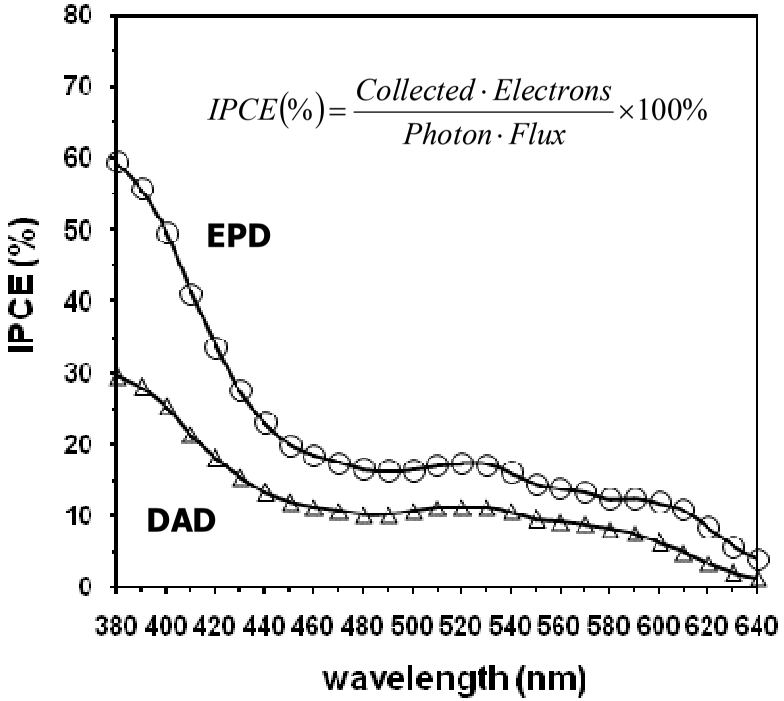
Electrophoretic deposition of PIX



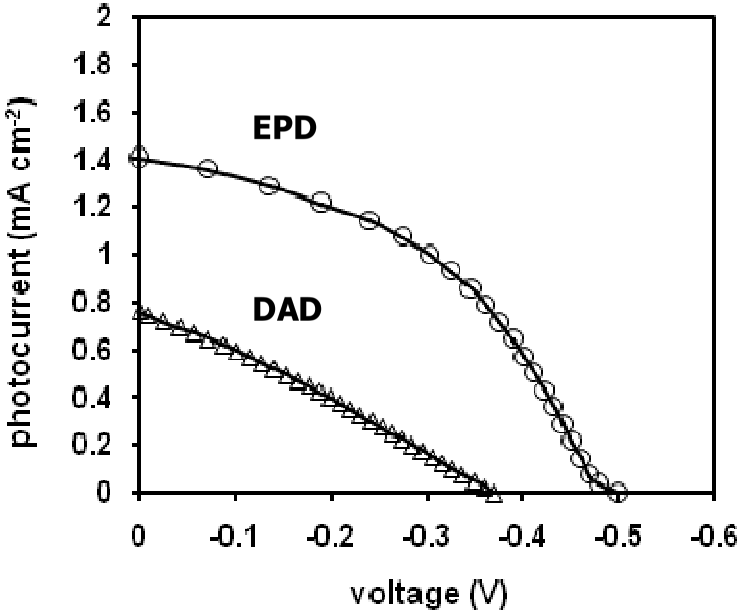
DSSC

UV-Vis and Photocurrent Spectroscopies





Current-Voltage Curves



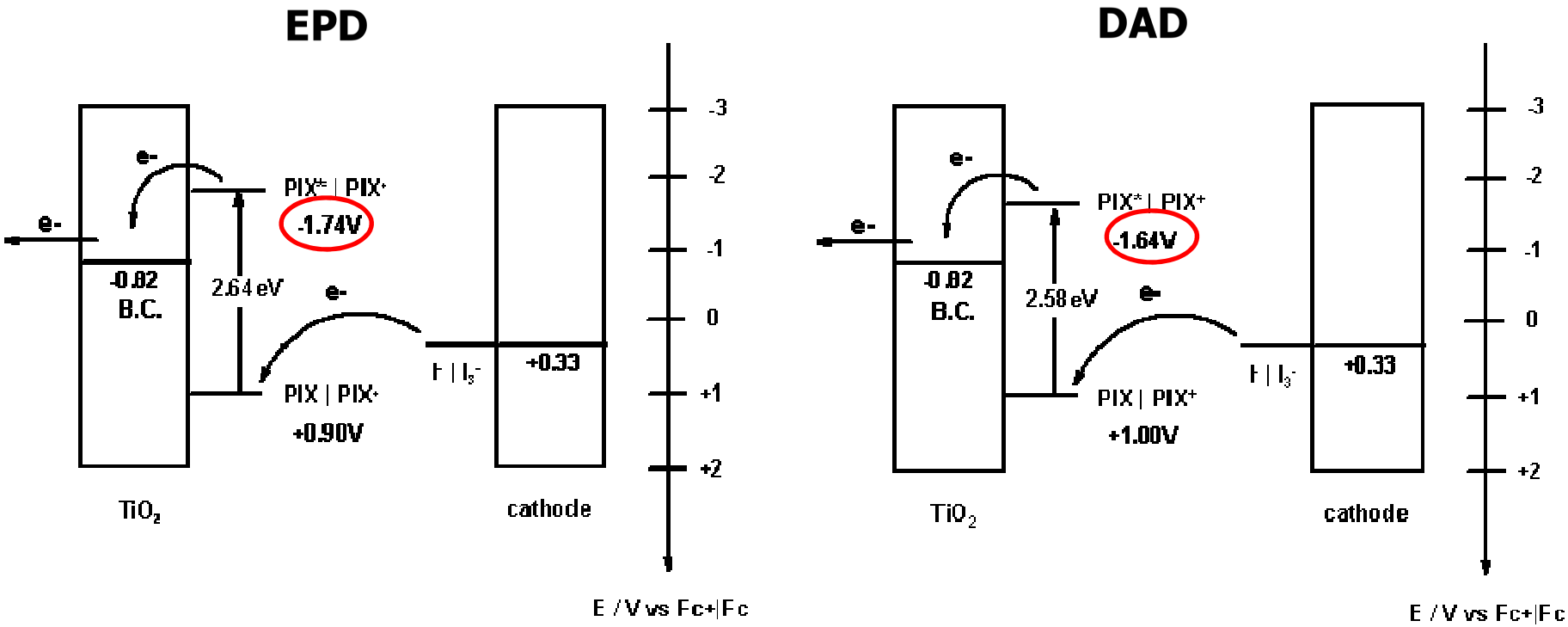
Junction	$-E_{OC}$ (V)	j_{SC} (mA/cm^2)	ff [a]	η [b] (%)
OTE/TiO_2/**EPD**-PIX	0.50	1.40	0.43	4.0
OTE/TiO_2/**DAD**-PIX	0.37	0.76	0.28	1.0

[a] *Fill factor was calculated using the relationship* $ff=P_{max}/E_{OC}\times j_{SC}$, *where* P_{max} *is the maximum output power and* j_{SC} *is the short-circuit-photocurrent.*

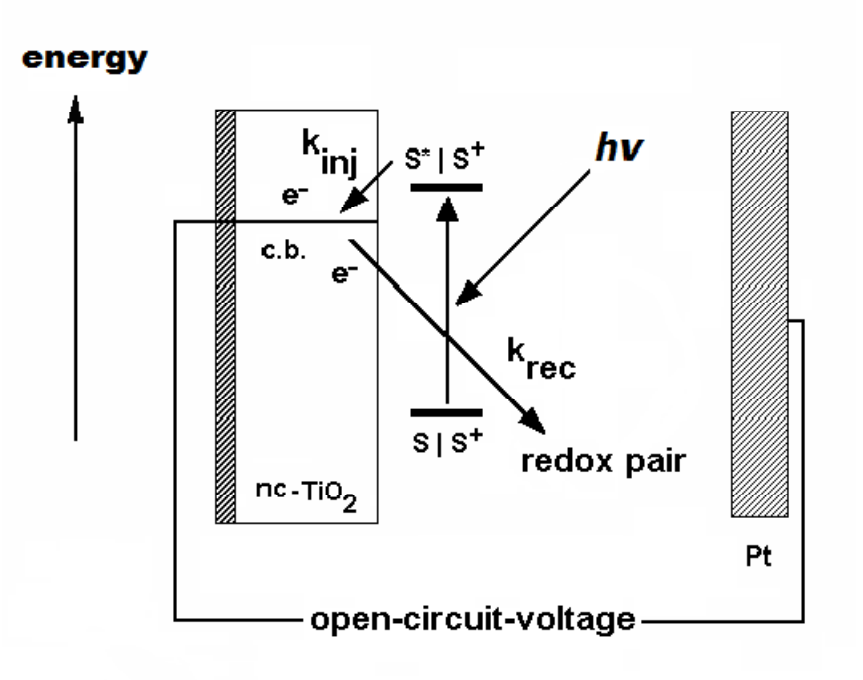
[b] *Global cell photoconversion was calculated using the relationship* $\eta=P_{max}/P_{input}$, *where* P_{input} *is the power of the incident photon flux.*

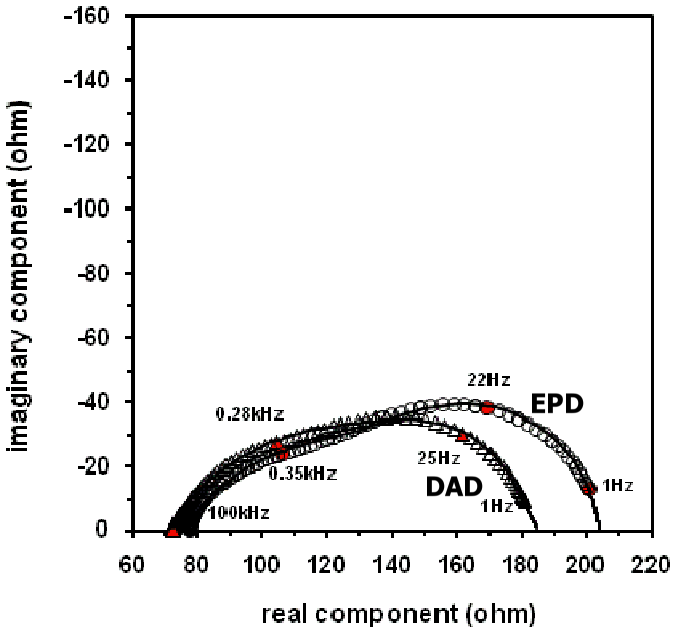
Why perpendicular orientation promoted by EPD of PIX is better than parallel orientation?

Thermodynamics



Photoelectrochemical Impedance Spectroscopy





k_{inj} = first-order kinetic constant for electron-injection

k_{rec} = first-order kinetic constant for electron-recombination

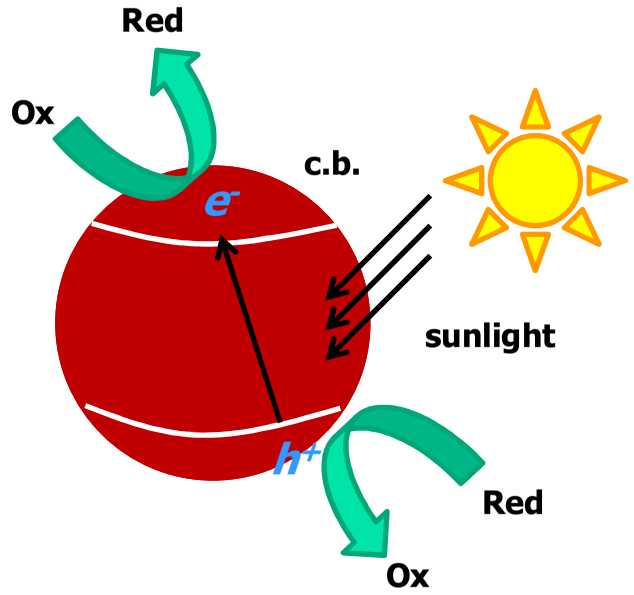
Junction	k_{inj} (s^{-1})	k_{rec} (s^{-1})
OTE/TiO_2/**EPD**-PIX	21350.7	141.8
OTE/TiO_2/**DAD**-PIX	7979.7	193.0

Preliminar Conclusion

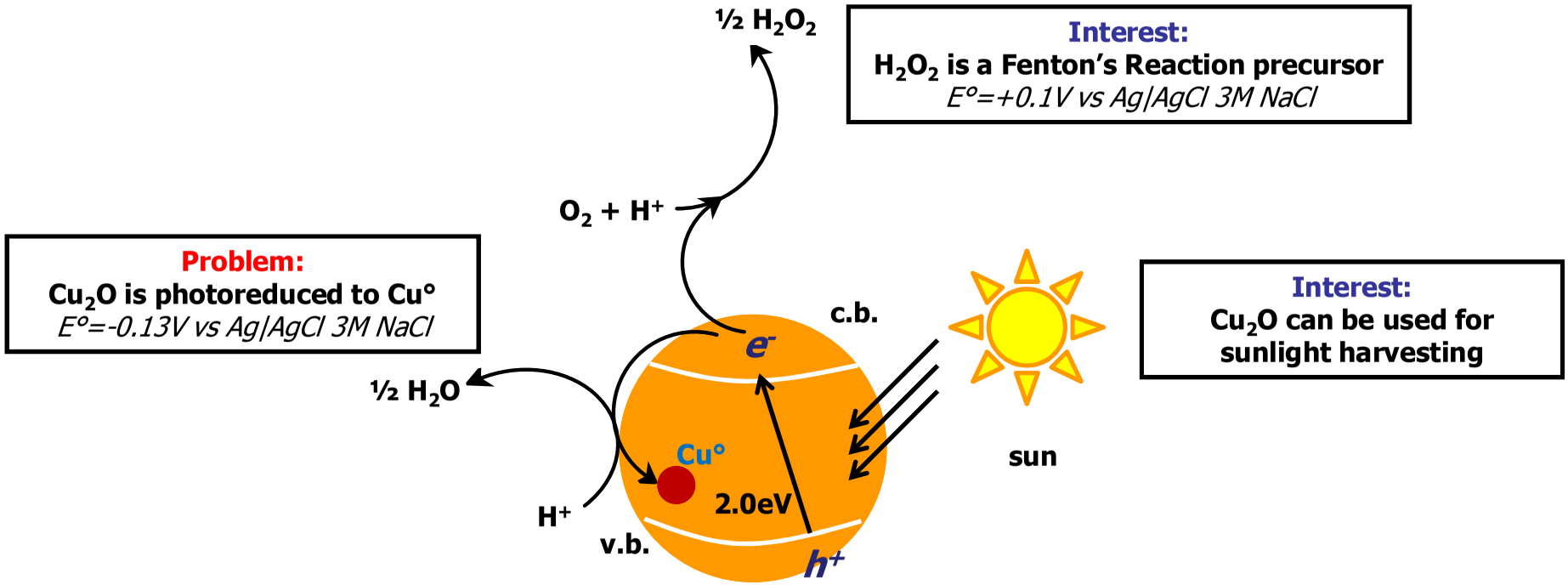
The dimensions as well as the electrical and photochemical properties of nanosized oxide semiconductors allow achieving a good balance between organization and functionality for the DSSC development.

Photoelectrocatalysis

One-Step Synthesis of Nanosized Cu_2O Crystals and their Response for the Photoelectrochemical Reduction of Oxygen



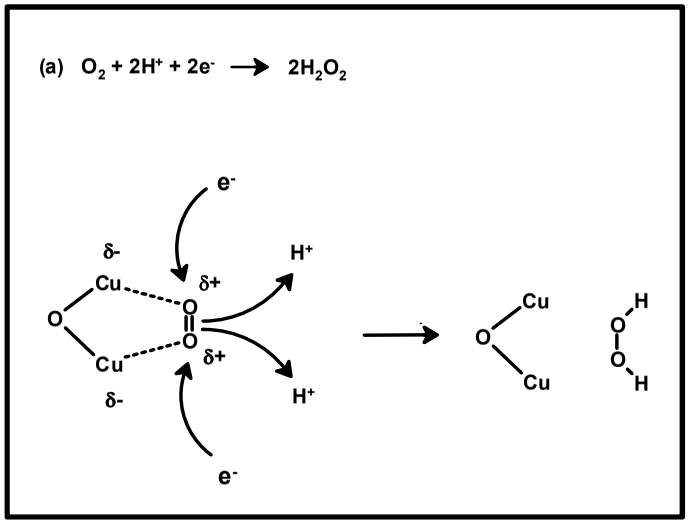
Nanosized Cu_2O : Why it's an interesting material?



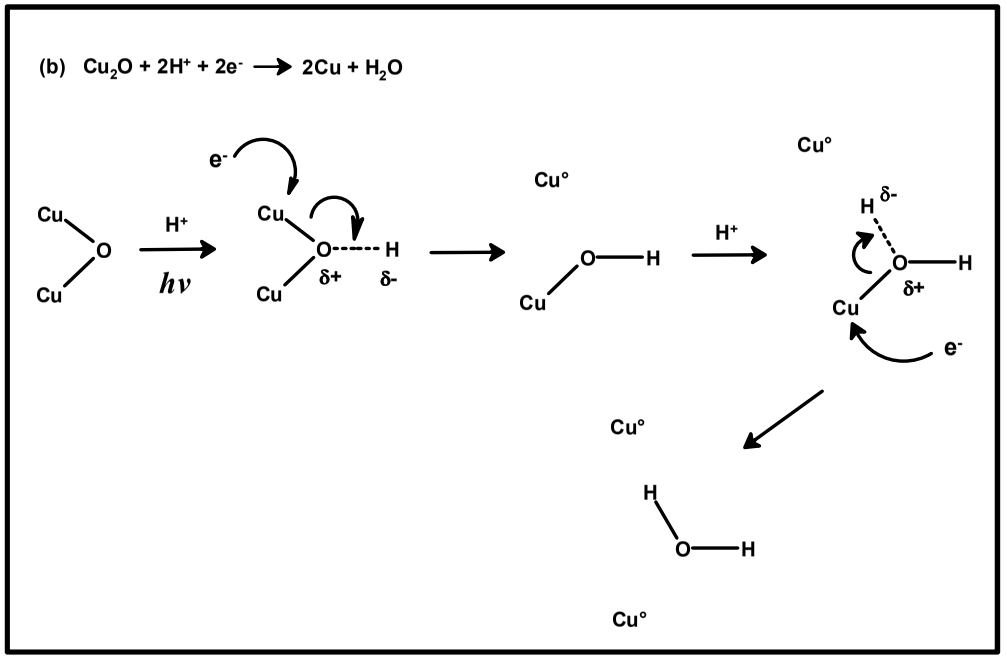
10-20nm Cu_2O nanoparticles

It has been reported that crystallographic planes (211) and (311) in Cu_2O have a high content of photoreducible sites.

How to solve it?



Vs.



Solution

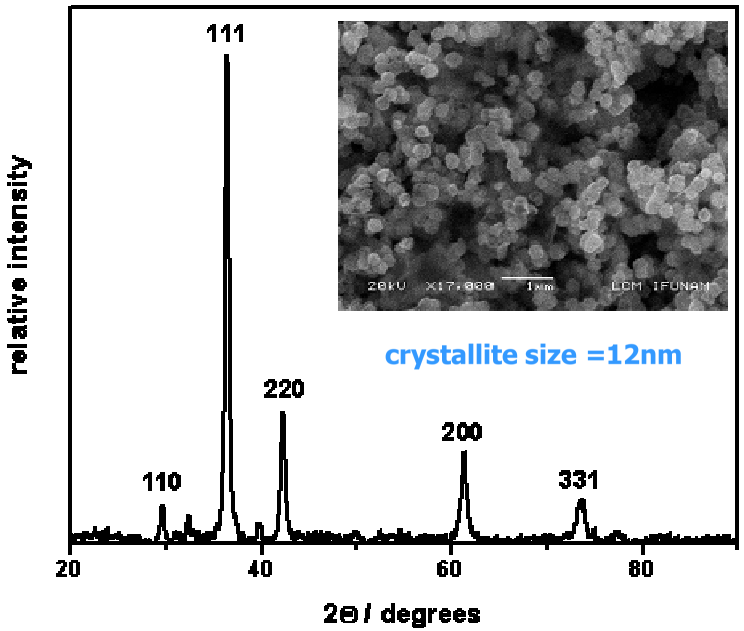
Locking for new one-step synthesis routes that allow obtaining nanosized Cu_2O having low levels of crystallographic planes (211) and (311).

Thermal hydrolysis of CuCl in aqueous DMSO

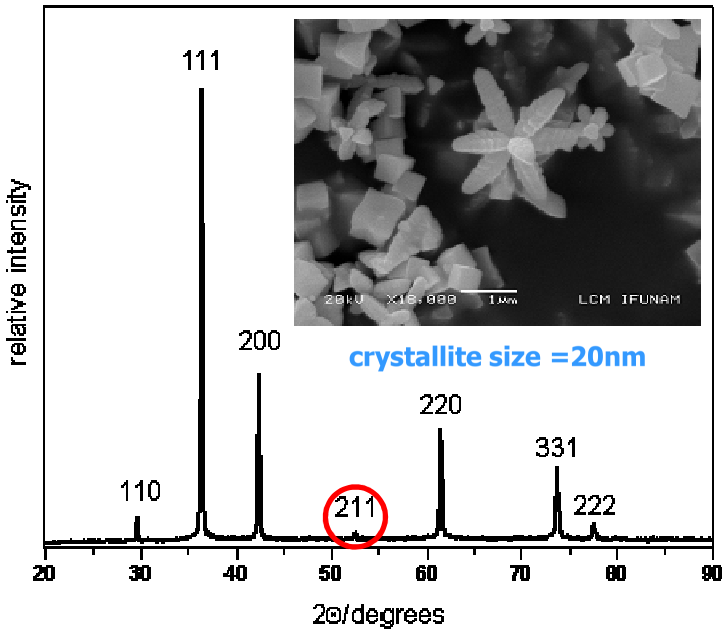
Vs.

Benedict's Reaction

$$2Cu^{+} + H_2O \xrightarrow[80°C]{DMSO} Cu_2O + 2H^{+}$$

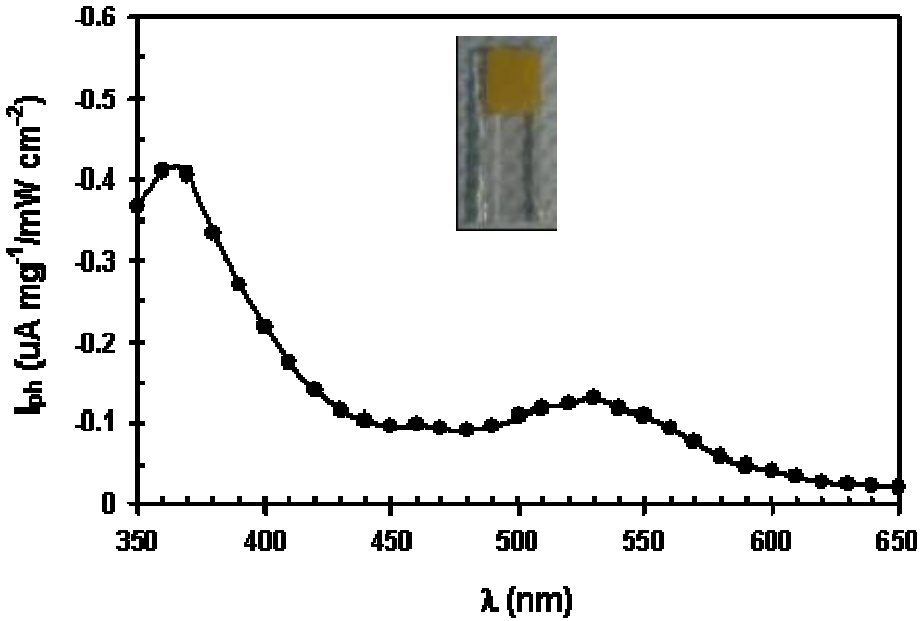


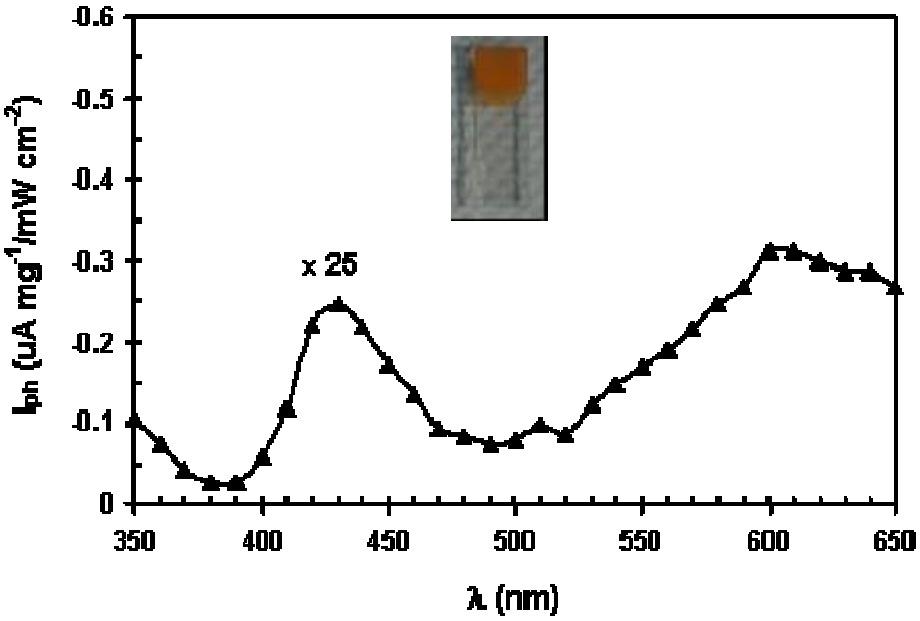
$$2Cu^{+} + 2OH^{-} \xrightarrow{glucose} Cu_2O + H_2O$$



Photocurrent Spectroscopy

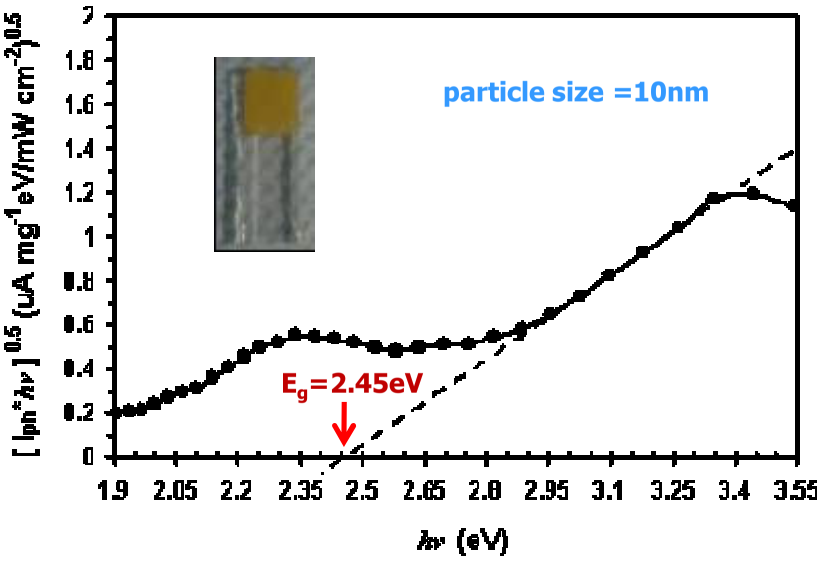
Thermal hydrolysis of CuCl in aqueous DMSO **Vs.** **Benedict's Reaction**

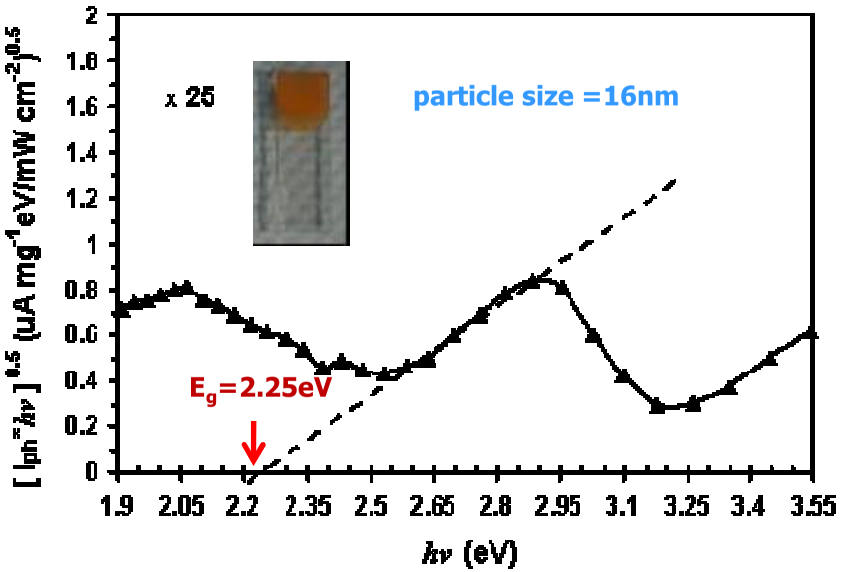




Photocurrent Spectroscopy

Thermal hydrolysis of CuCl in aqueous DMSO **Vs.** **Benedict's Reaction**



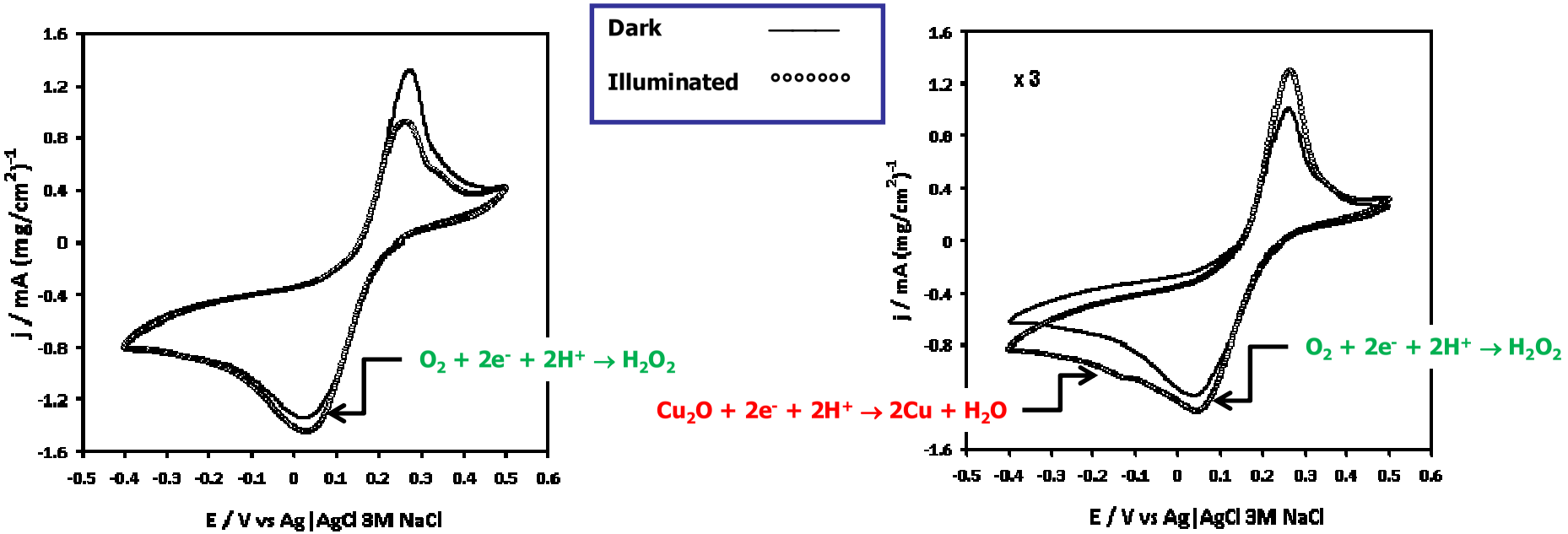


H_2O_2 photogeneration Vs. Cu_2O photoreduction

Thermal hydrolysis of CuCl in aqueous DMSO

Vs.

Benedict's Reaction



Preliminar Conclusion

The photoassisted reduction of nanosized Cu_2O was minimized using the thermal hydrolysis of CuCl in aqueous DMSO involving a one-step.

The photoelectrocatalytic O_2 reduction by Cu_2O which was obtained through the thermal hydrolysis demonstrated to be 3 times better than the respective response of Cu_2O obtained by the Benedict's Reaction.

General Conclusions

Commercial TiO_2 and synthesized Cu_2O were used for assembling functional electrodes having promising applications in photovoltaics and photoelectrocatalysis.

However, it is important to promote the creation of new centers of research dedicated to the synthesis and commercialization of nanometric materials.

Acknowledgments

To Rubén J. Lazos-Martínez and Janet Lindemann

To CENAM

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