ISTITUTO ITALIANO DI TECNOLOGIA
CENTER FOR NANO SCIENCE AND TECHNOLOGY

# Characterization of Hybrid Conjugated Polymer / Electrolyte Interfaces for biology and energy

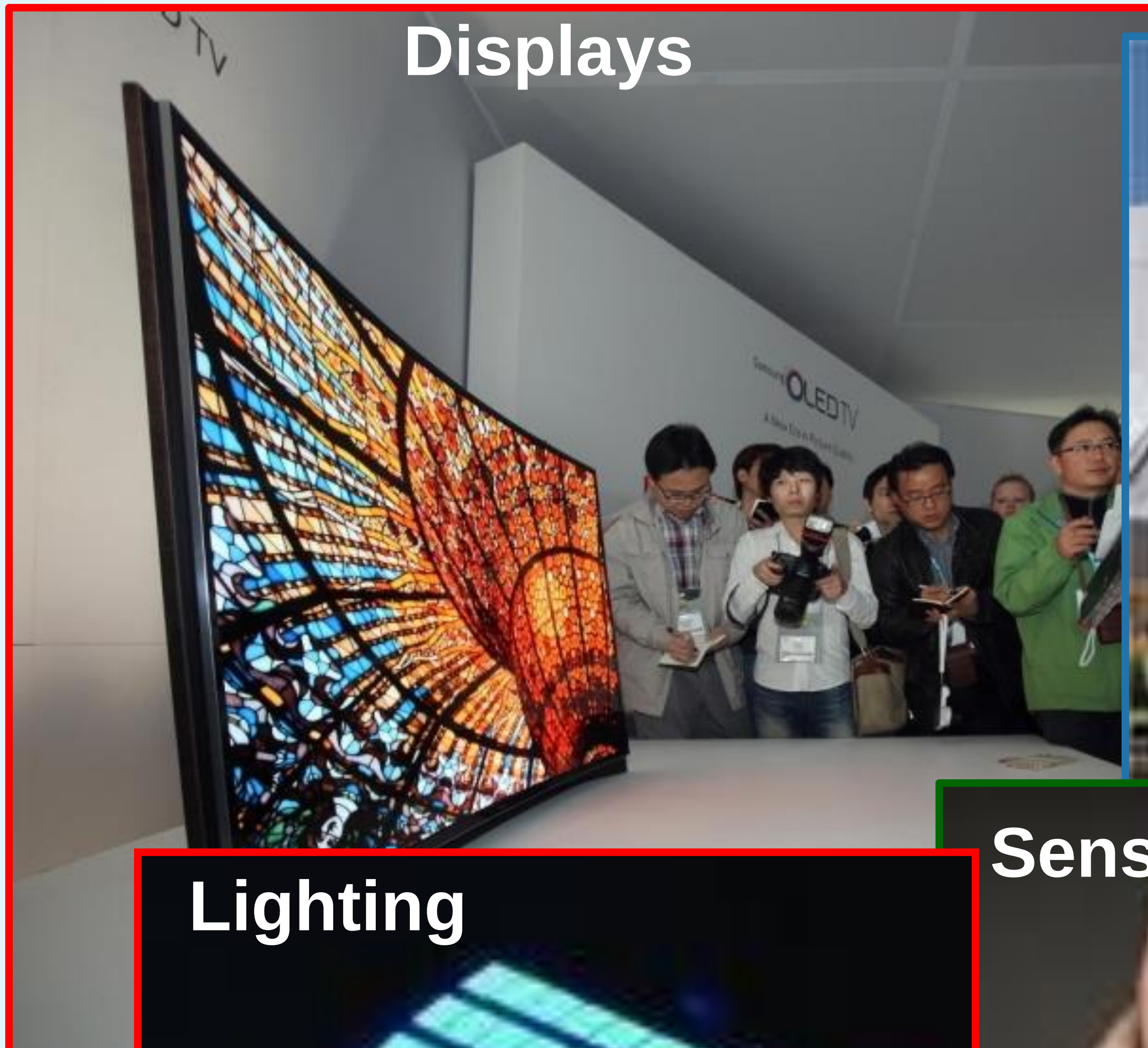
*Maria Rosa Antognazza*

**Organic Electronics: Principles, Devices and Applications**

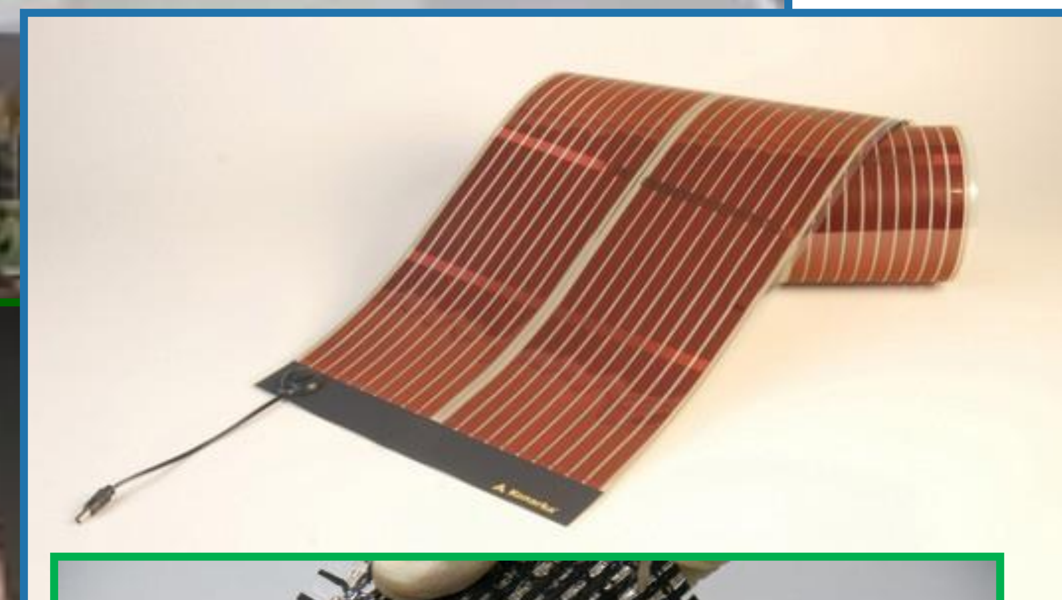
**Milan, 25th November 2015**

# Conjugated polymers



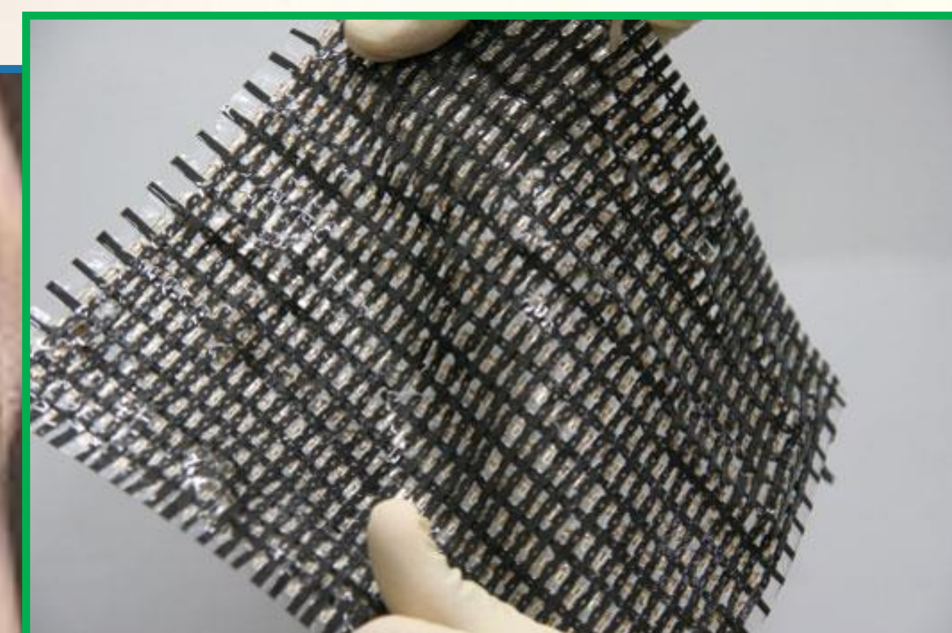

Displays


Photovoltaics




Lighting


Sensors



*"In creating and expanding the 4th generation of polymers, we attempted to understand nature with sufficient depth that we could achieve materials with novel and unique properties, that are not otherwise available.*

*This was (and is) an elegant and somewhat dangerous exercise; elegant because it requires the synthesis of knowledge from chemistry, physics and materials science, and dangerous because when working on the boundary of three disciplines, one is always pushing beyond the knowledge and experience of this background.*

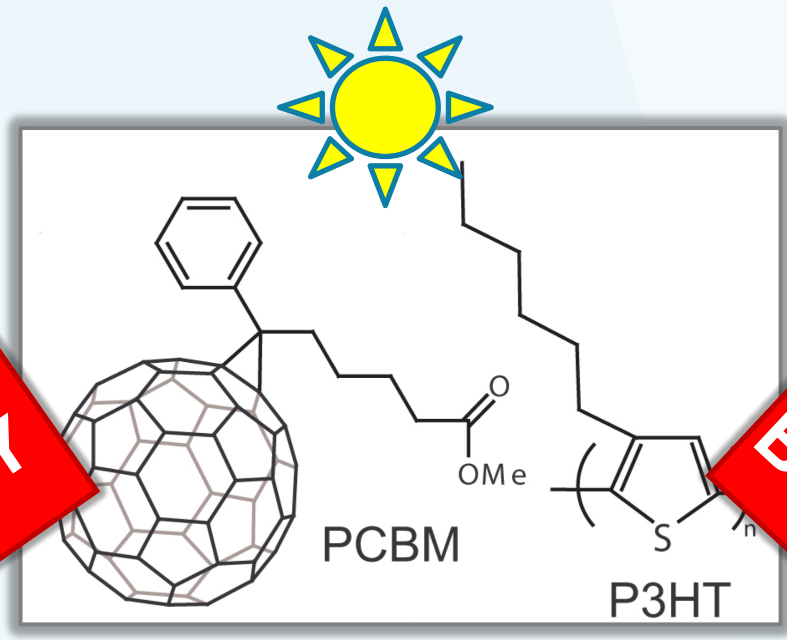
*To our research in this interdisciplinary field has had sufficient impact on chemistry to be recognized by the Nobel Prize gives us, therefore, particular satisfaction."*

Alan J. Heeger (on occasion of giving him the Nobel Prize for Chemistry in 2000)

# Time to target new applications



- ✓ *Visible light absorption*
- ✓ *Easy processability*
- ✓ *Conformable, light devices*
- ✓ *Chemical engineering*
- ✓ *Photovoltaic regime*

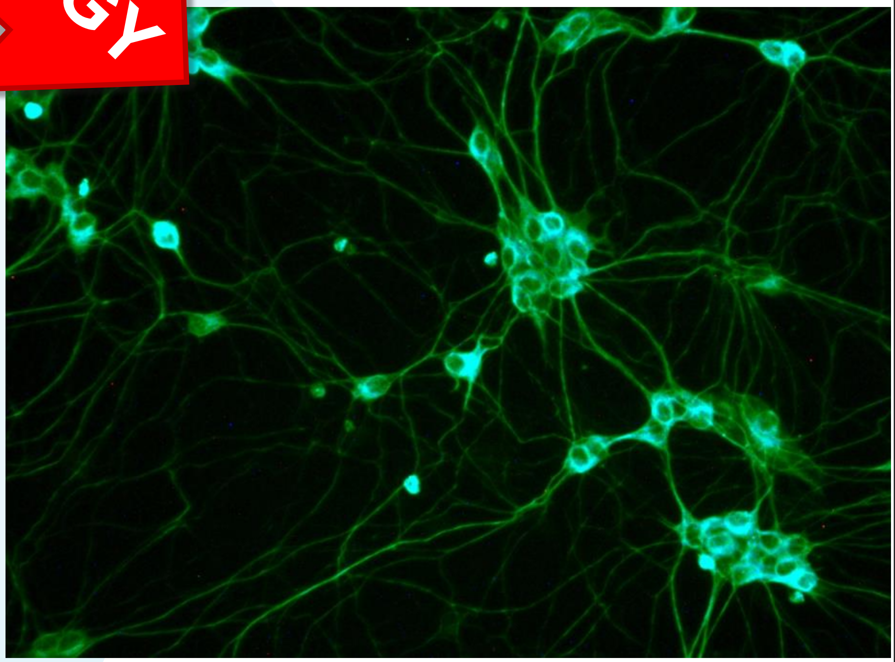



ENERGY

BIOLOGY

Photo-catalytic
Water Splitting

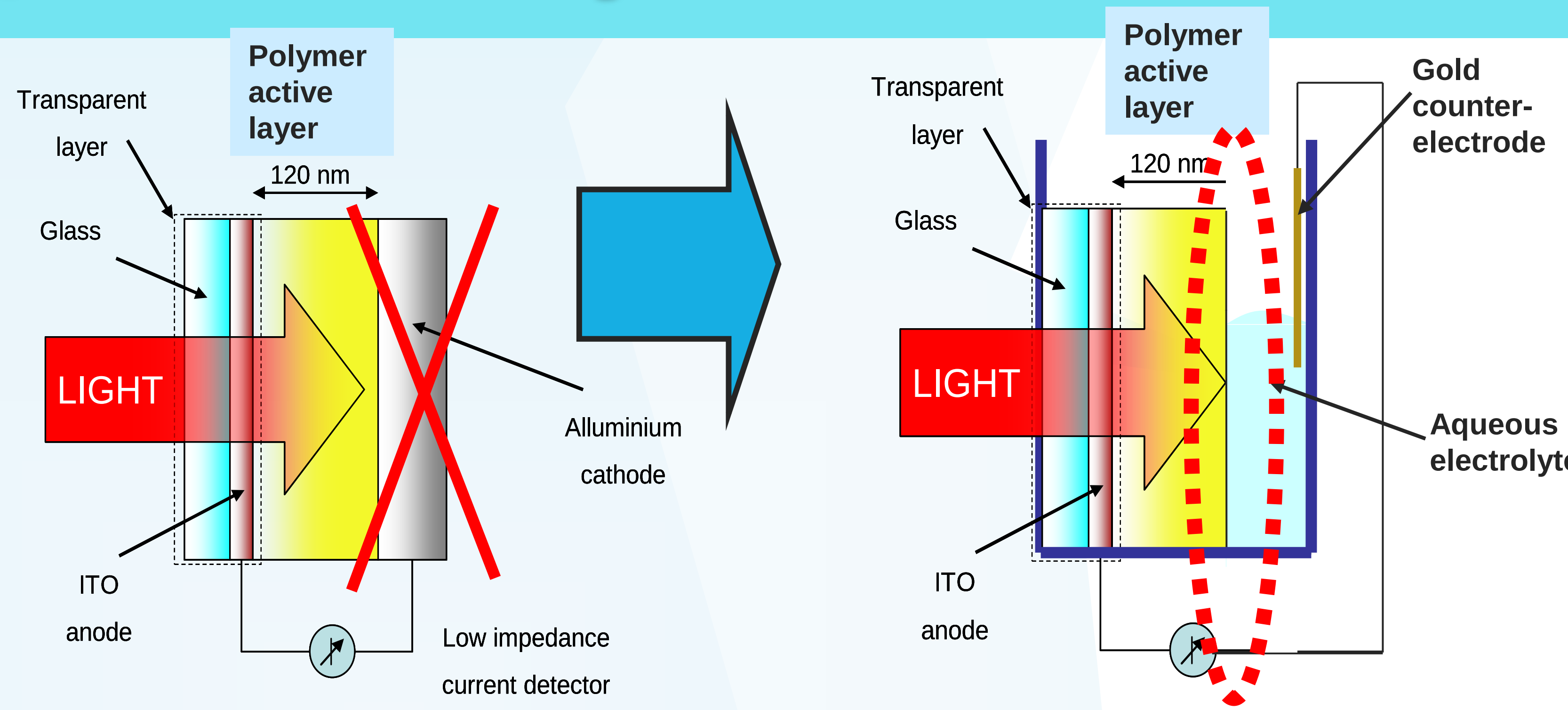
Functional Interfaces
for cell optical stimulation



***"…the synthesis of knowledge from chemistry, physics and materials science…." + electrochemistry… + biology…. + neuroscience…+ medicine***

# Polymer/electrolyte interfaces





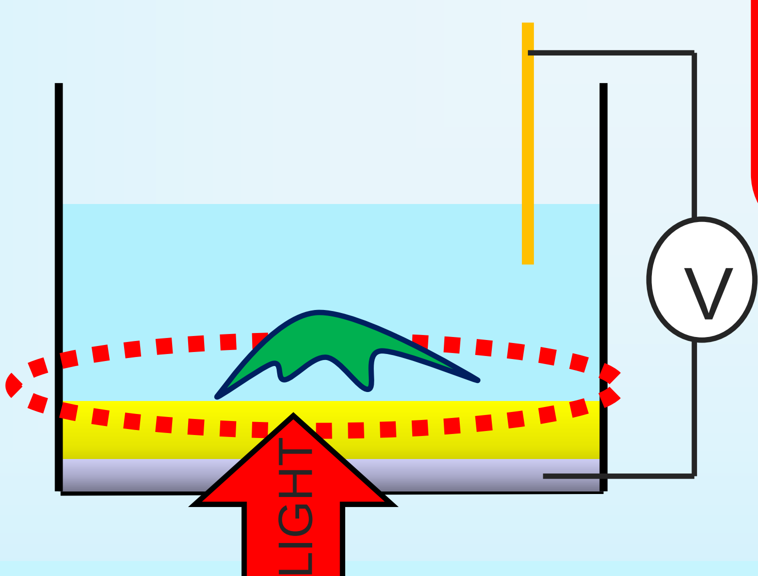

*Electrolytes:*

*- Aqueous solutions of ionic salts, w/wo electrocatalysts;*

*- Extracellular or buffer solutions;*

*- Physiological media*

OUTLINE:




1- Characterization of the water effect on polymer properties(degradation)

2- Use as an electrochemical cell

***Today work***

3- Interface with different biological cells in vitro

4- In vivo implantation for sight restoration (retinal prosthesis) + other perspectives

***On Friday***

# What is ‘degradation’?

**……Every kind of INSTABILITY, related to *chemical-physical* changes**

**For example:**

- **Decrease of absorption / photoluminescence effciency**
- **Decrease of charge generation efficiency**
- **Decrease of charge transport properties**
- **Decrease of charge collection**
- **Overall decrease of device performance and lifetime**
- **….**

**Origin and dynamics of degradation in P3HT thin films and devices are still controversial**

**-role of singlet oxygen, triplet oxygen and ozone**
**-role of moisture**
**-role of UV and VIS light**
**-role of temperature**

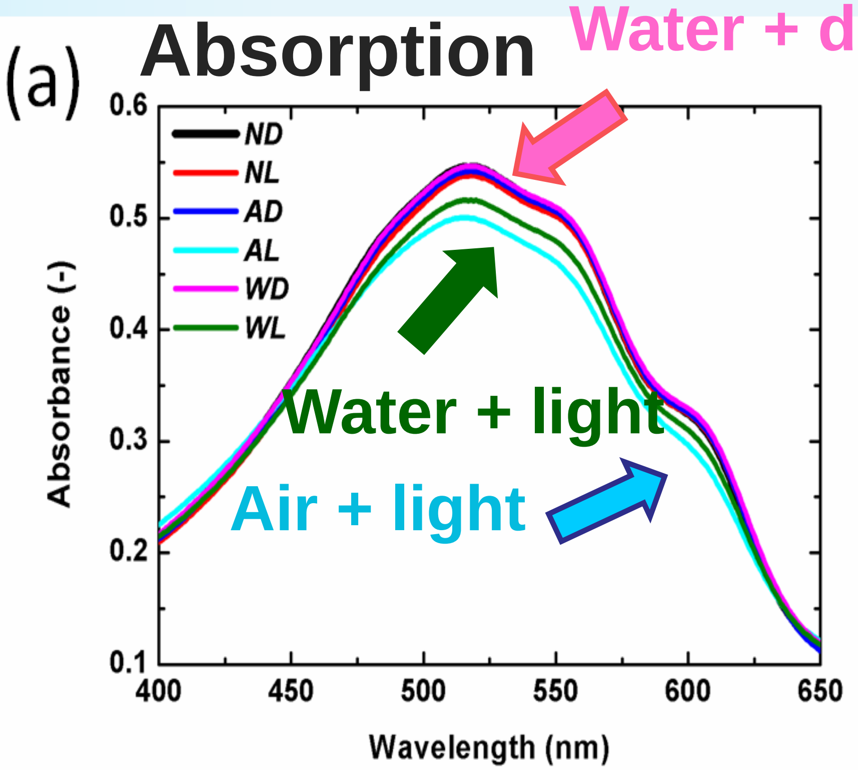
# Reversible and irreversible degradation

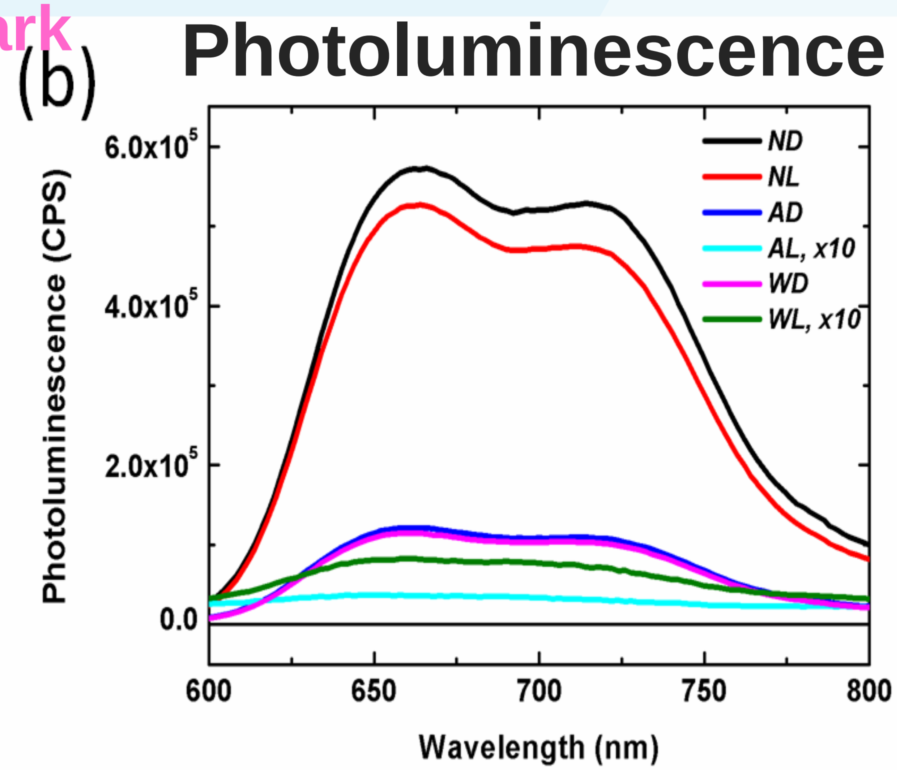


(A) Irreversible: Chemical degradation >> loss of conjugation; chain scission; side chain and backbone oxidation - Activated by UV light

(B) Reversible: Formation of P3HT/oxygen reversible complexes

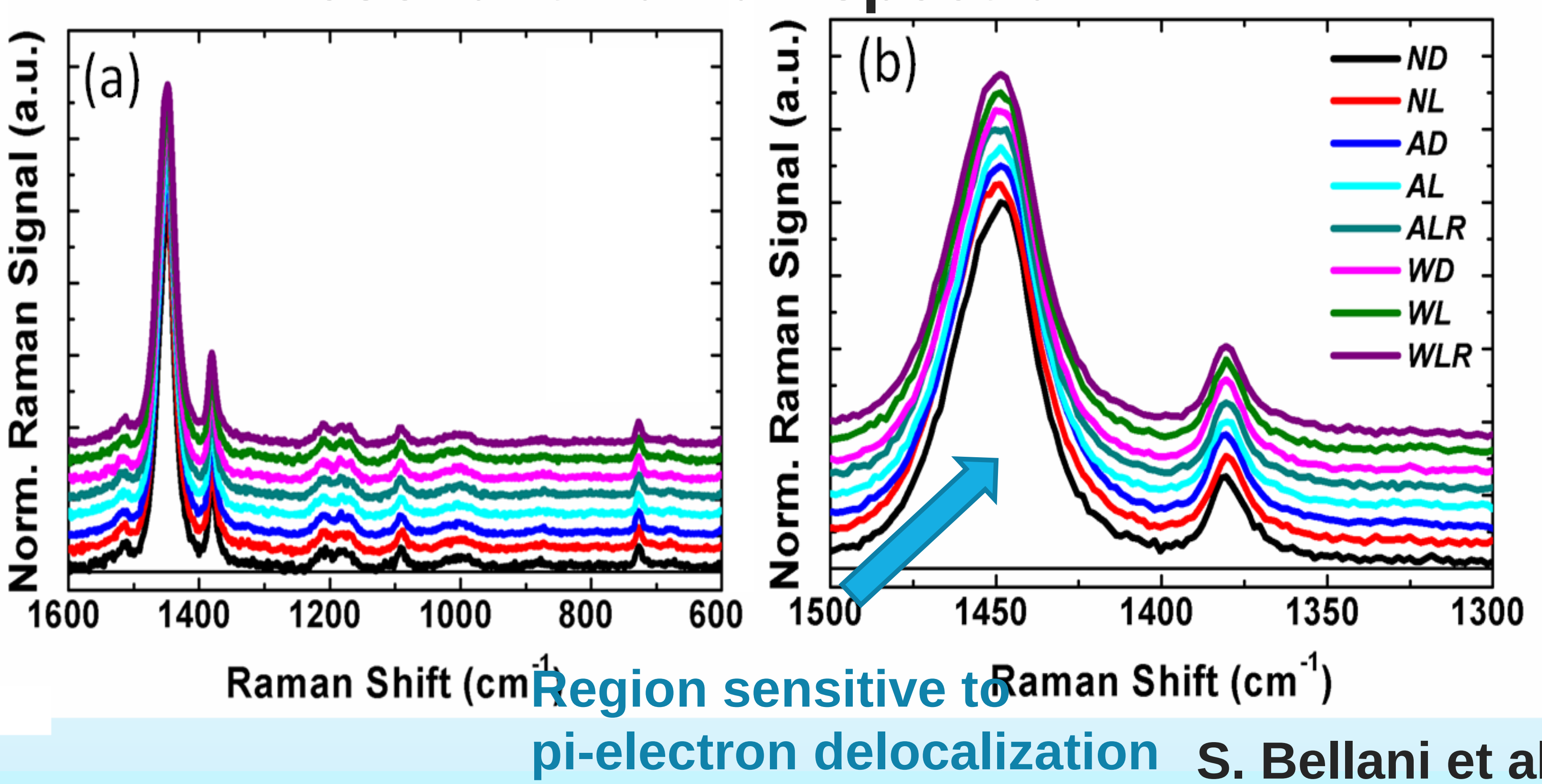
# The hybrid interface: optical spectroscopy




- Limited irreversible degradation.
- *Reversible* degradation due to the combined exposure both to oxygen and light

## Resonant Raman spectra

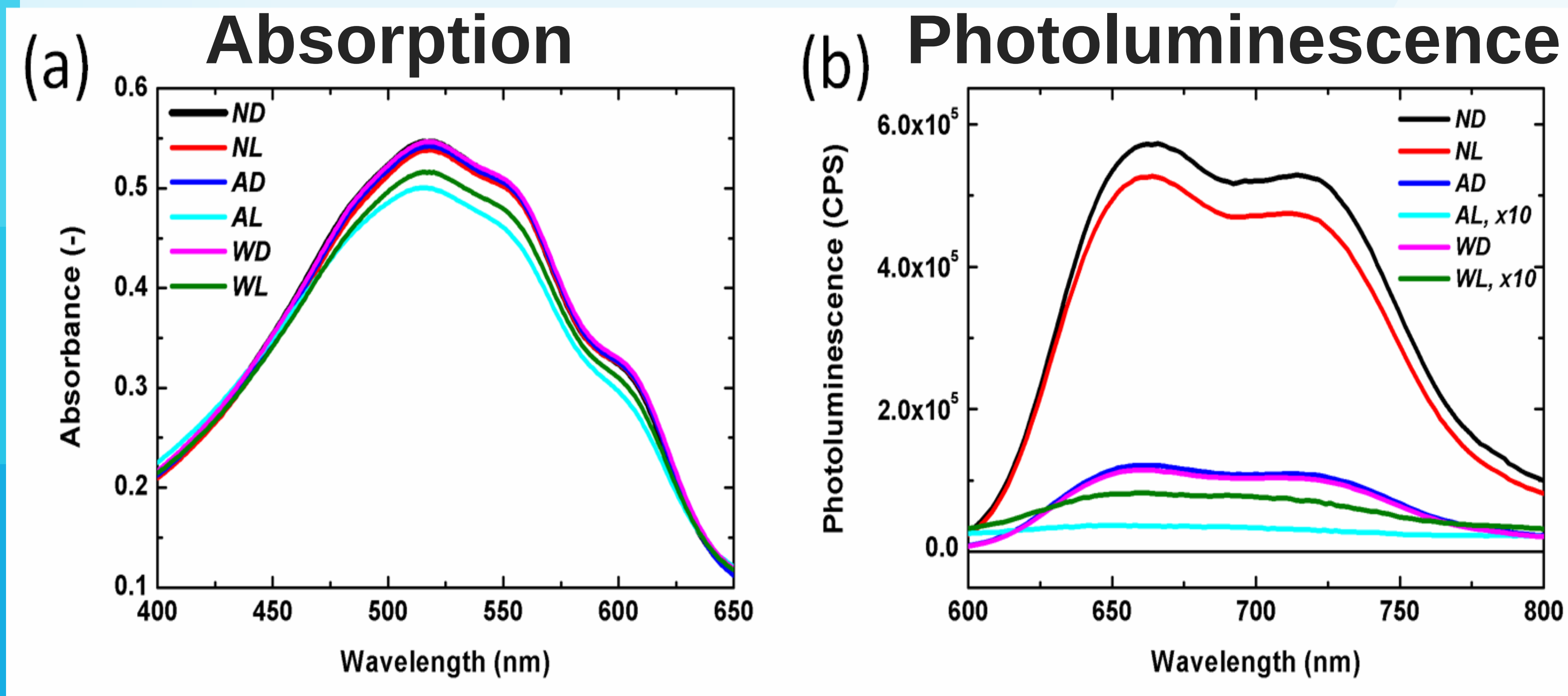



- No chain modification or conjugation break
- Reduced effect in water compared to air!

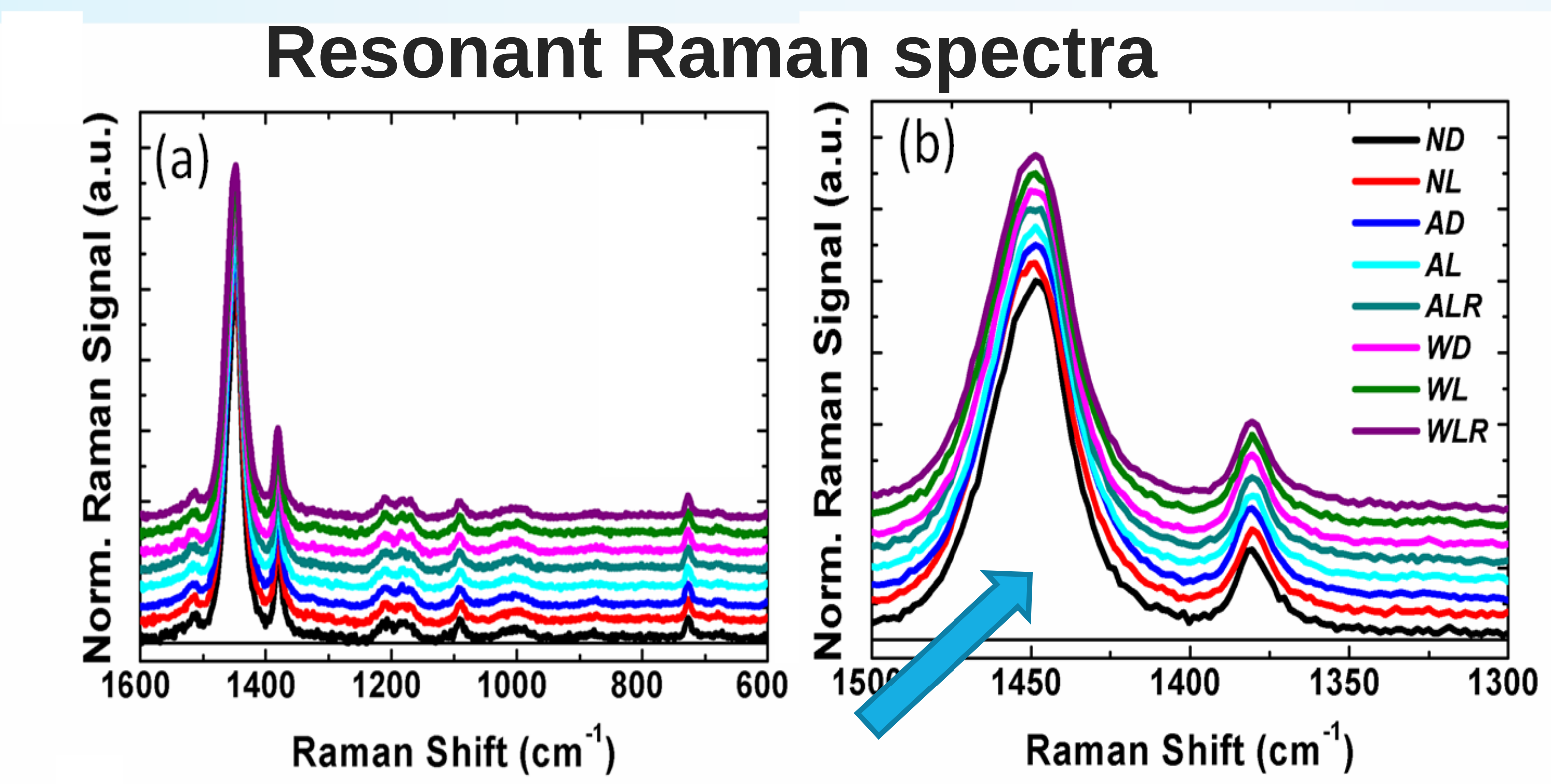
S. Bellani et al., J. Phys. Chem. C (2014)

# The hybrid interface I: optical spectroscopy






- Limited irreversible degradation.
- Huge Reversible degradation due to the combined exposure both to oxygen and light.




Region sensitive to p-electron delocalization

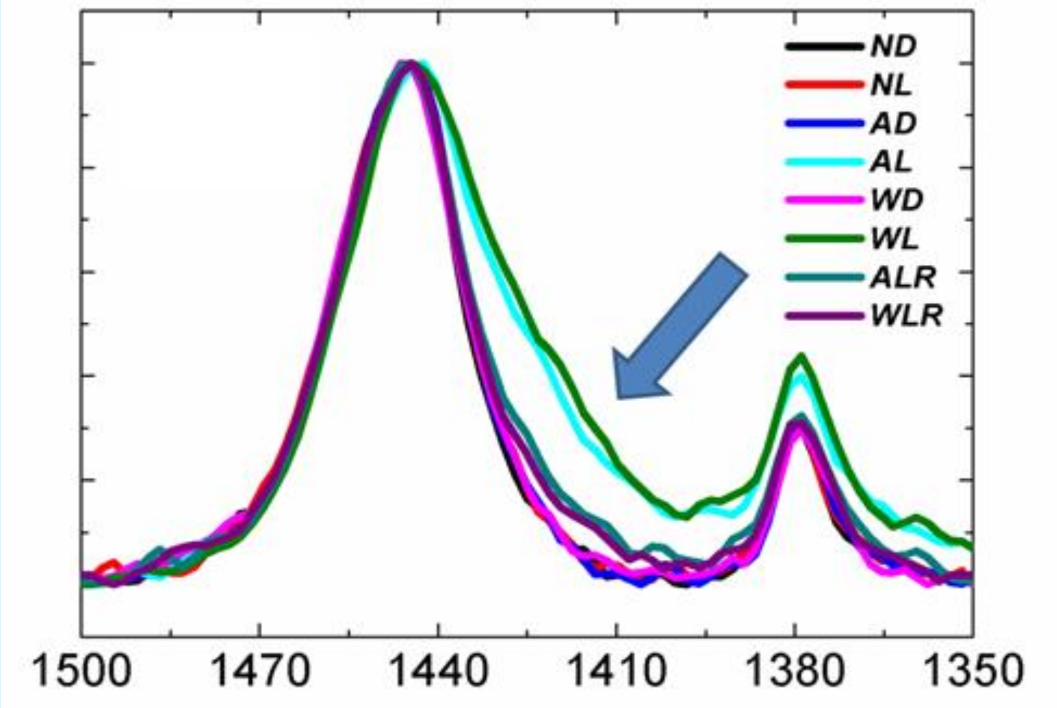
- No chain modification or conjugation break
- Reduced effect in water compared to air!

S. Bellani et al., J. Phys. Chem. C (2014)

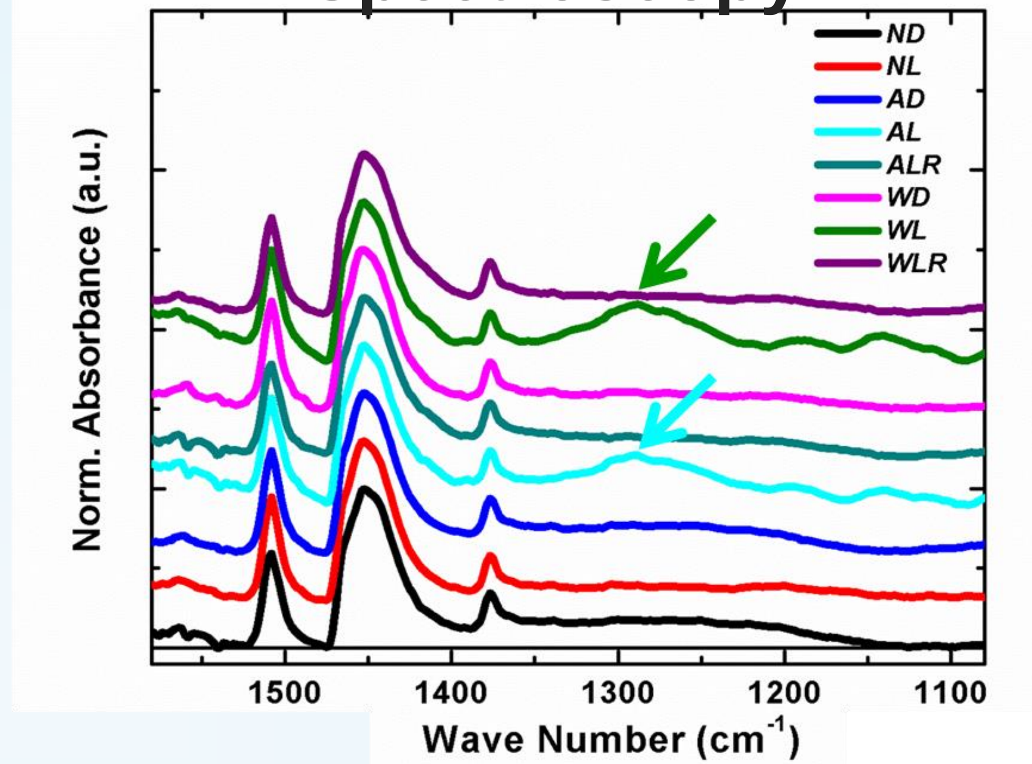
# The hybrid interface I: optical spectroscopy



## Non-Resonant Raman

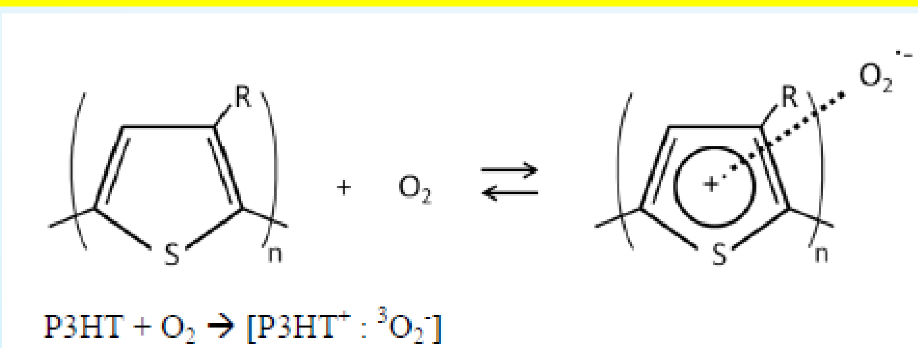


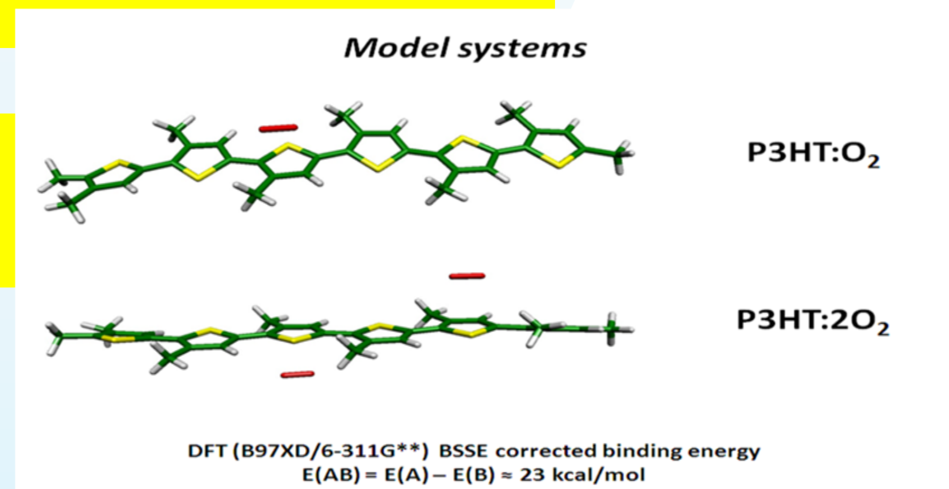

## IR Spectroscopy




- Combined action of visible light and oxygen
- Direct contact with water does not add specific degradation effects
- Reversible photoactivated doping is comparable

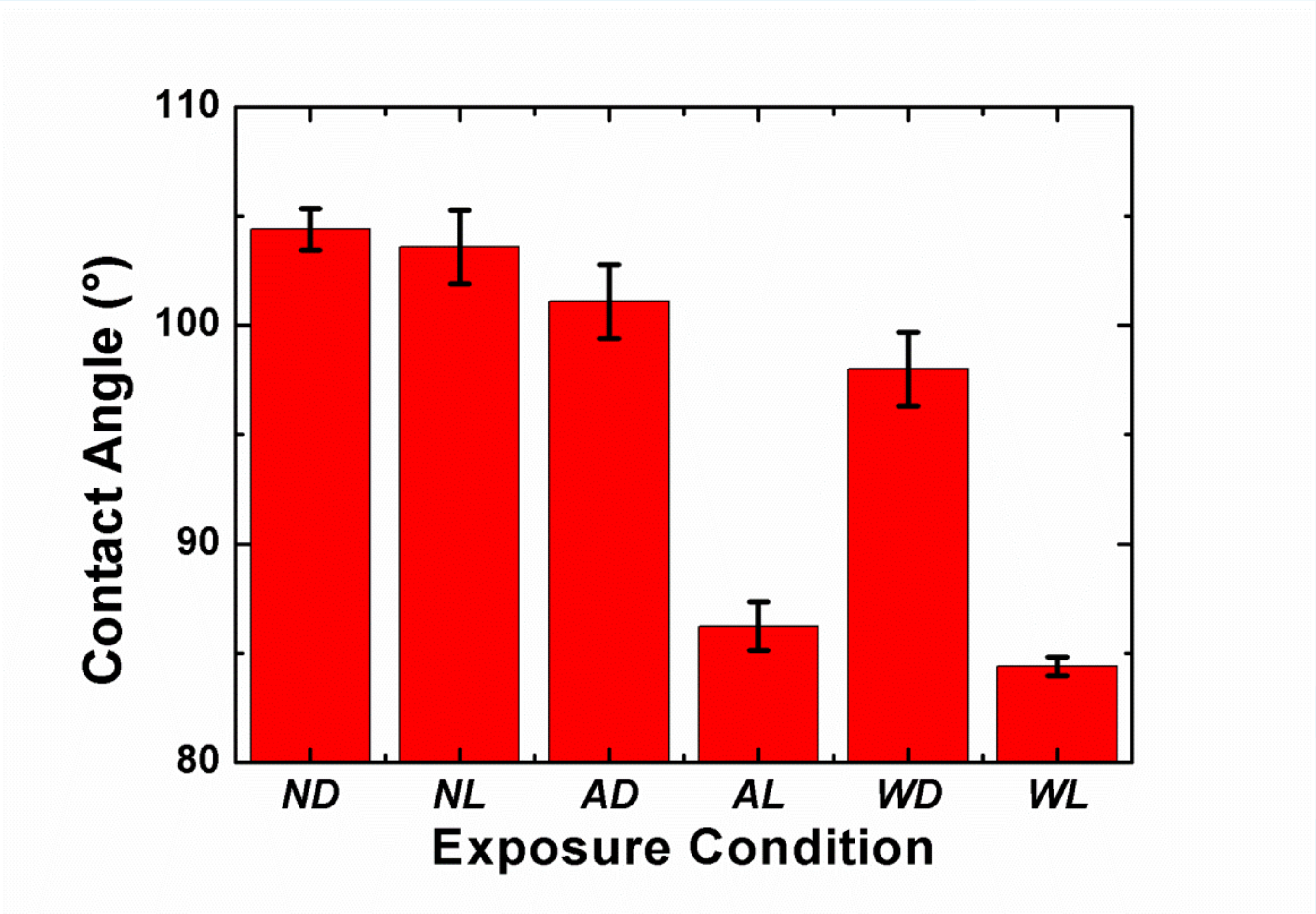
$$P3HT + O_2 \rightarrow [P3HT^+ : O_2^-]$$



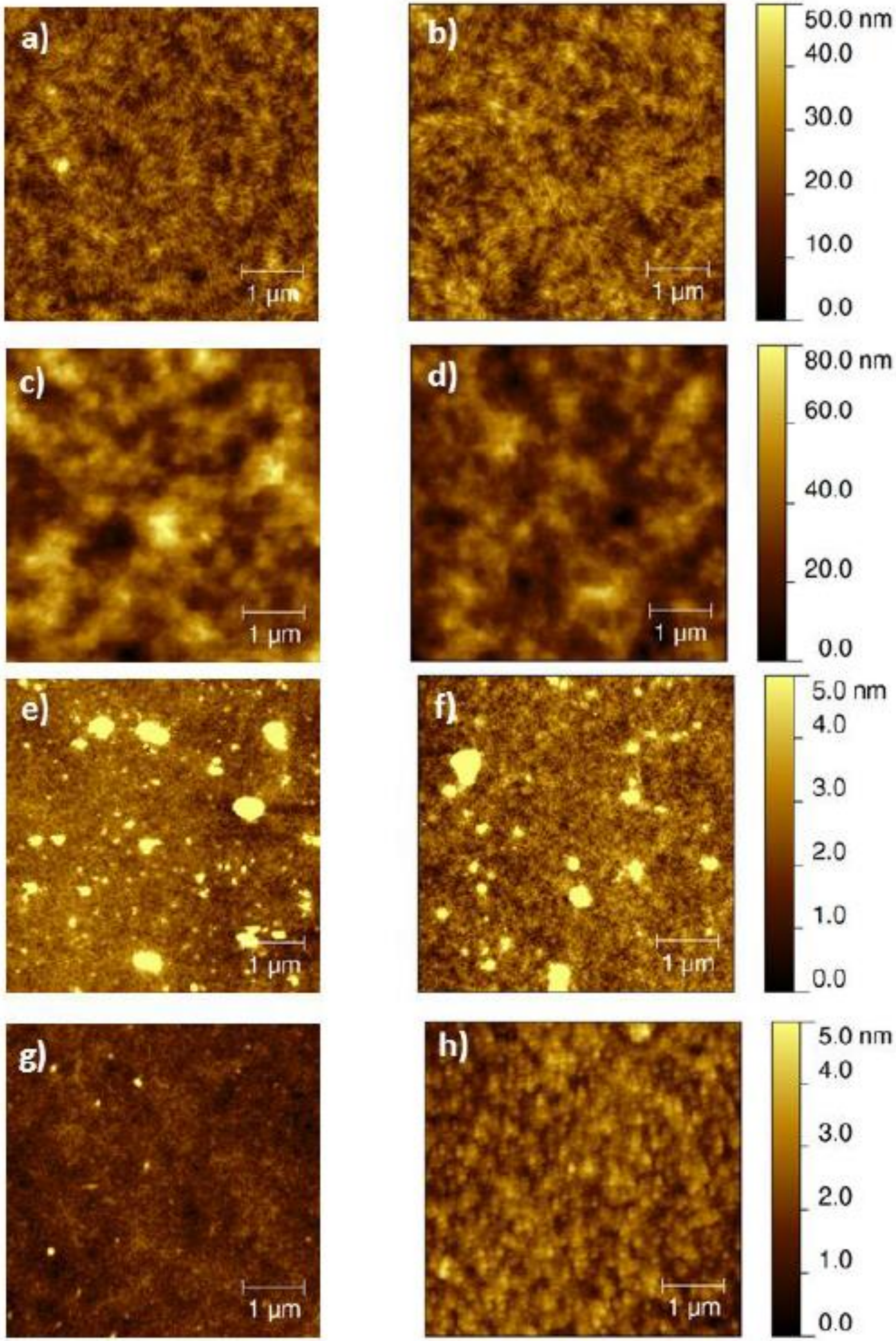

S. Bellani et al., J. Phys. Chem. C (2014)

# Contact angle measurements




Contact angles dramatically decrease (meaning a more hydrophilic surface) for COMBINED exposure to oxygen and light; no remarkable effect of water compared to air

# What about topography?



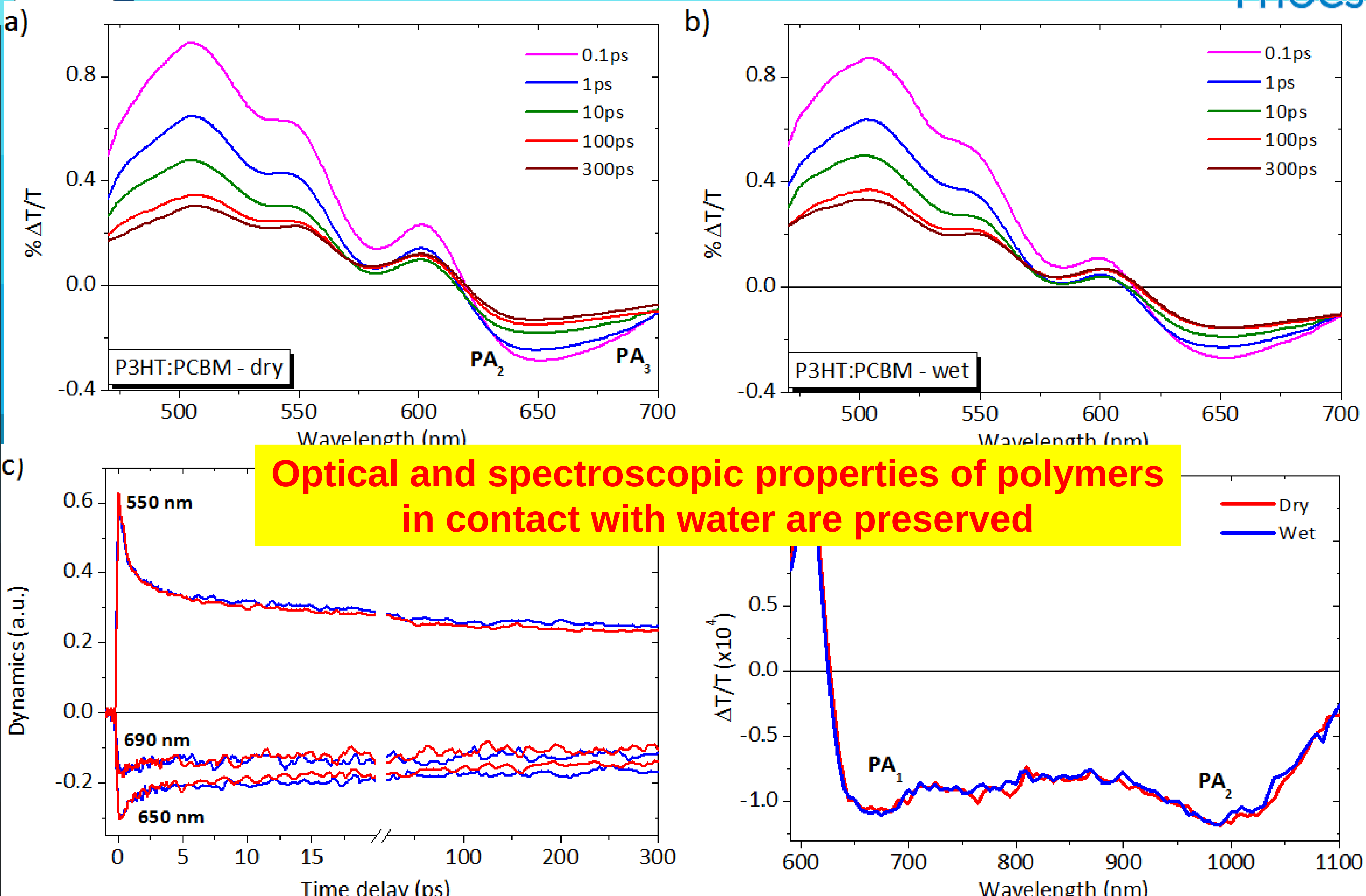

PCPDTBT

Rr-P3HT

MEH-PPV

PFO

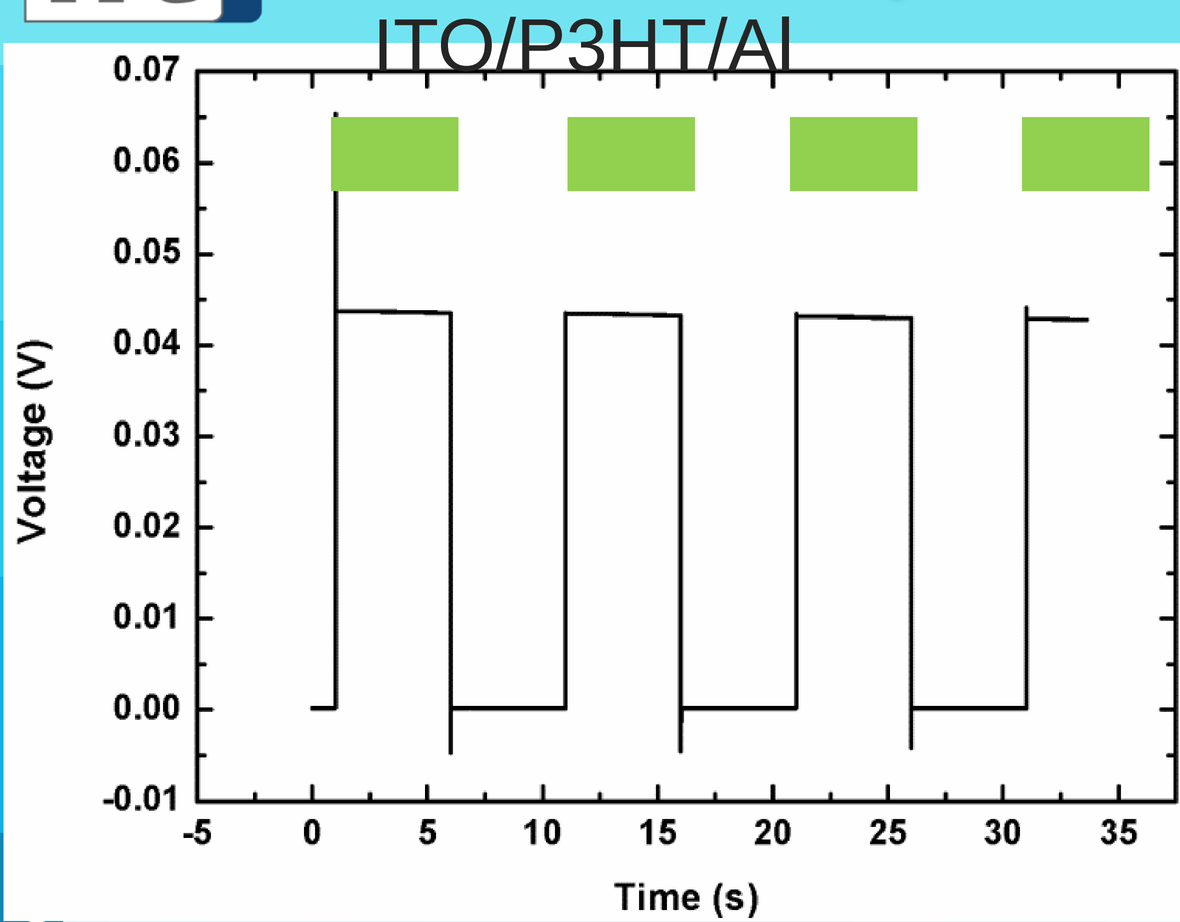
# Charge generation and recombination

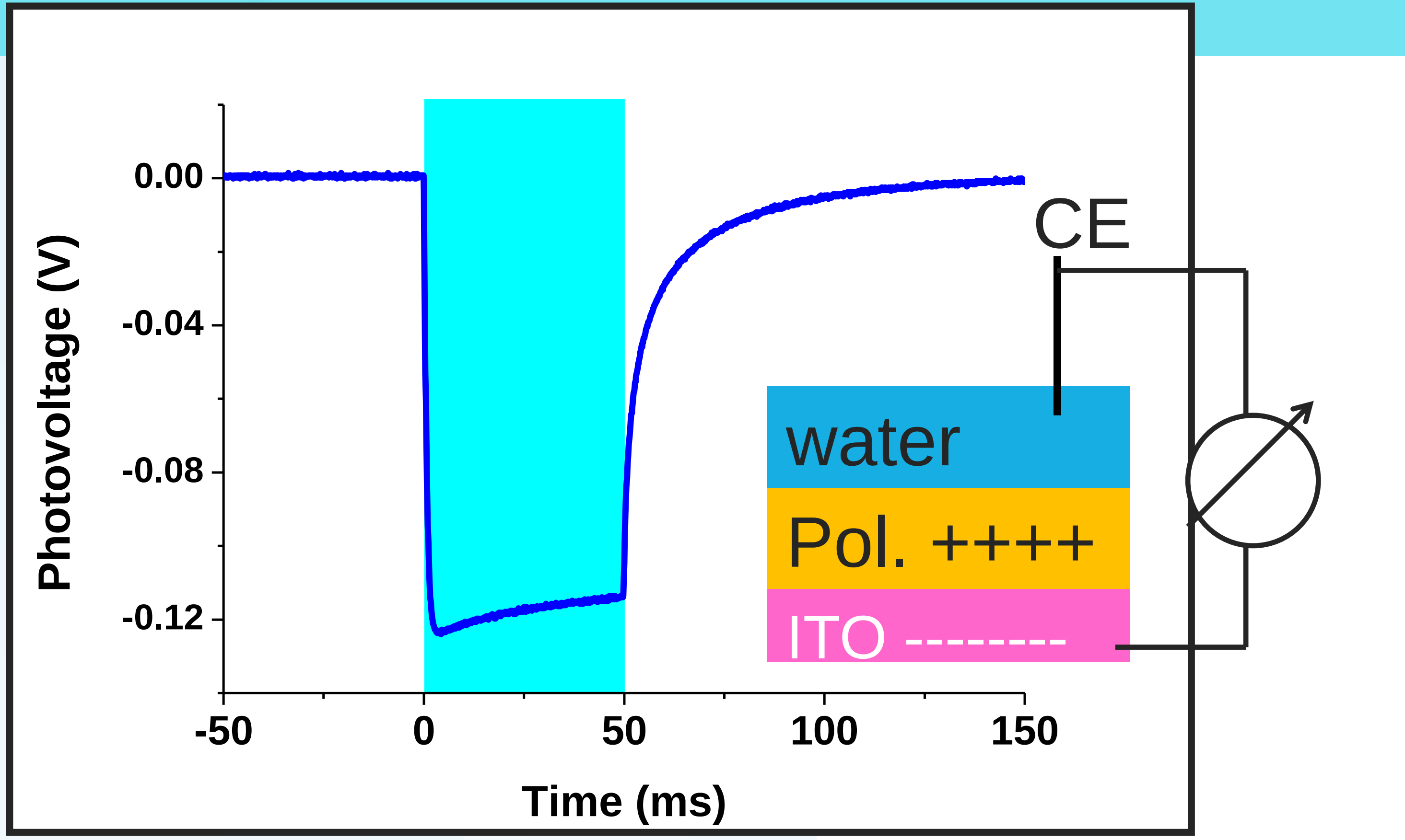



**Optical and spectroscopic properties of polymers in contact with water are preserved**

M. R. Antognazza et al., APL 2012; A. Guerrero et al., En. Environ. Sci. 2014

# Photocurrent , Photovoltage and Surface Potential

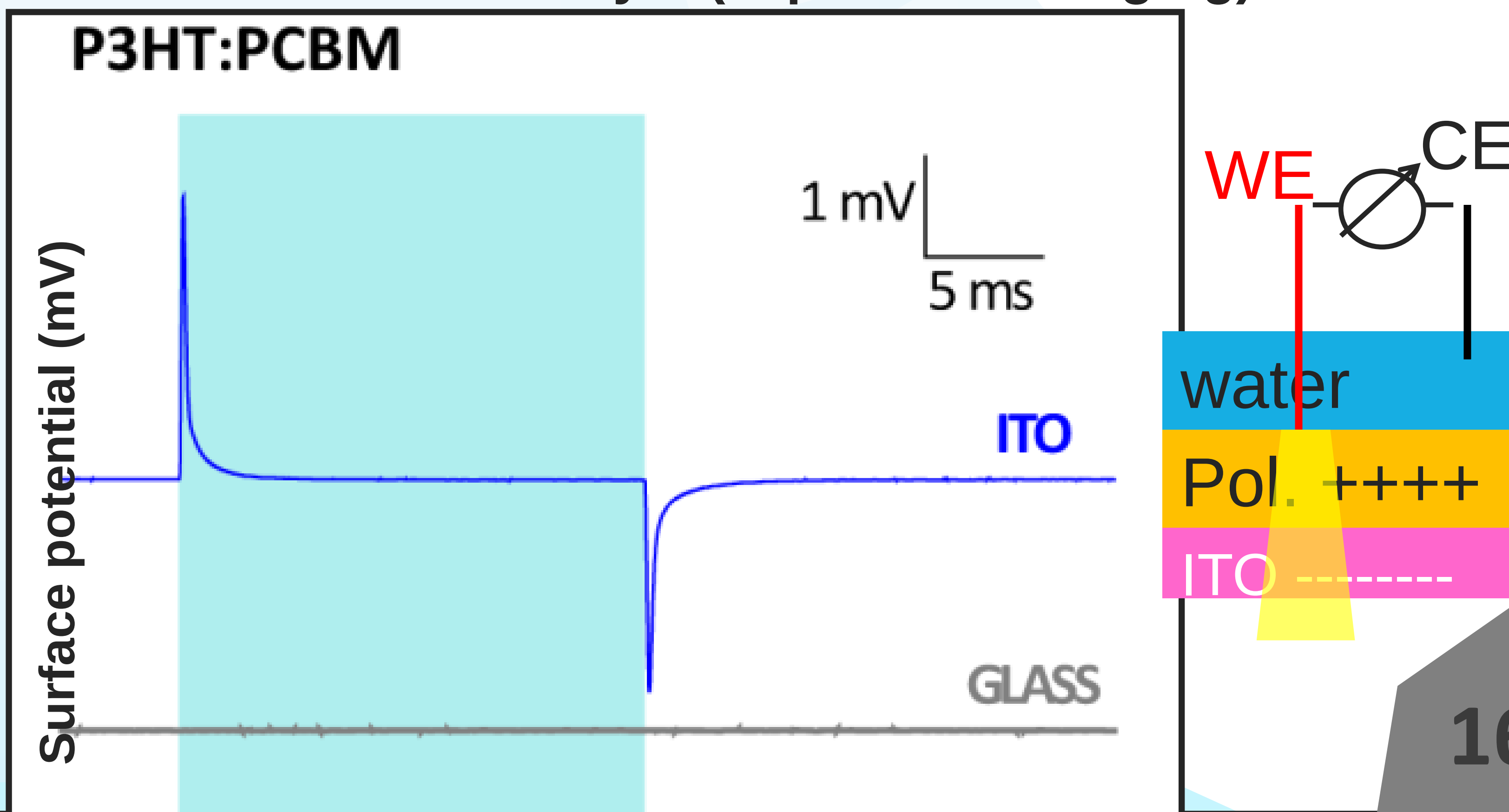



**Holes accumulate at the interface with the electrolyte (capacitive charging)**

✓Light intensity
✓**Light duration**
✓Incidence direction
✓Polymer thickness
✓Electrolyte composition
✓ pH
✓ Blend Morphology and phase segregation

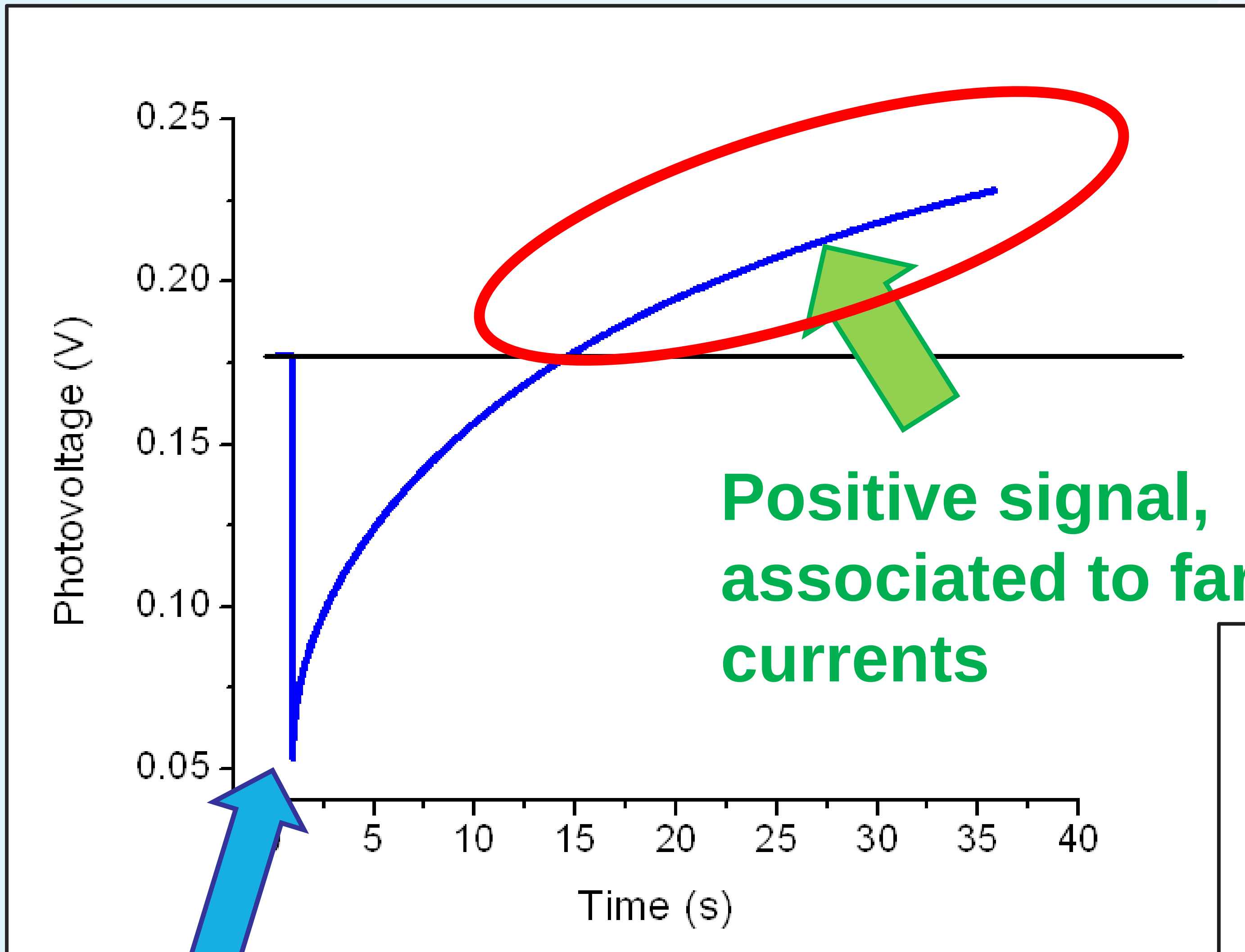
......still work in progress




1- Water effect on polymer prop

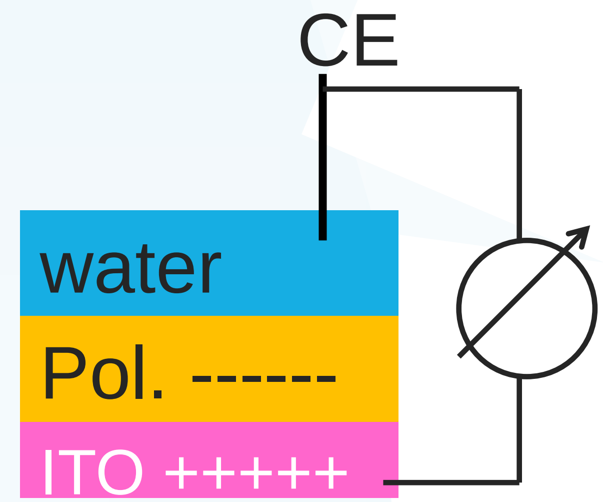
# Charge extraction: Photocurrent  and Photovoltage

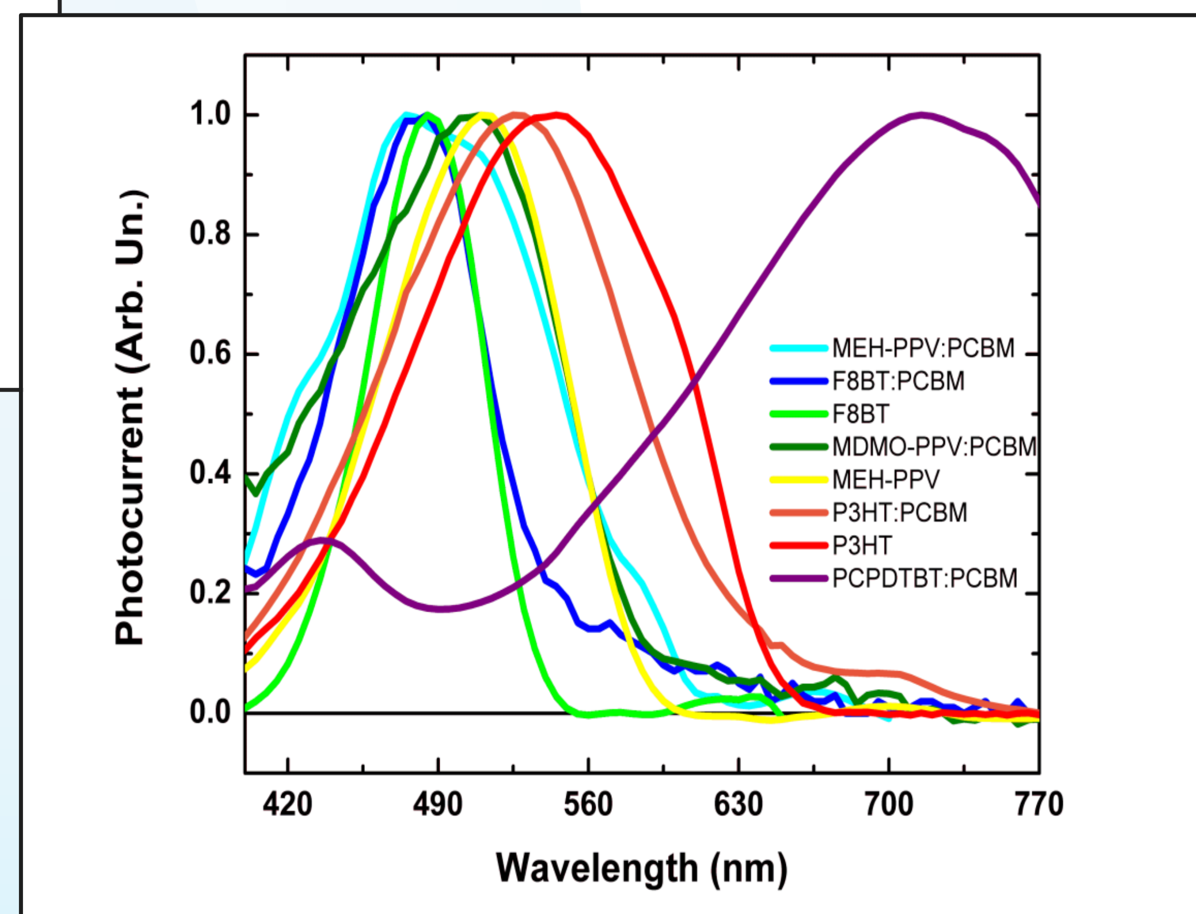





**Positive signal, associated to faradaic currents**

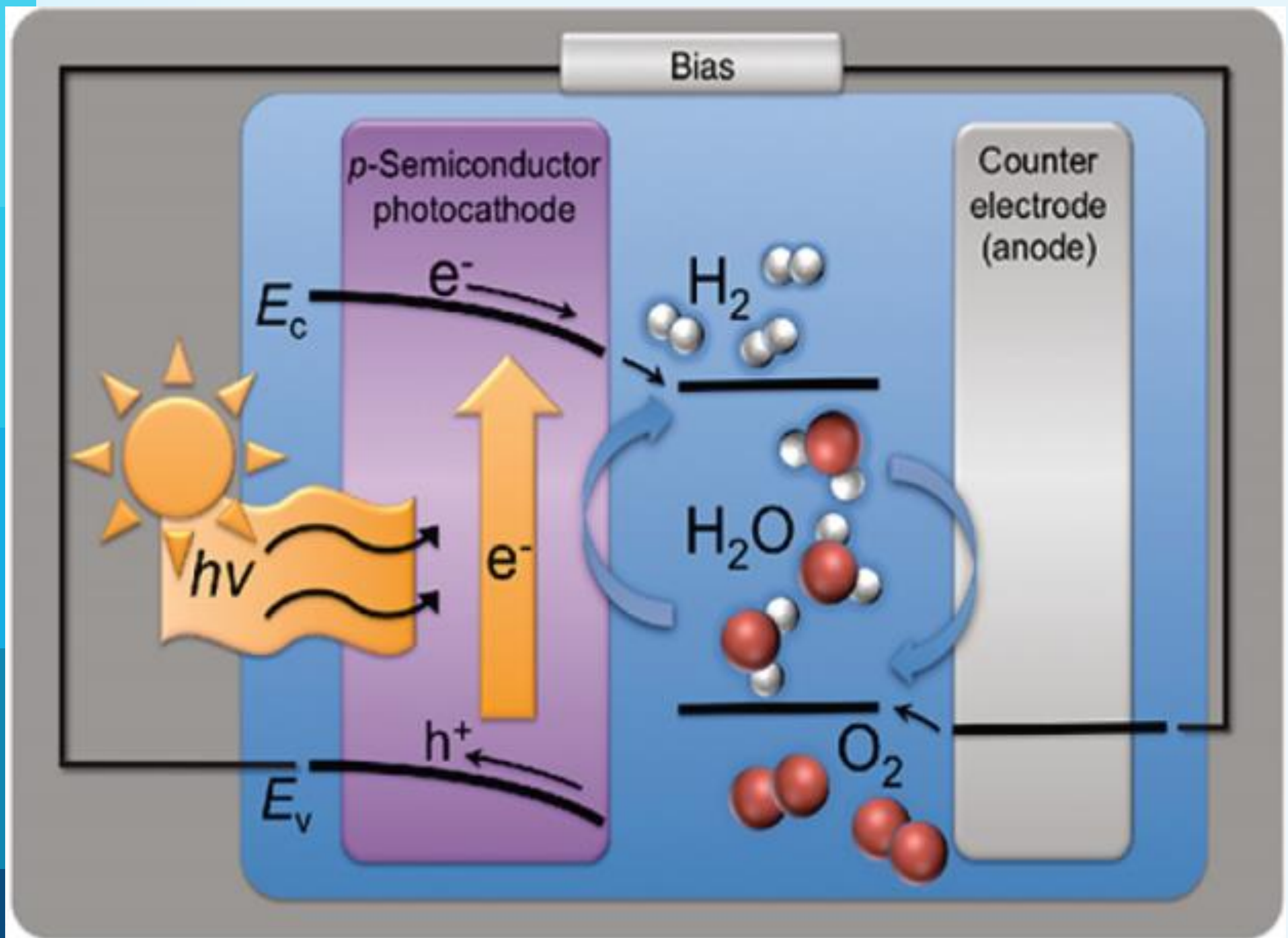
**Capacitive peak**




**E. Lanzarini et al., J. Phys. Chem. C 2012; S. Bellani, M. Porro, N. Martino et al., in preparation; A. Guerrero et al., Energy & Environmental Science 2014**

# PEC cells

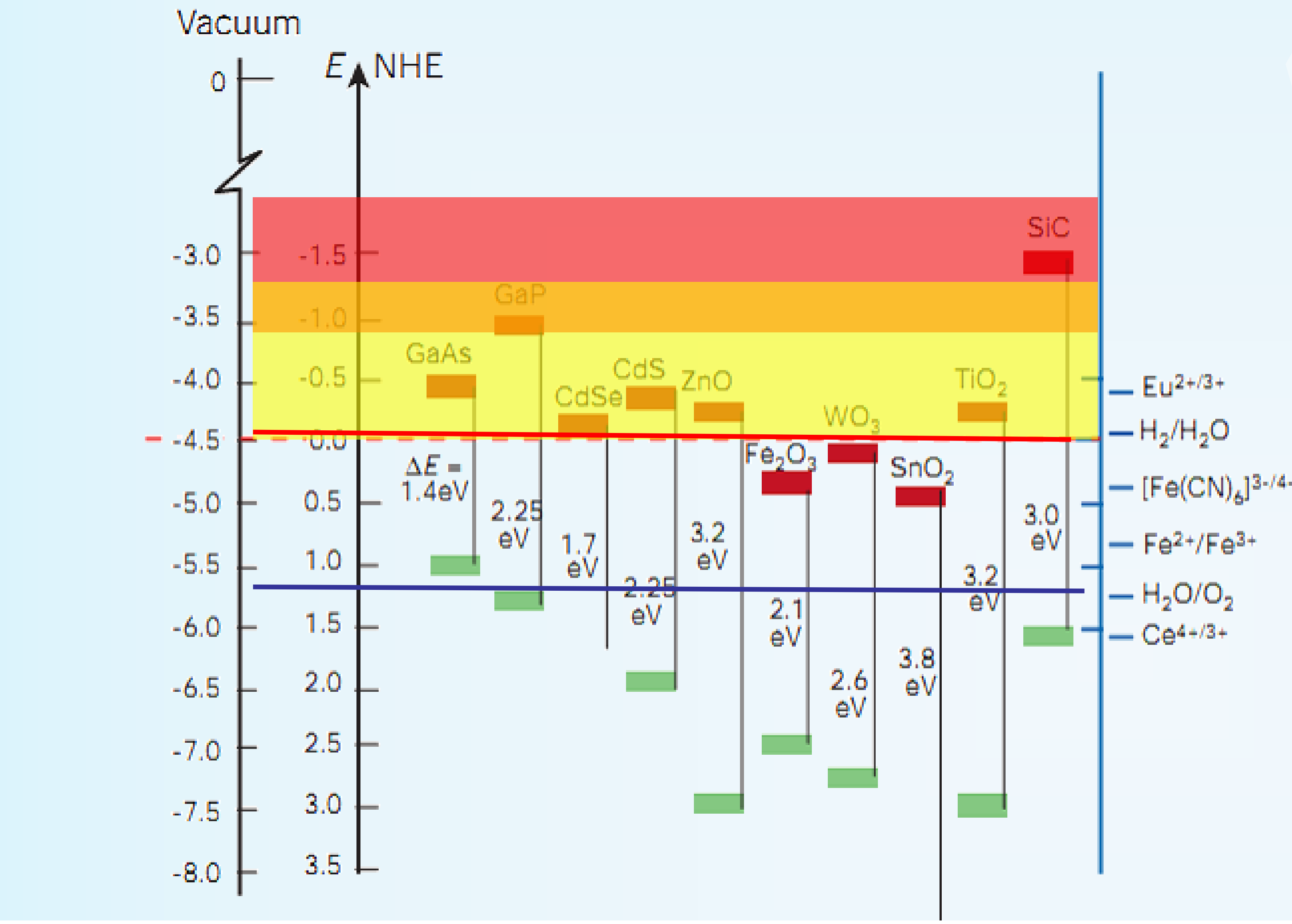


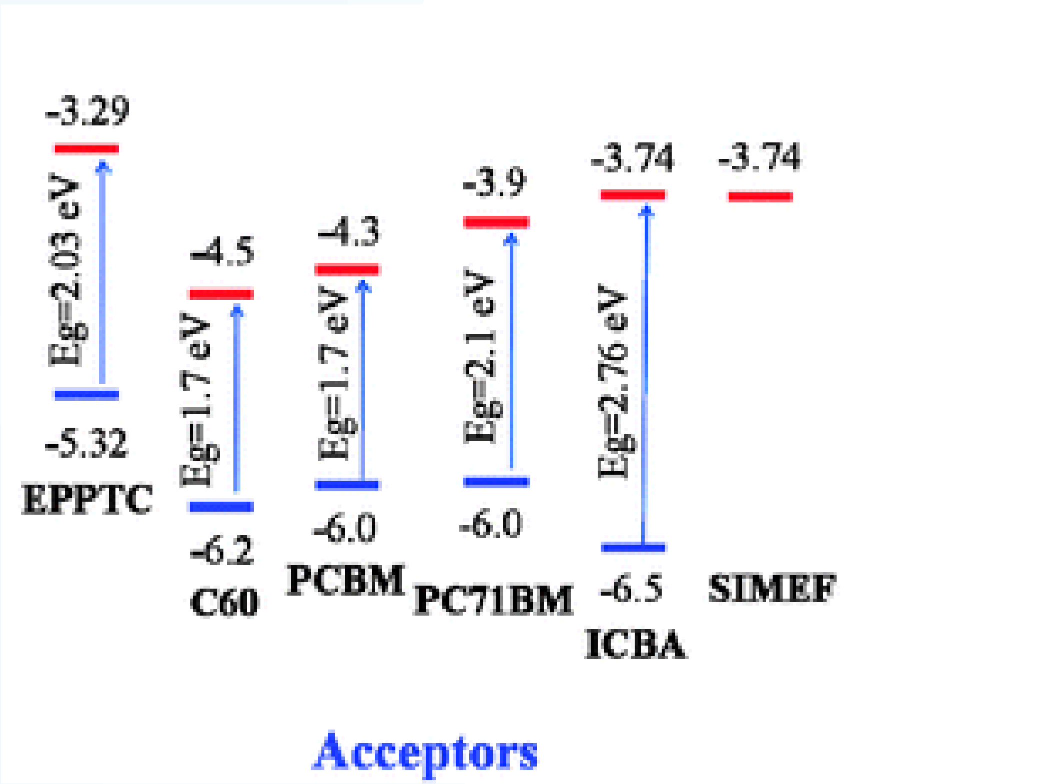

***Requirements:***

- ✓ suitable band alignment
- ✓ band gap 1.8-2.1 eV for full WS
- ✓ photoelectrochemical stability
- ✓ low cost, scalable device

***Great challenge for material scientists!***

# The perfect material…not yet found

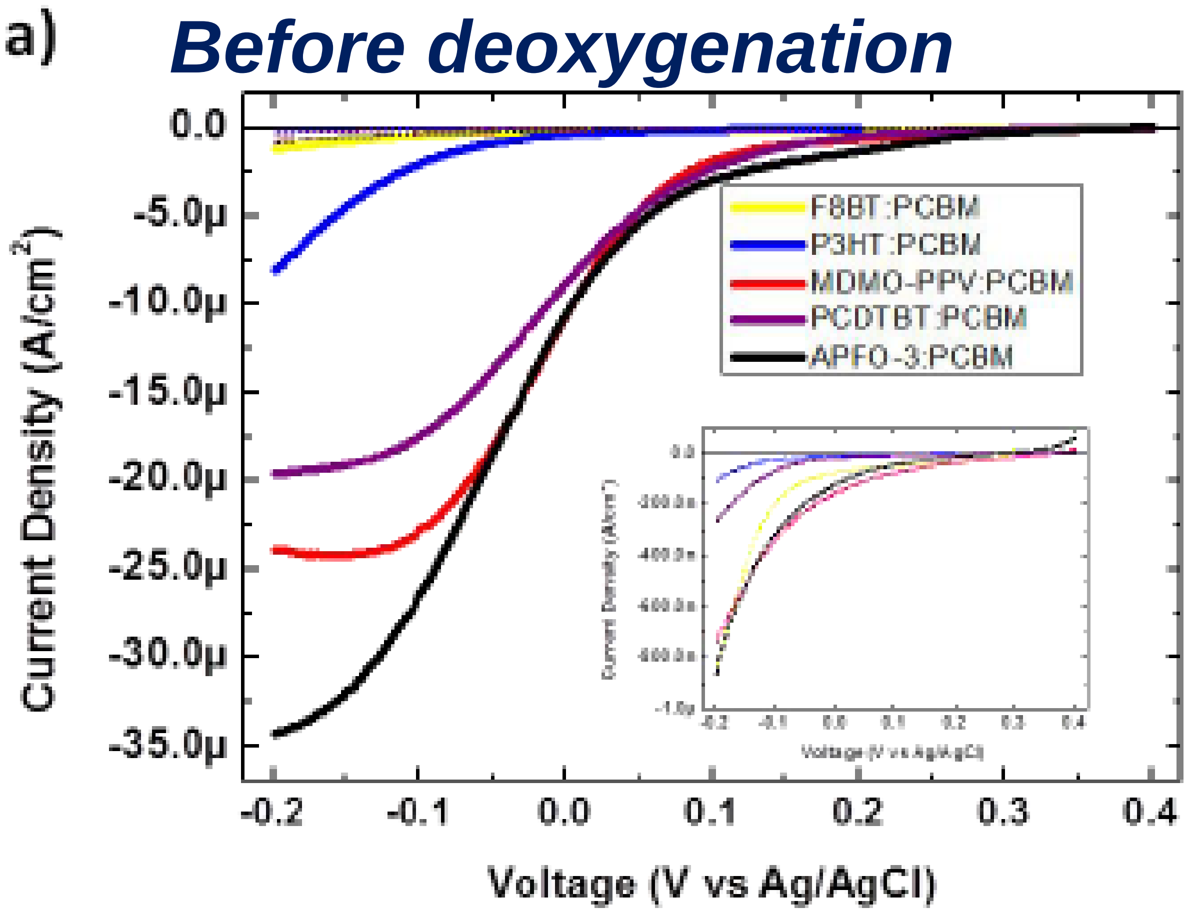


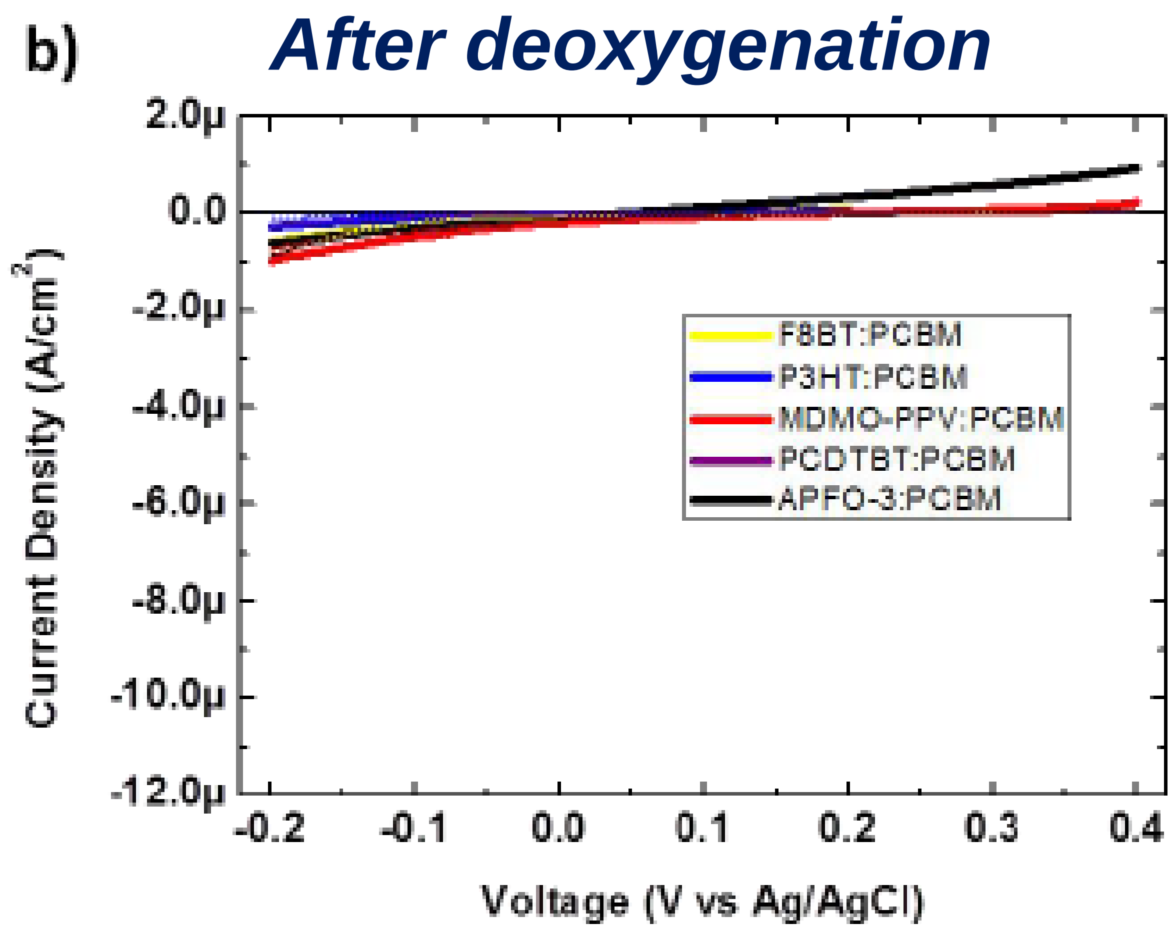



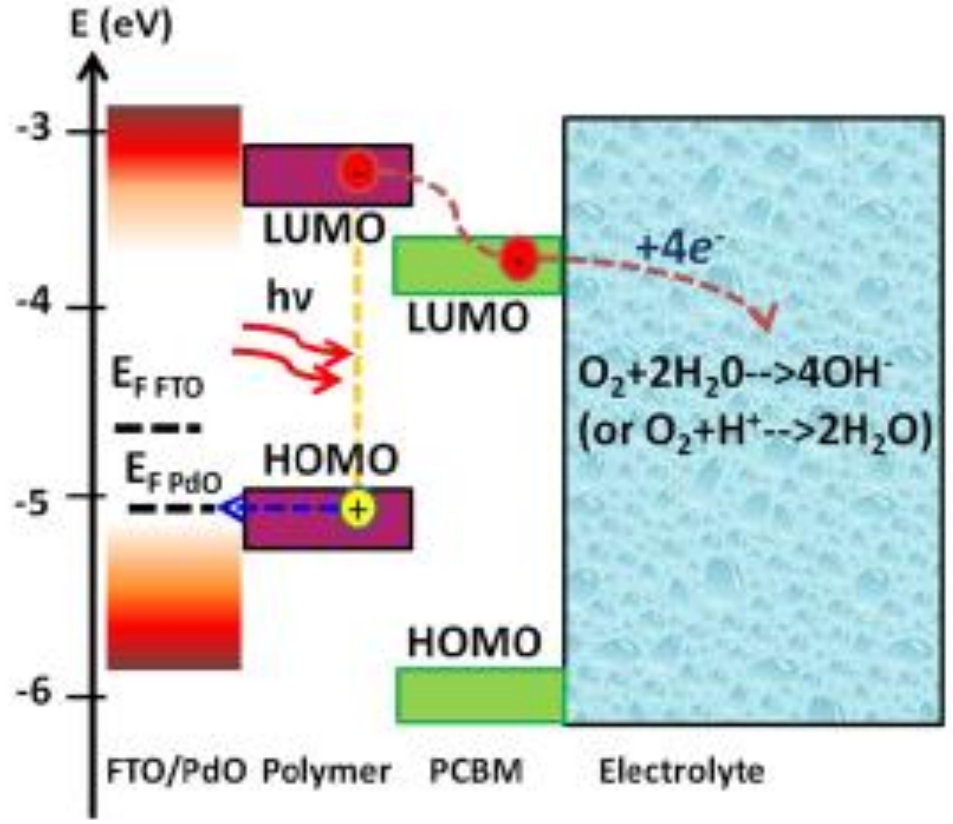


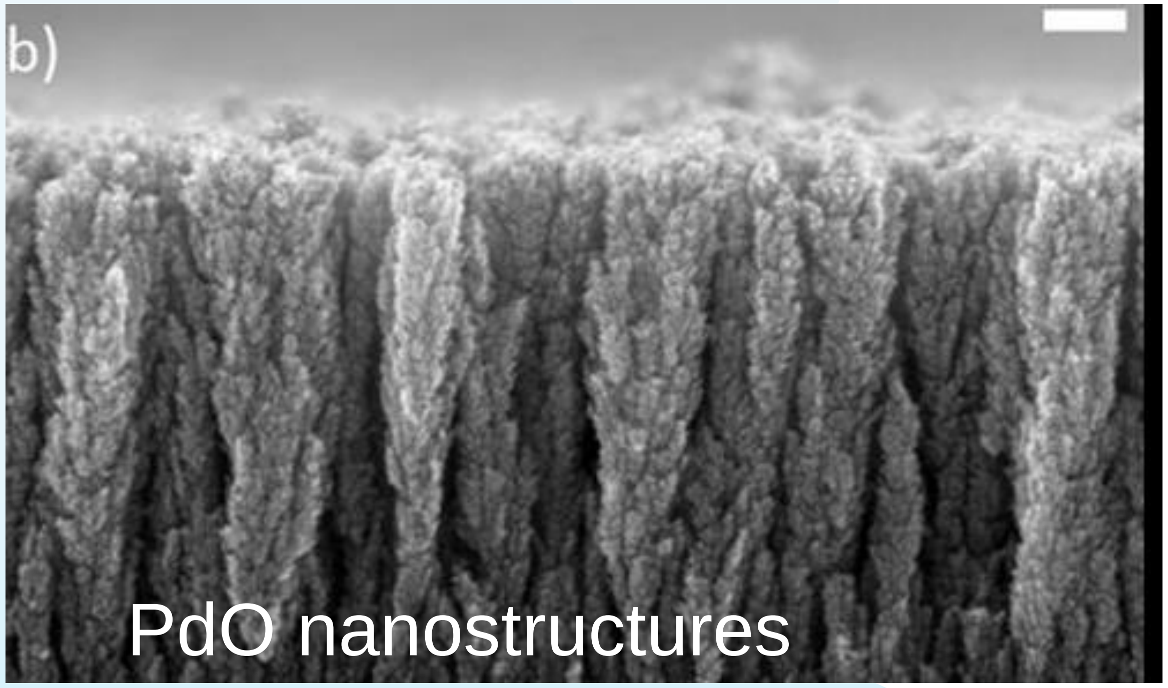
**Let's give CP a chance as new photocathodes!**

# Oxygen counts

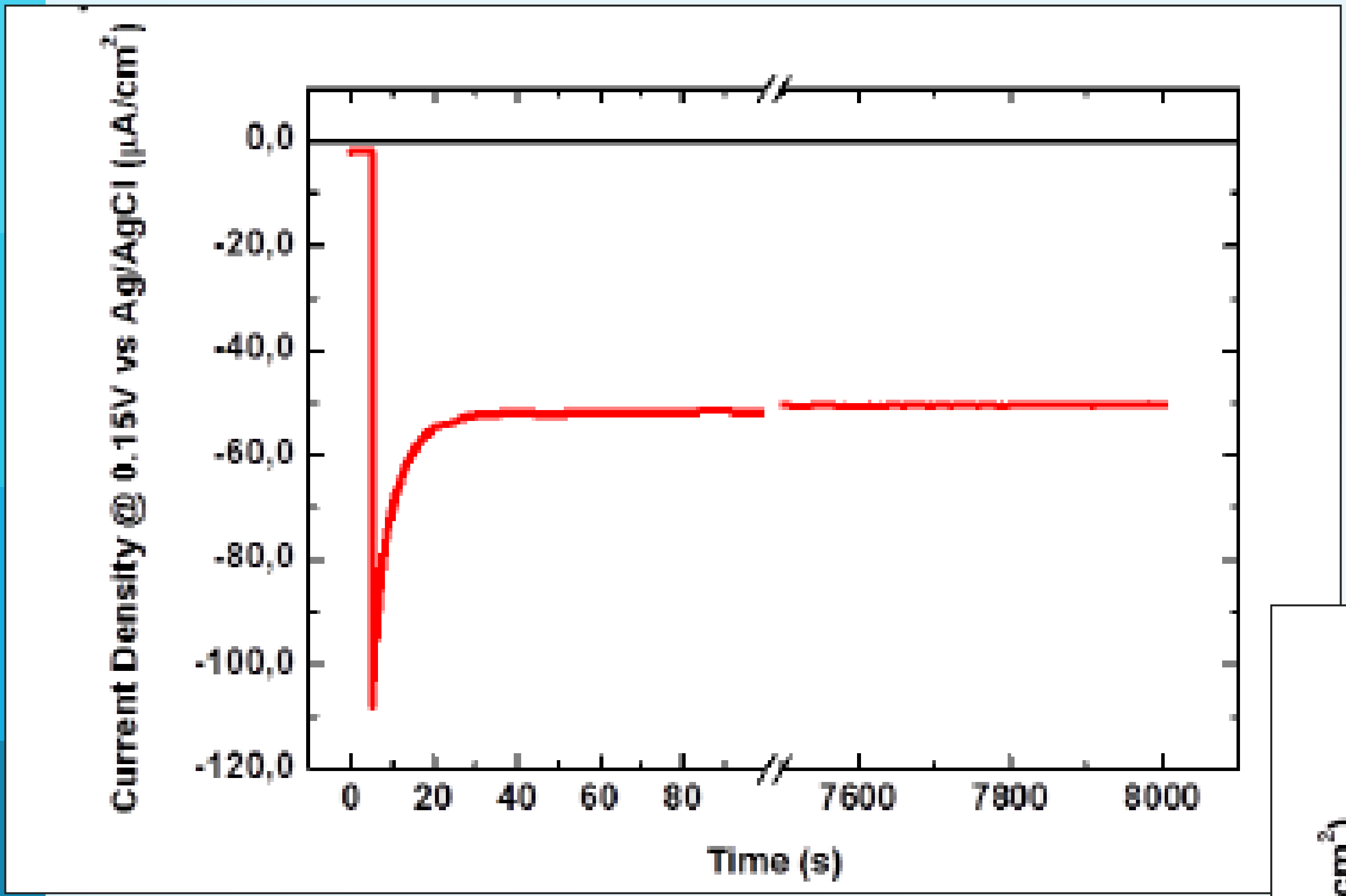


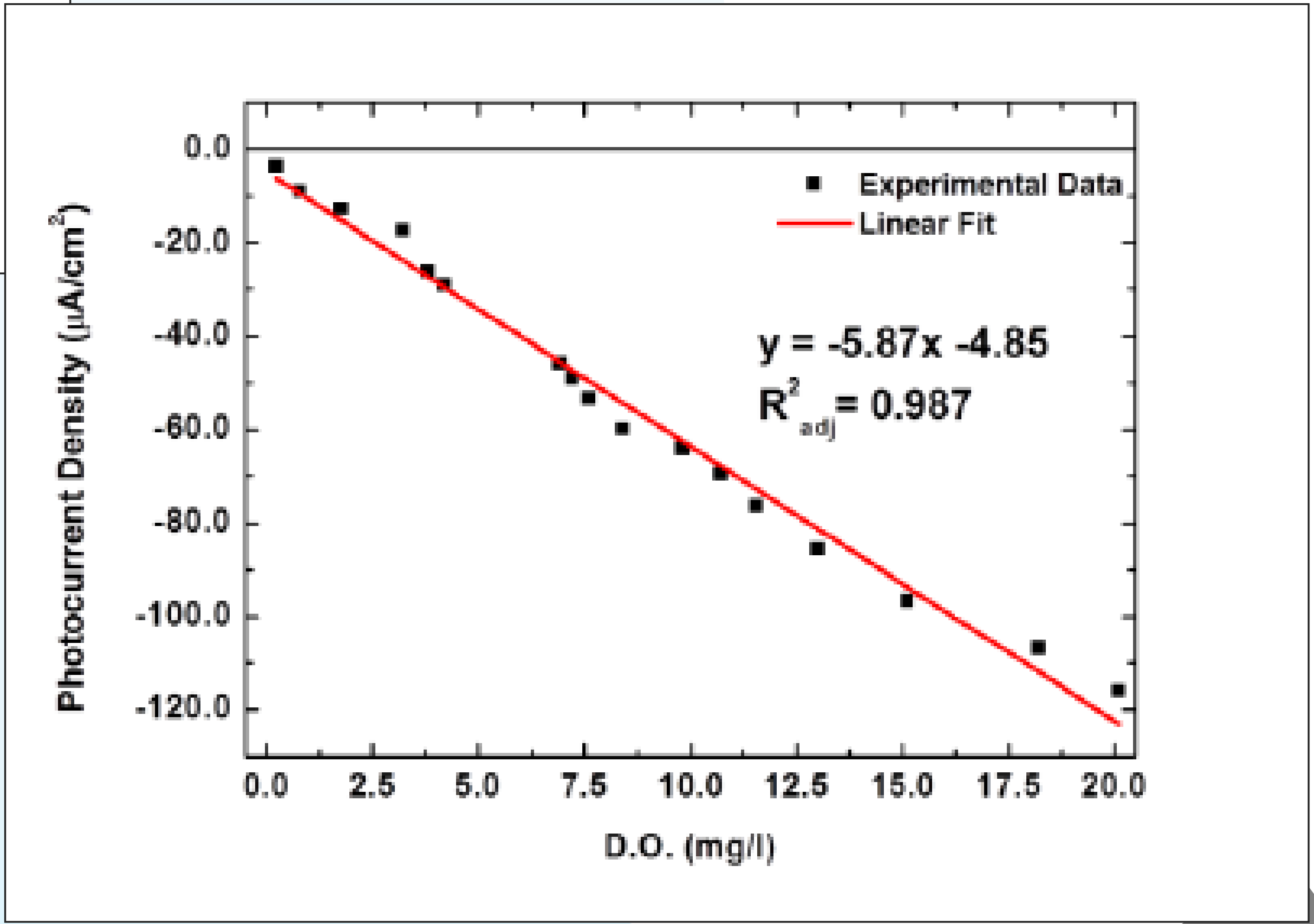



# Photoelectrochemical sensor for dissolved oxygen




Stability >2h continuous operation;
Sensitivity: -5.9 uAcm$^{-2}$/ppm;
Very low background signal;
Possibility of operation at different pH

*S. Bellani et al., Adv. Funct. Mater. 2015*

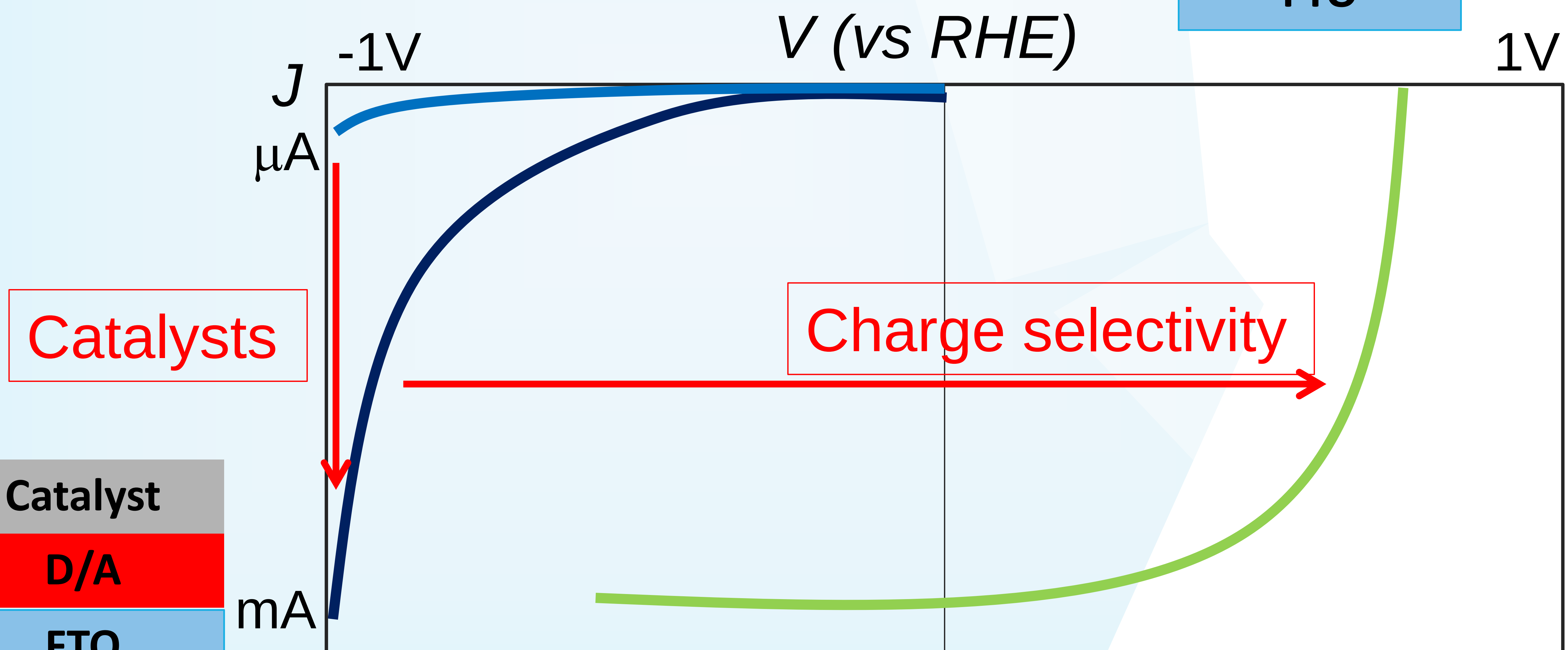
# The roadmap

*INTERFACIAL LAYER*

**Polymer as *PHOTOCATALYST***

| |
|---|
| D/A |
| FTO |

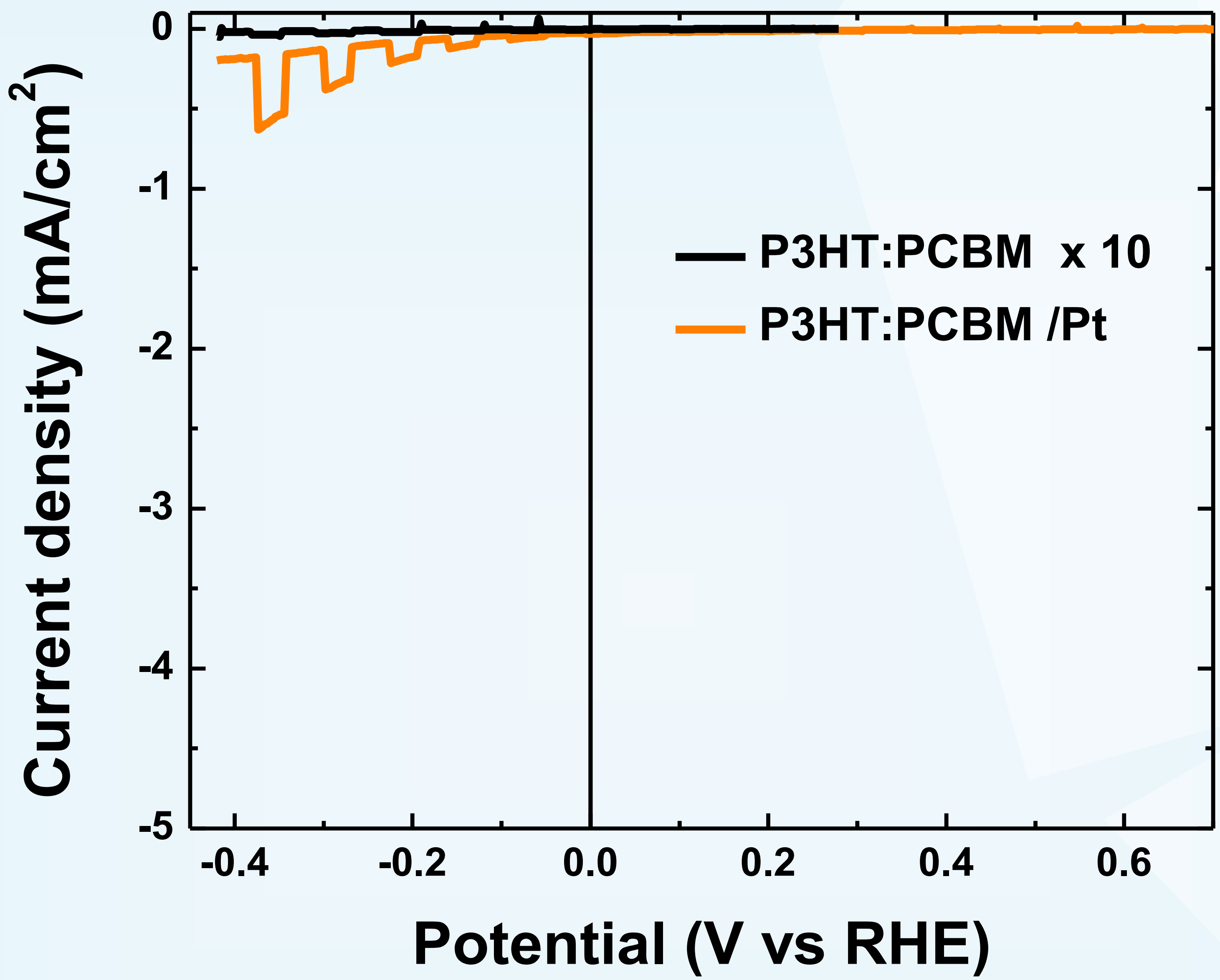
| |
|---|
| Catalyst |
| ESL |
| D/A |
| HSL |
| FTO |




| |
|---|
| Catalyst |
| D/A |
| FTO |

**Polymer as *CO-CATALYST***

# Towards hydrogen production (i)

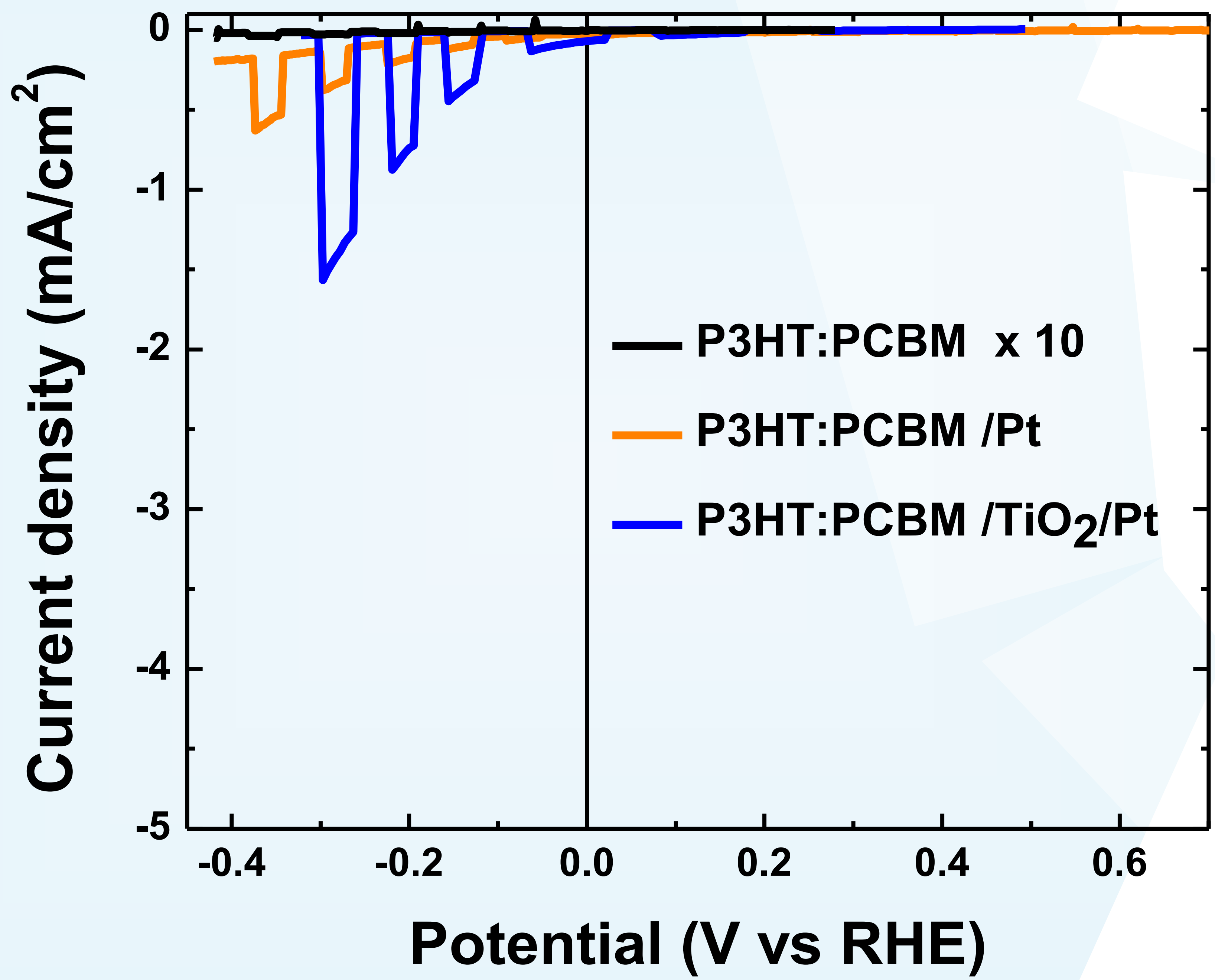



*1- Conjugated polymers as catalysts:* negligible current

*2- Conjugated polymers & Platinum:* current slightly increases, but onset potential is negative

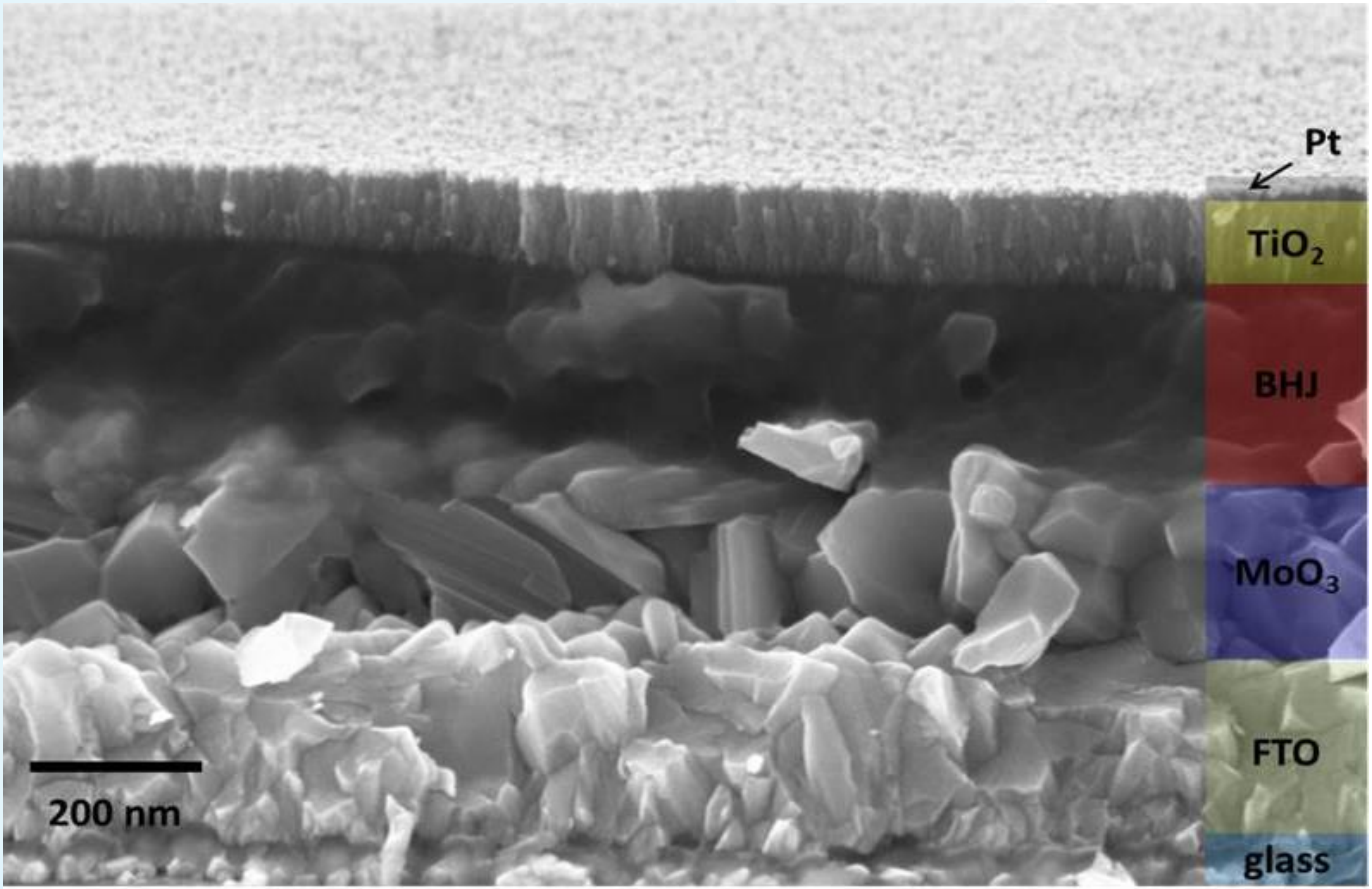

*M. R. Antognazza et al., APL 2012; E. Lanzarini et al., J. Phys. Chem. C 2012; A. Guerrero et al., En. Environm. Sci. 2014*

# Towards hydrogen production (ii)



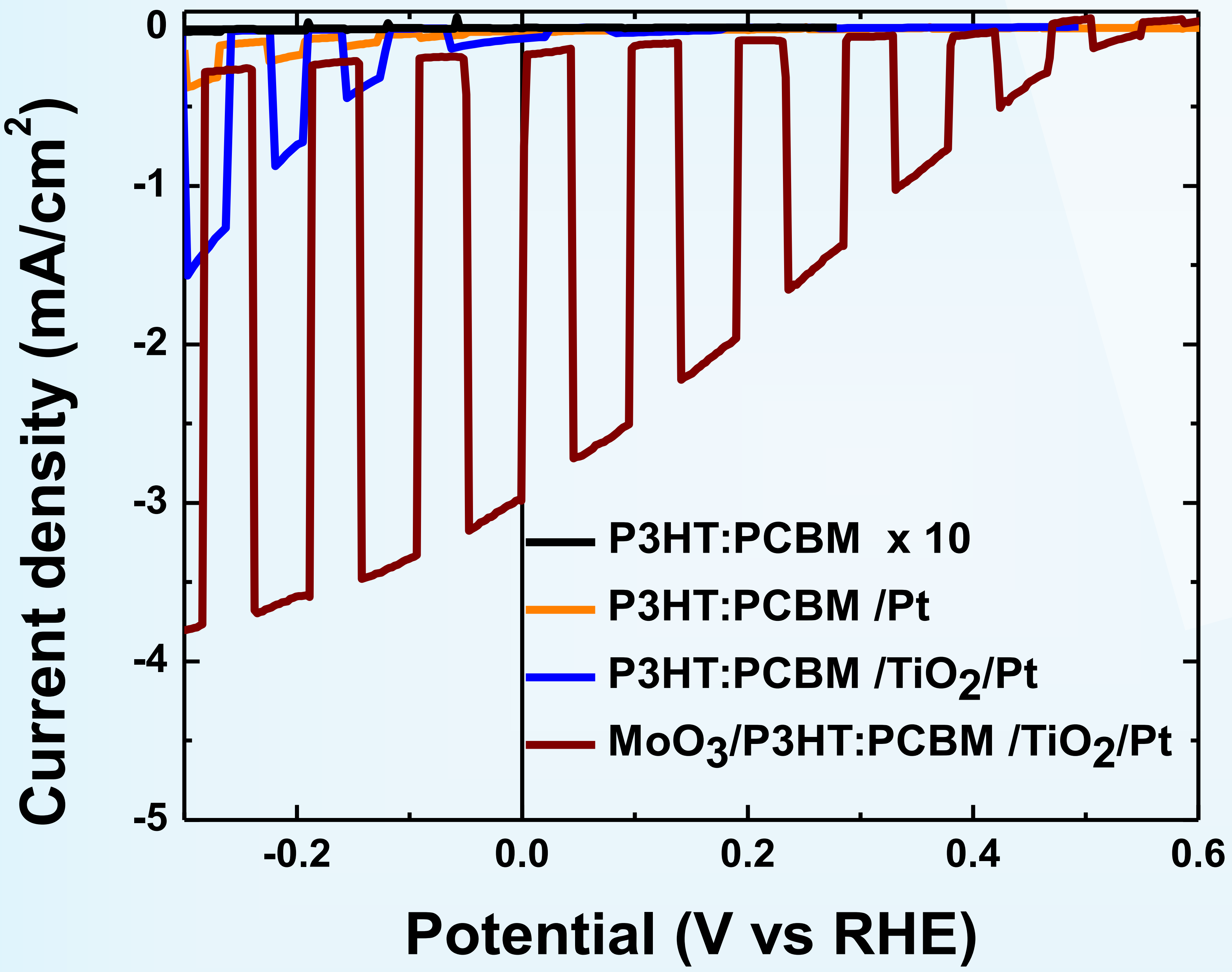

*3 - Introduction of the ESL:* further increase in the current, but onset potential is still negative

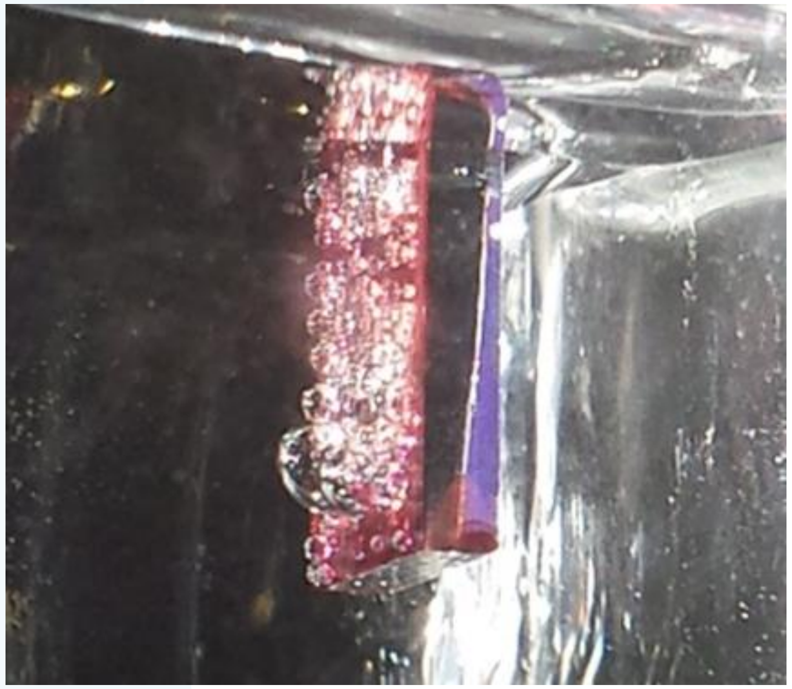
# Towards hydrogen production (iii)




*F. Fumagalli et al., submitted*

# Efficient hydrogen generation

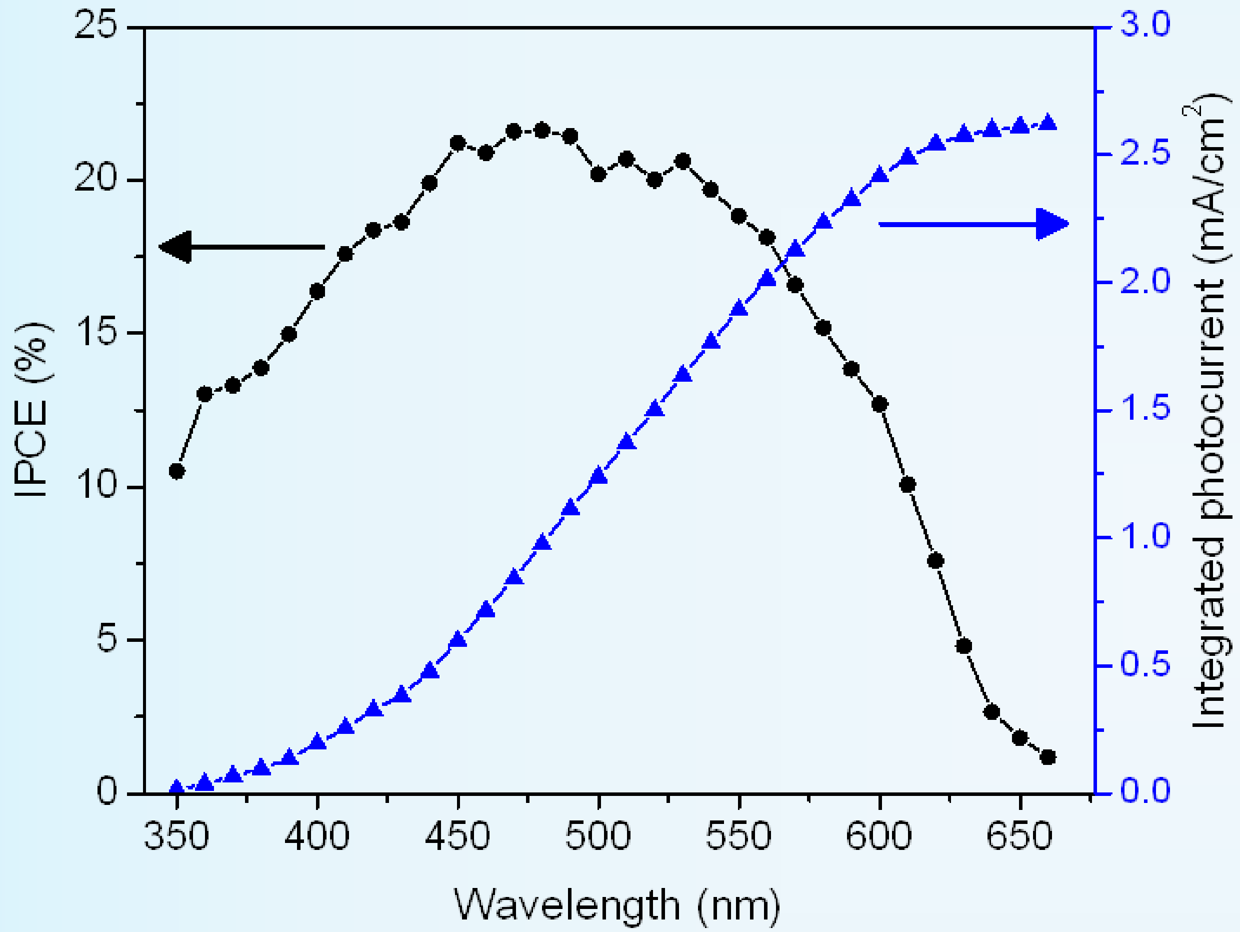


*F. Fumagalli et al., submitted*

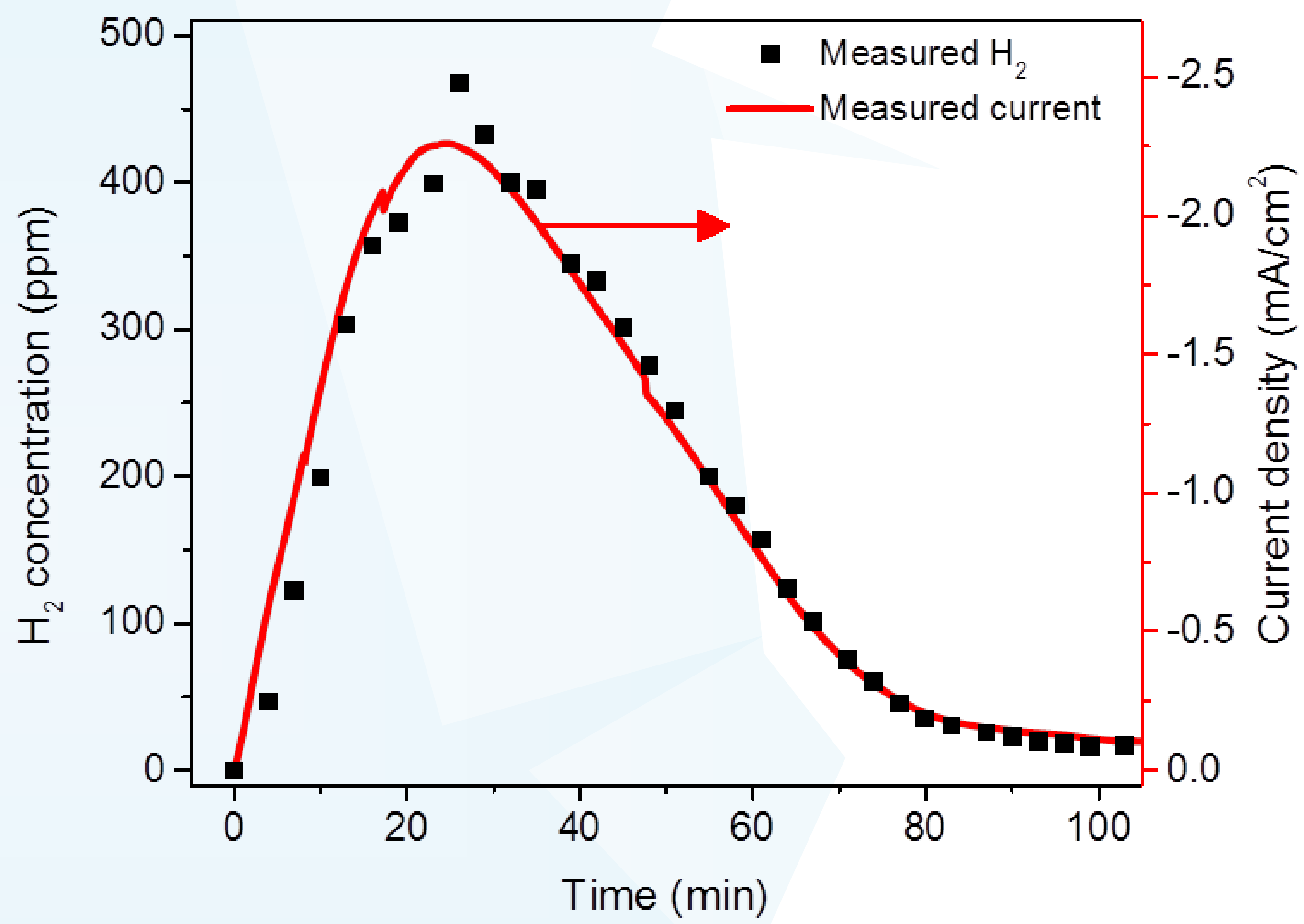
# Photocathode characterization

## IPCE



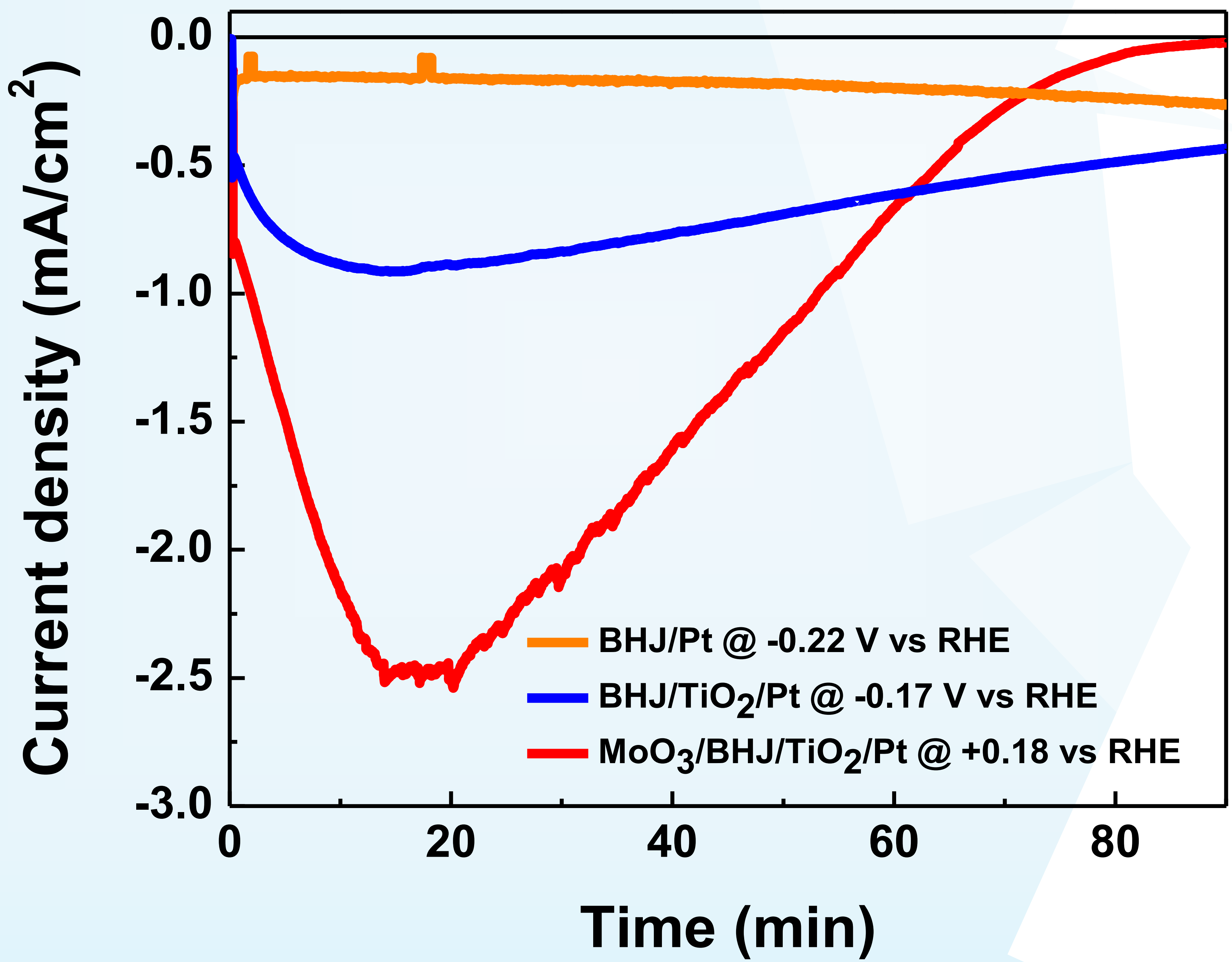

-V = 0.18 V vs RHE
-P3HT is the photo-active part
-IPCE integration matches J

## Hydrogen measurements (GC)

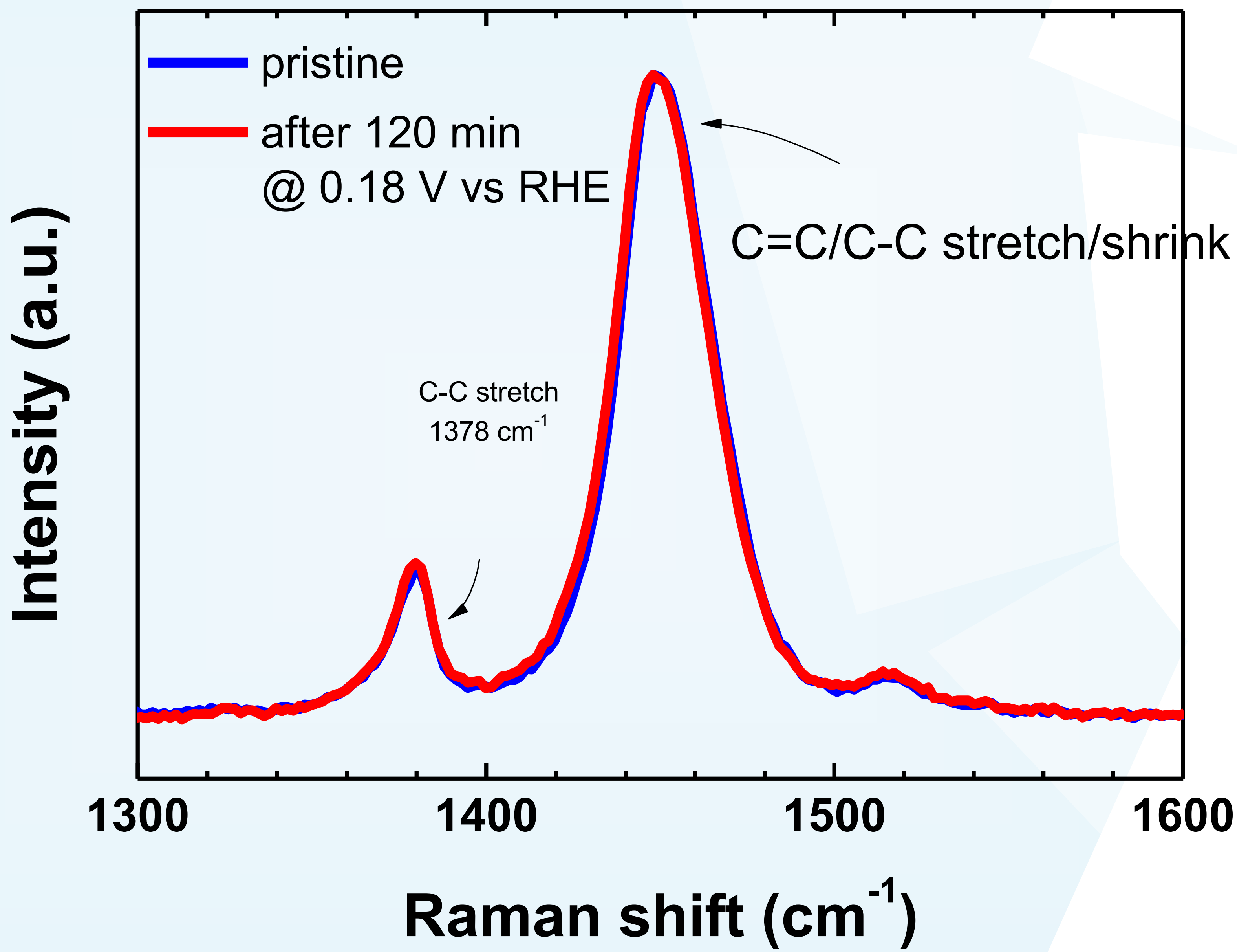



-V = 0.18 V vs RHE
-100% Faradaic Efficiency
-dynamics?

# Temporal stability



# Polymer stability




**No polymer photodegradation**

S. Bellani et al., J. Phys. Chem. C (2014)

# Conclusions……

- CP can sustain the contact with water
- CP in water preserve their optoelectronic properties in terms of charge generation efficiency
- Morphology is not seriously affected
- Polymer photo-activated doping (rev degradation) counts
- Interfacial effects are critical
- Anyway, standard picture of an organic photodetectors is not suitable (mixed electronic + ionic)

- Organic semiconductors can be reliably used in PEC cells for WS
- Charge selective contacts are essential
- 3mA/cm$^2$ @0.18 V vs RHE (now 8mA/cm2 @0.65V vs. RHE)
- Stability issue mainly related to the HSL/catalyst

# ....and Perspectives

- ✓ Improvement of stability and efficiency
- ✓ Investigation of other organic and inorganic materials
- ✓ Avoid the use of precious catalysts (molecular catalysts)
- ✓ Capability to work at neutral pH
- ✓ Coupling to nanostructures to enhance active area available for PEC reactions
- ✓ Printable, large area polymer-based PEC cell
- ✓ **Basic understanding of a new device in the large arena of CP**