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Using Cold Plasmas to Improve Electrochemical Sensors and vice versa

Camille Colin, Vasilica Badets, Fanny Girard-Sahun, Pauline Lefrançois, U Botsos-Margerit, Dodzi Zigah, Sylvie Blanc, Neso Sojic, Franck Clement, Stéphane Arbault

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Using Cold Plasmas to Improve Electrochemical Sensors and *vice versa*

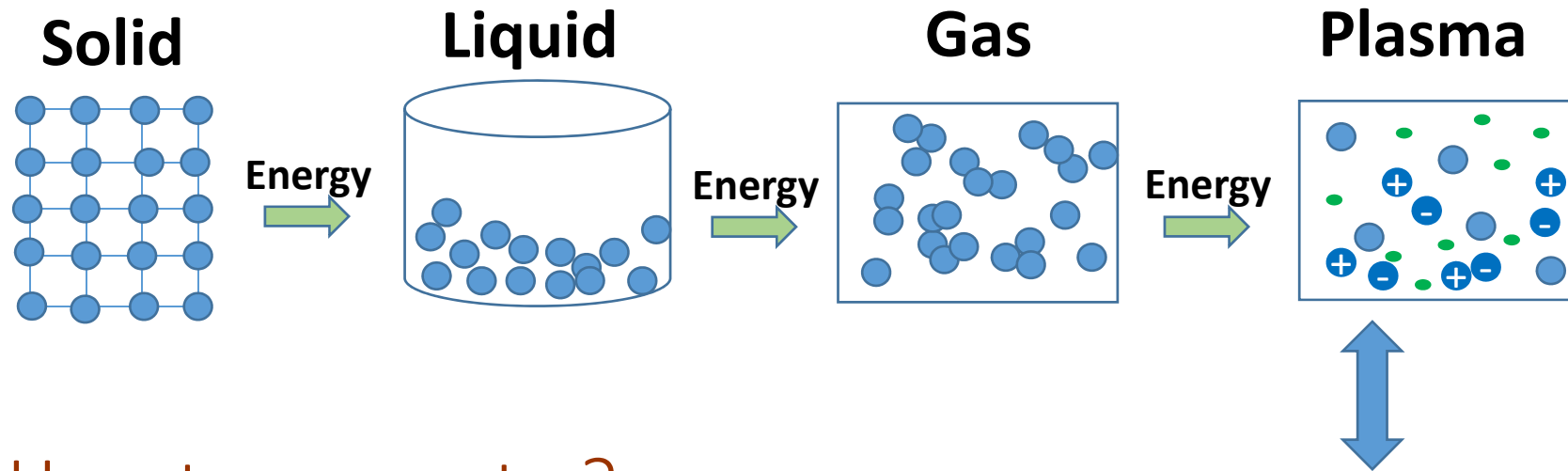
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Botsos-Margerit Ugo,¹ Zigah Dodzi,¹ Blanc Sylvie,²
Sojic Neso,¹ Clément Franck,² Arbault Stéphane¹

1. *University of Bordeaux, Institute of Molecular Sciences, NSysA lab.
CNRS UMR 5255, ENSCBP, Pessac, France*

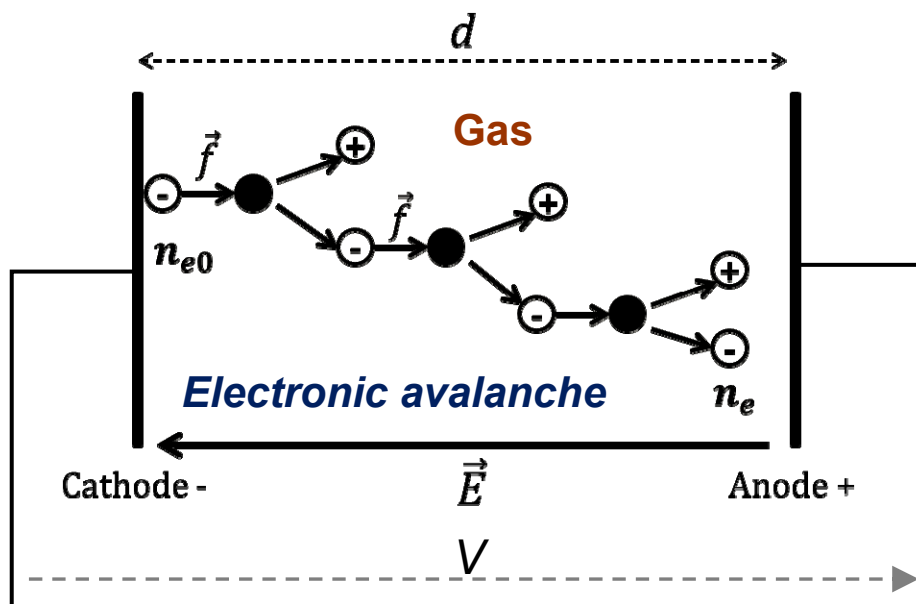
2. *UPPA, IPREM, CNRS UMR 5254, 2 avenue Président Angot, 64000 Pau, France.*



What is a plasma ?

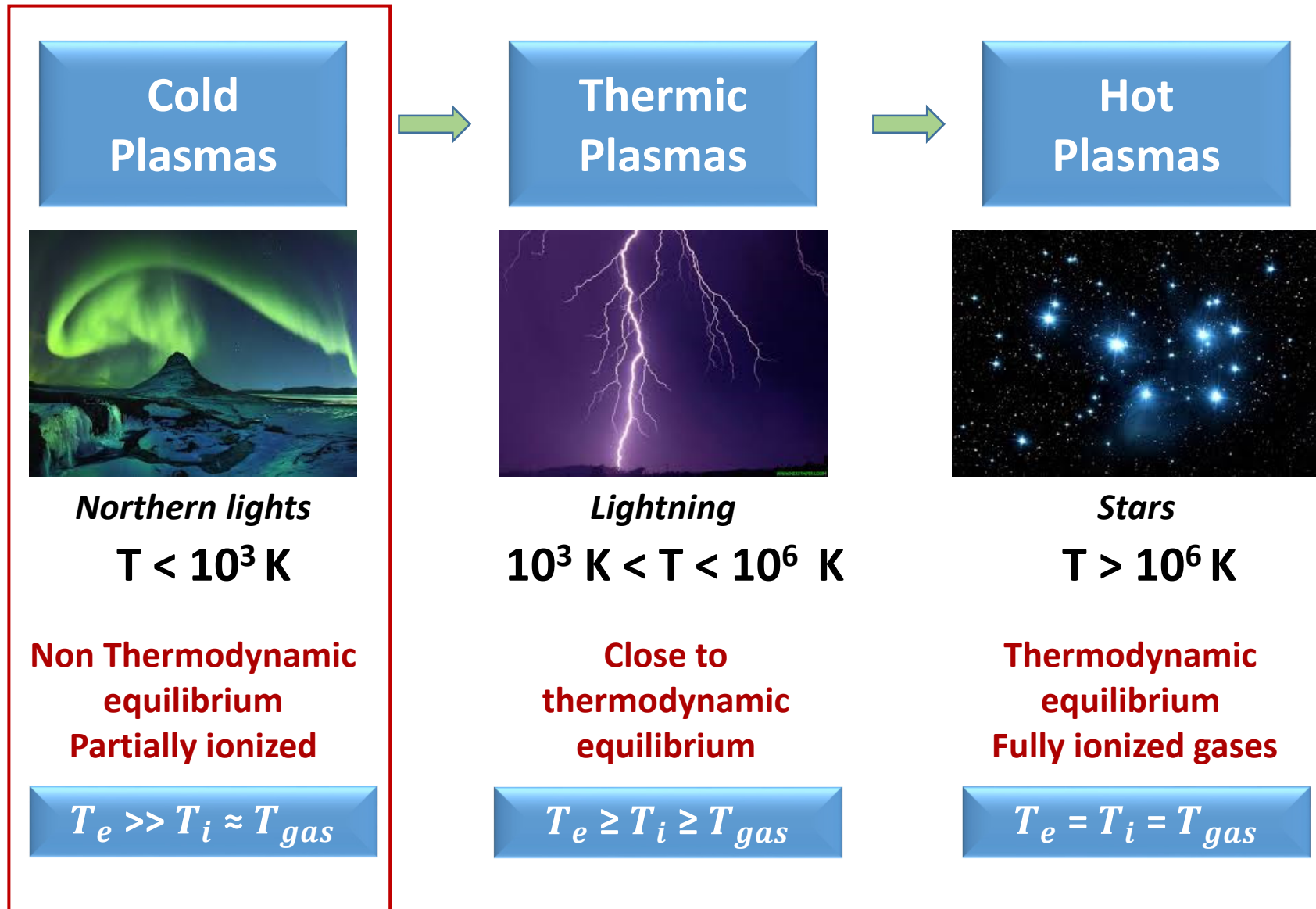


How to generate ?



- Electrons
- Ions @ fundamental / excited states
 - Neutral atoms and molecules @ fundamental / excited states
 - Photons

Types of plasma :



Ionization degree : $\alpha < 10^{-4}$

Easiest way to work with plasmas ?

Glow discharge plasmas : Room T°- gases at Low pressure (vacuum) – RF field



Typical uses :

1. removal of hydrocarbons - Micro-cleaning - degreasing in oxygen plasma
2. Mechanical cleaning :
Due to the kinetic energy of impacting ions, atoms and molecules forming coatings can be gradually removed.
3. Structuring - physical etching
4. **Formation-Reduction of oxide layers – surface chemical activation**

Advantages :

- **Plasma cleaning has unique advantages :**
- Cleaning even in the finest cracks and gaps
- Cleaning of all component surfaces in a single step
- Residue-free removal of degradation products by vacuum suction
- No damage to solvent-sensitive surfaces by chemical cleaning agents
- Also removes fine molecular residues
- Immediate further processing is possible (and beneficial). No venting and removal of solvents required
- Low process costs
- **Modulation of hydrophilicity/hydrophobicity**



Detection in biochemical buffers of Hydrogen Peroxide With Platinized Microelectrodes

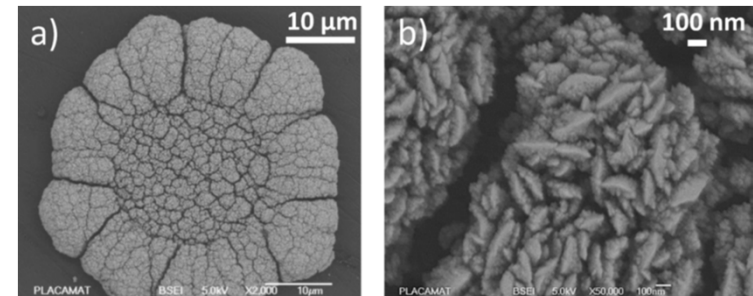
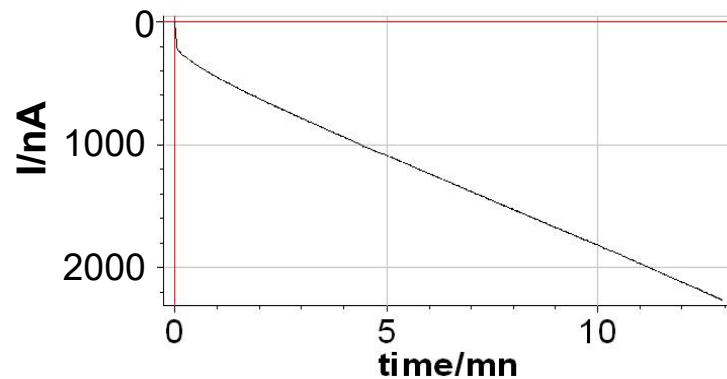
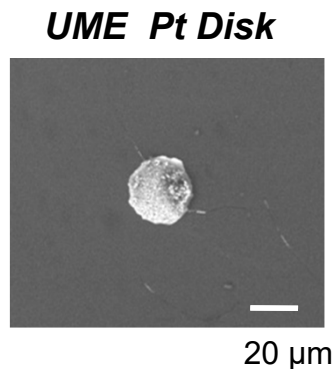
➤ Operating conditions :

- selective detection of H_2O_2 between $\approx 10 \text{ nM}$ to $100 \mu\text{M}$
- analyses in specific buffers (Manitol, Phosphates, EGTA...)
- response time $\leq 1 \text{ sec}$; steady-state monitoring

⇒ Microelectrode with a nano-structured Platinum surface : high Surface/Area

Electrodeposition of « Black Platinum »

$E = -60 \text{ mV vs. Ag/AgCl}$

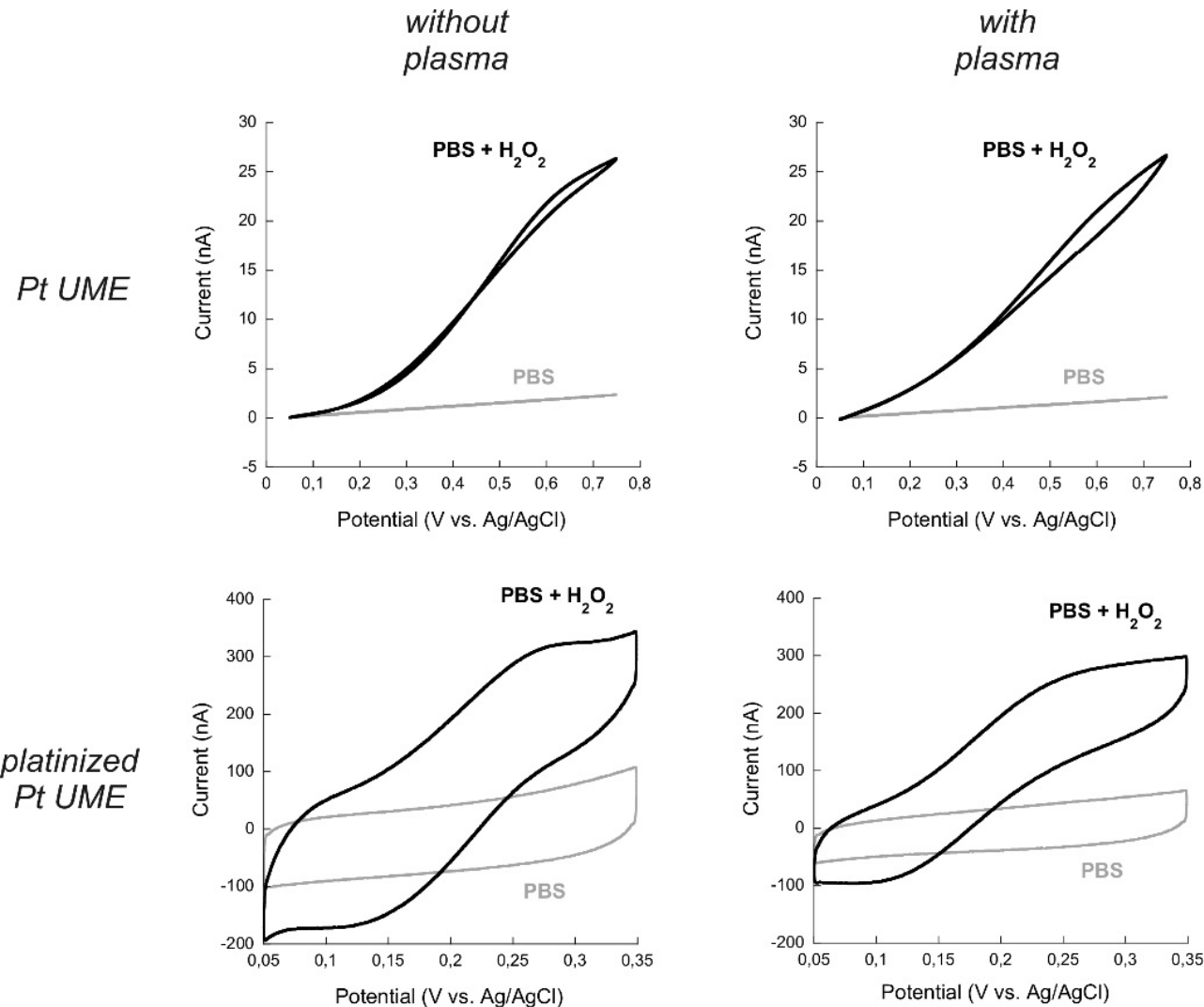


⇒ active surface x 10-500

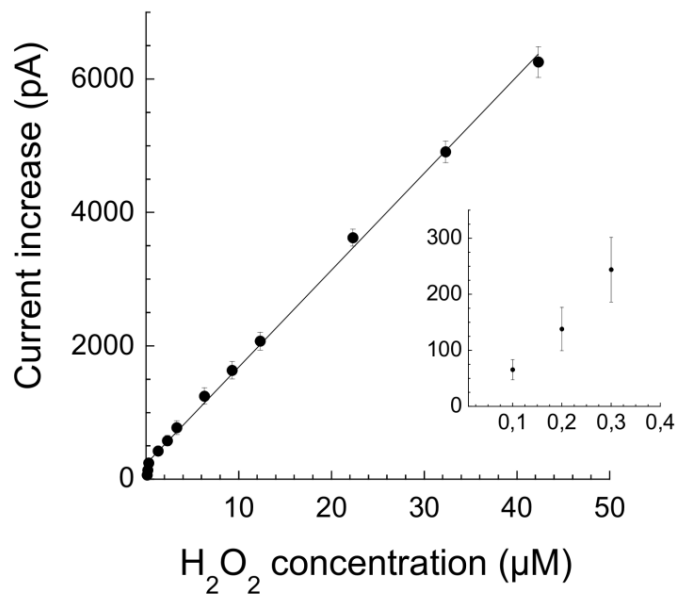
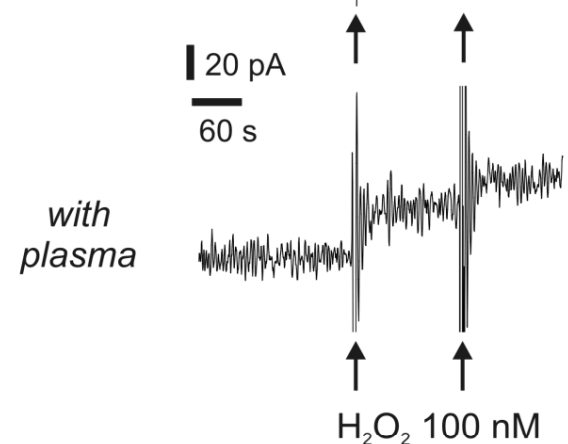
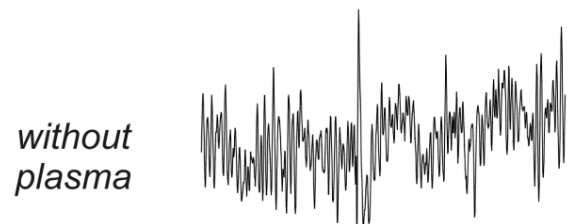
Sensitivity / H_2O_2 as f($[\text{H}_2\text{PtCl}_6]$, $[\text{Pb}(\text{CH}_3\text{CO}_2)_2]$, coulometric charge)

Effect of an Oxygen Plasma on Platinized Microelectrode Responses

➤ **Oxygen plasma treatment:** 30 W; 300 mTorr 100 % O₂; 20 min. (Harrick Plasma)



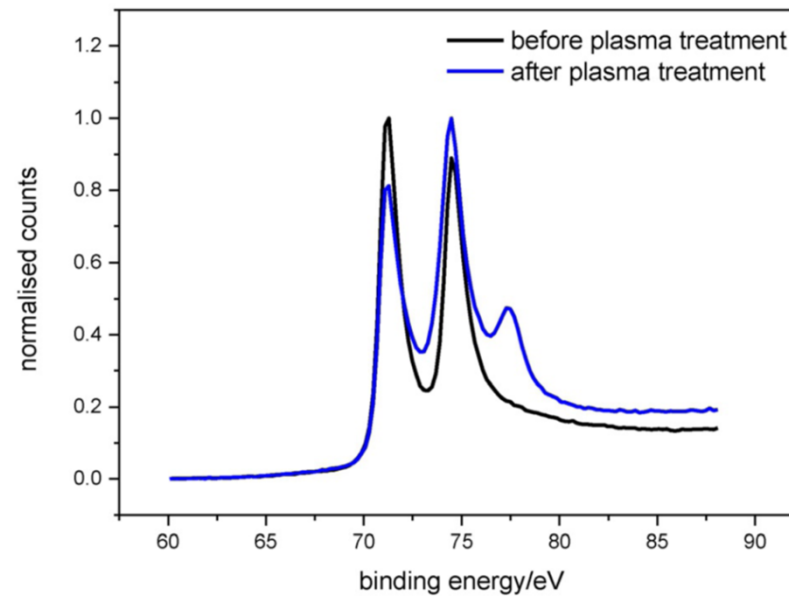
⇒ I_{faradaic} / I_{capacitive} ↗ 3-fold



Amperometric noise

⇒ better sensitivity (LOD = 100 → 30 nM)

XPS – Pt4f analyses

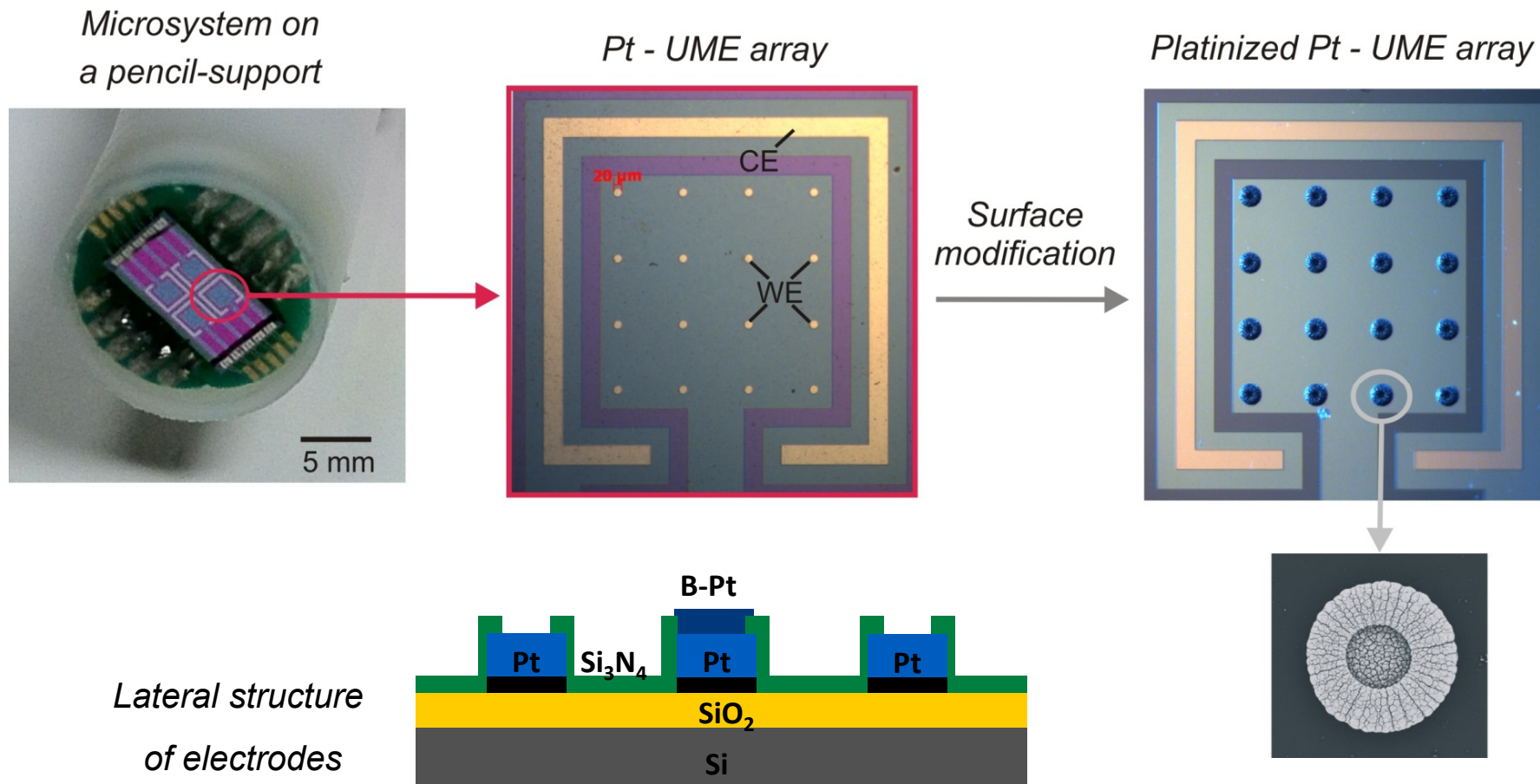


PtO₂ oxides increase / Pt⁰ and PtO

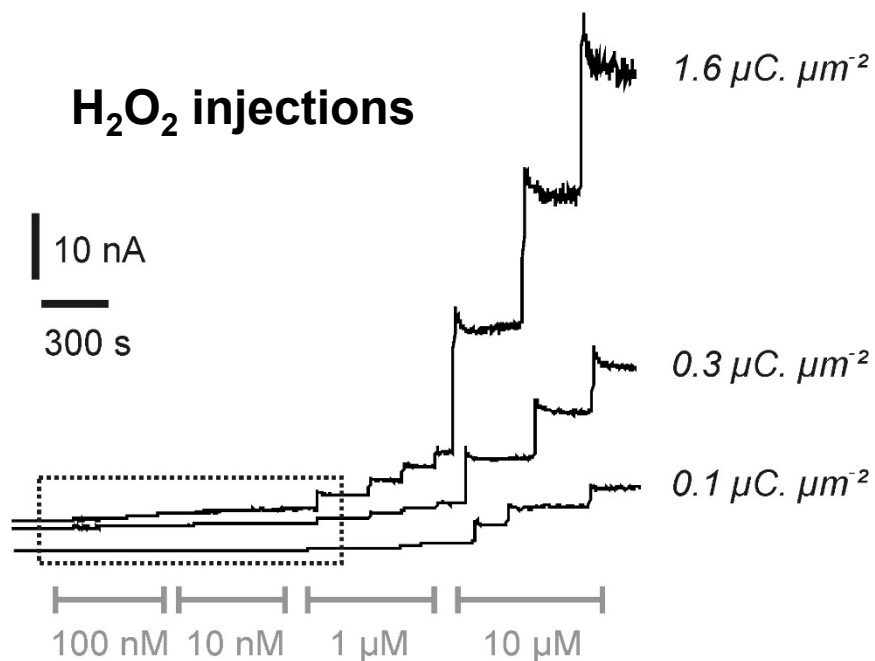
Outer-layer surface modification (few nm)

Development of Electrochemical Microchips for Bioenergetic Sensing

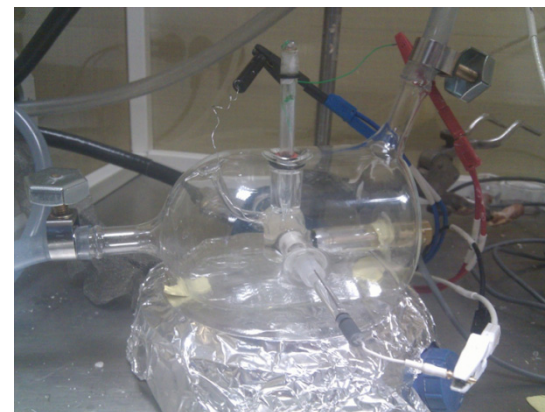
Multiple Electrochemical cells - ultramicroelectrode arrays on a silicon chip :



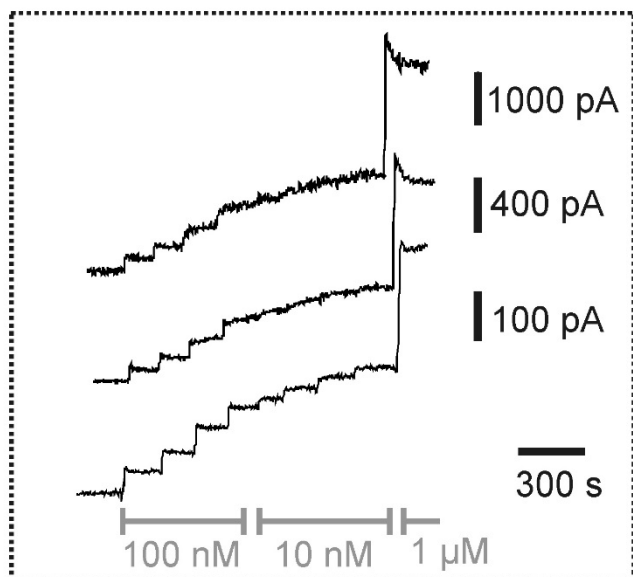
Chrono-amperometric responses to H_2O_2 as function of the platinization charge :



Test in an oxygraphy chamber



Mitochondrial phosphate buffer, $T=28^\circ\text{C}$, 900 rpm



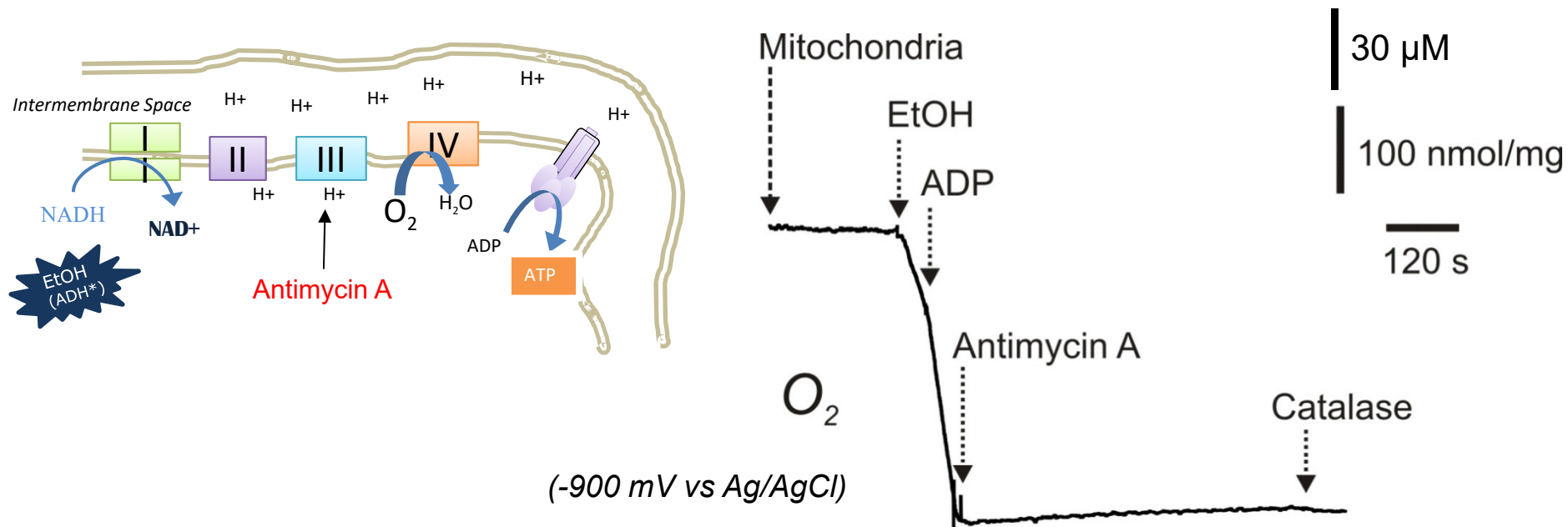
Sensitivity for H_2O_2 : 10 nM

Linearity of response : 30 nM – 100 μM

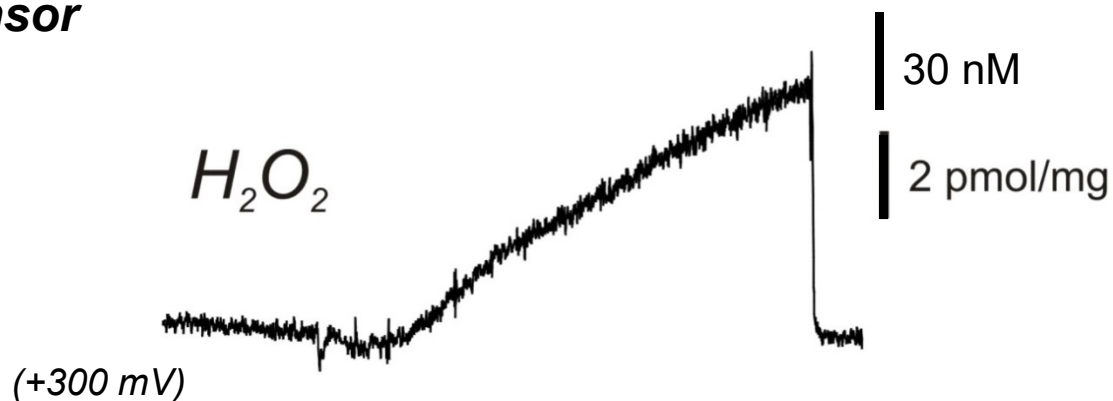
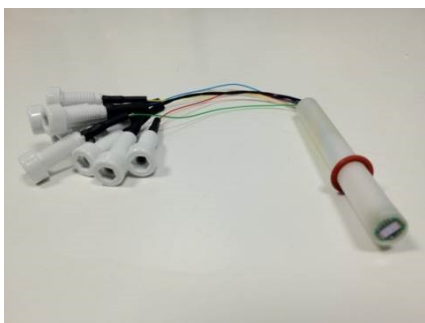
Response-time ≤ 1 sec.

Ben-Amor S et al. *Electrochimica Acta*, **2014**, 126, 171-178

Coupled Detection of O_2 and H_2O_2 on Yeast Mitochondria



Microelectrode array-based sensor

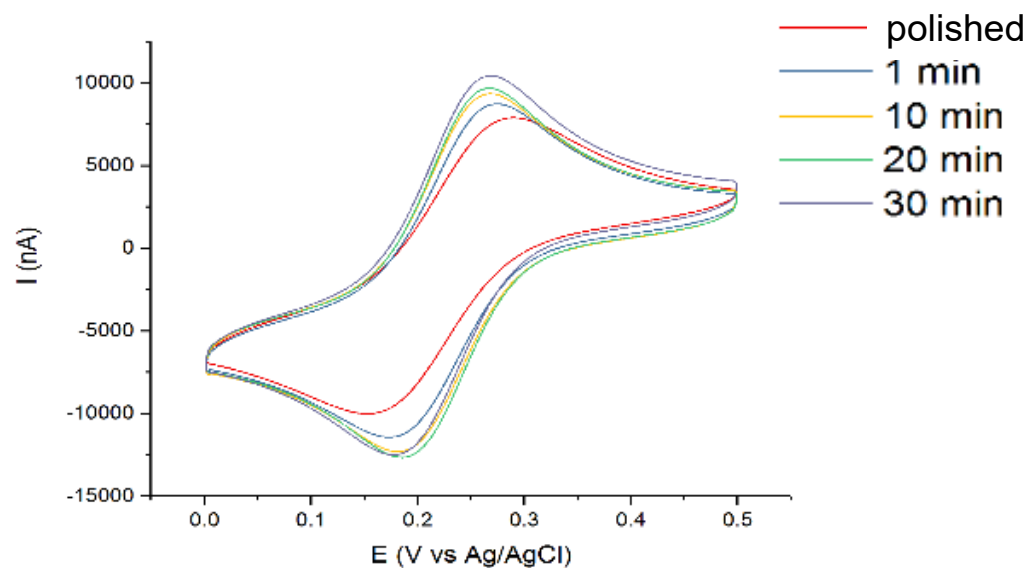


Direct quantification of H_2O_2 release / O_2 consumption

Effects of Oxygen Plasma on the Responses of Glassy Carbon Electrodes

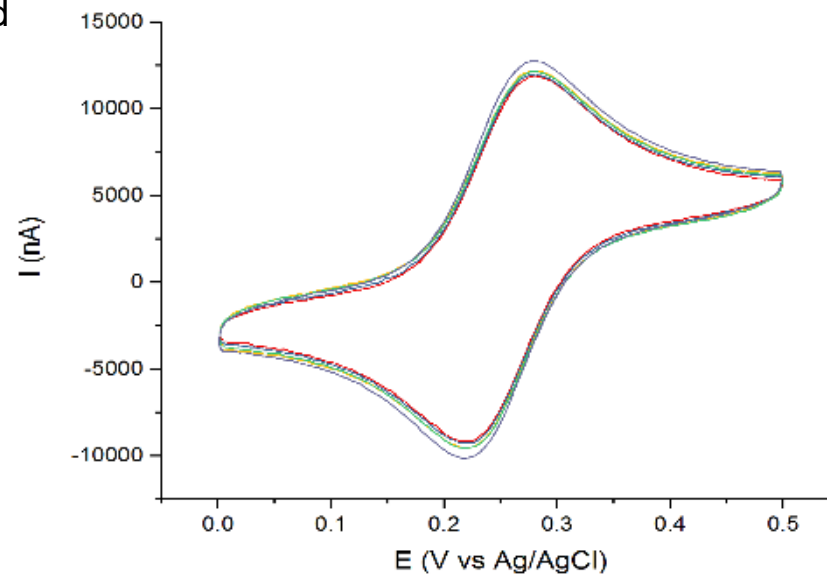
➤ **Oxygen plasma treatment:** 30 W; 300 mTorr 100 % O₂; different exposure times

Ferrocyanide (1 mM, KCl electrolyte)



Positive effects on peak amplitudes and transfer kinetics

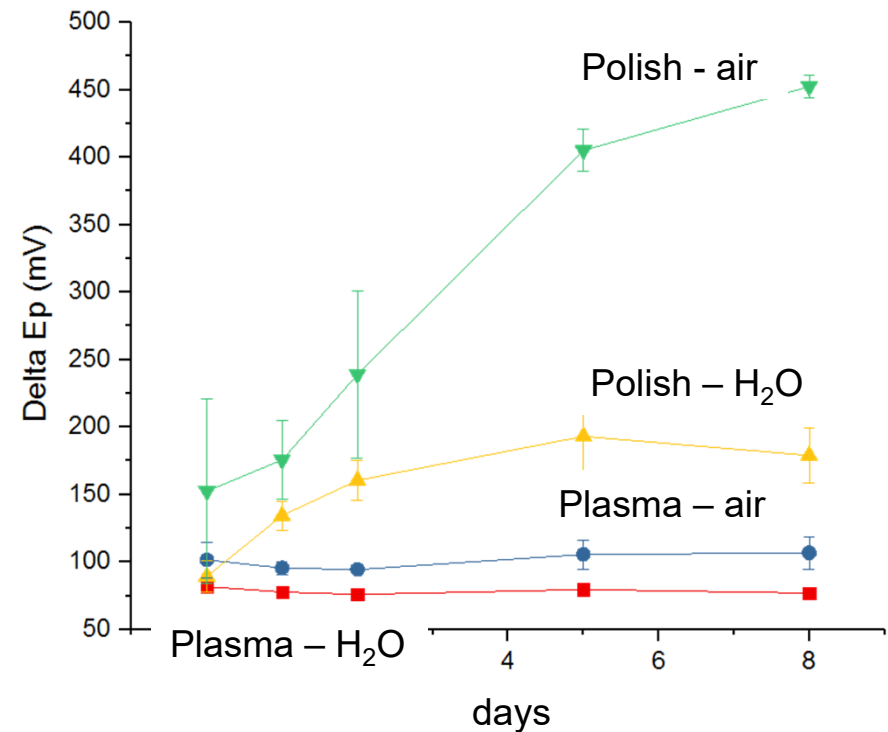
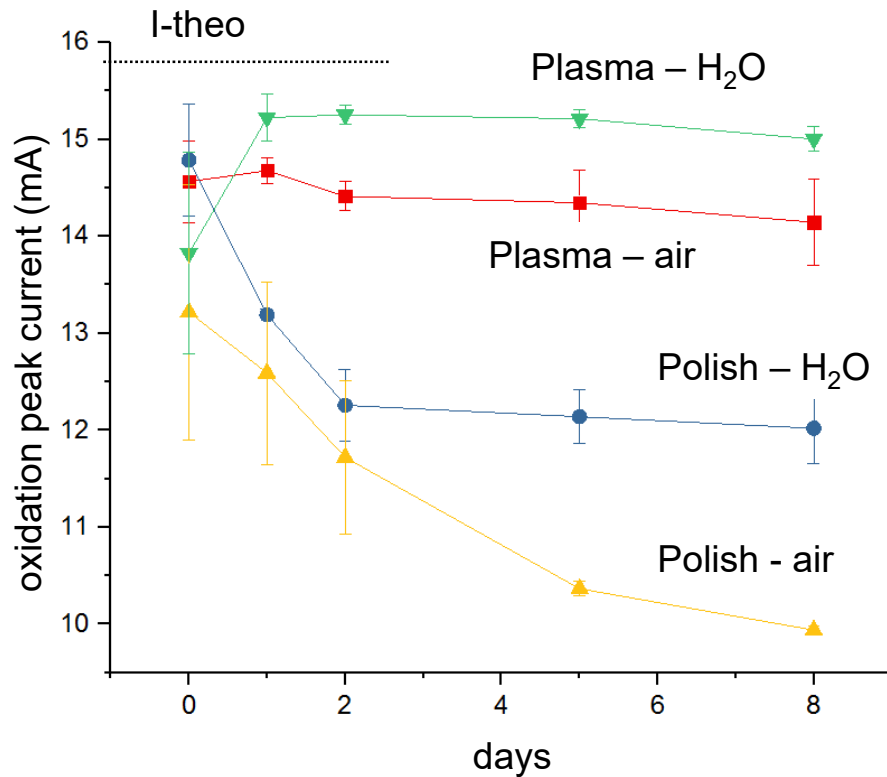
Ferrocenedimethanol (1 mM, KCl electrolyte)



Slight effects on peaks

➤ Stability of the oxygen plasma effects if electrodes are kept in water or at air

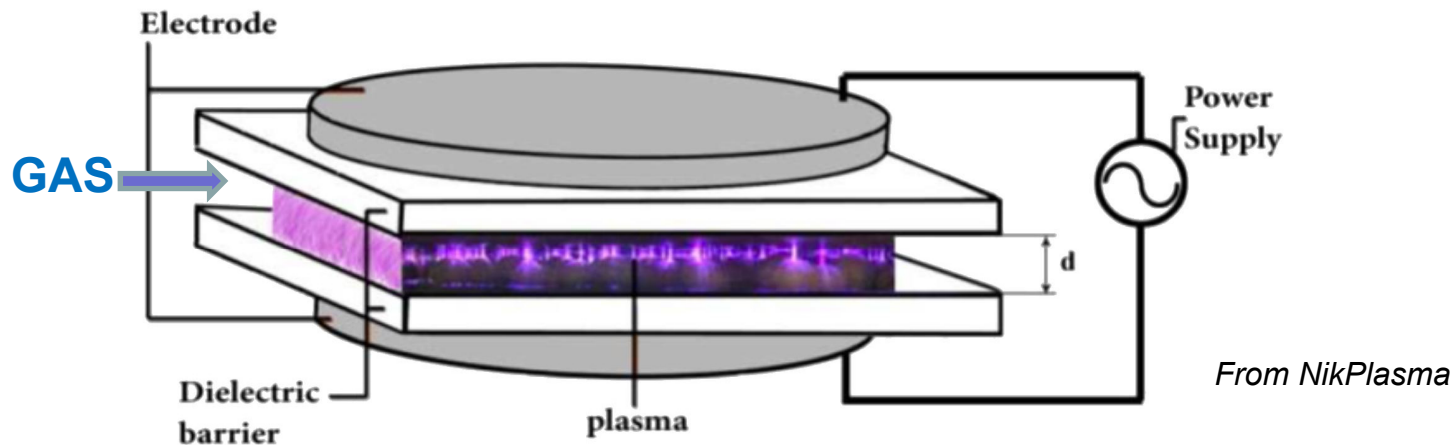
3 electrodes in each condition ; T0, +1 day, +2 days, +4 days, +8 days



- Plasma effects are conserved over a week when electrodes are kept in water
 - XPS analyses show increase of O1s /C1s (C=O, C-O functions)
- Surface hydrophilicity increased / allows to eliminate grafted layers (ex. diazonium)

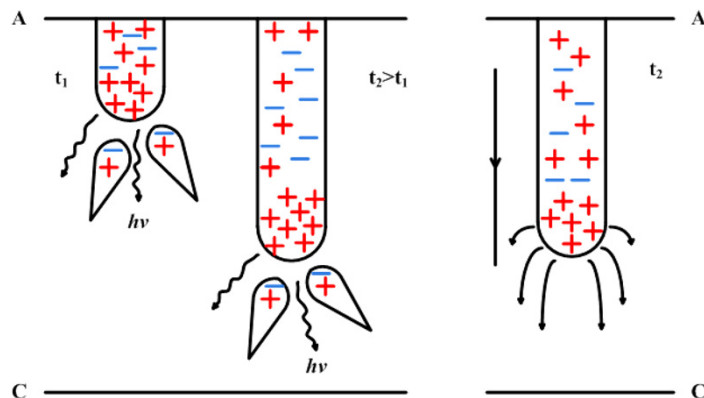
Generating Cold Atmospheric Plasmas (room temperature, ambient Pressure)

➤ **Dielectric barrier discharge setup :**

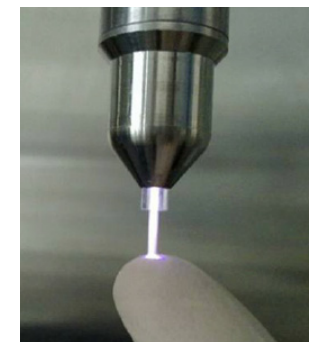


High voltage (current) AC field to ionize the gas at ambient P, T° : 10 kV/cm , kHz

Propagation of **ionization waves** in air



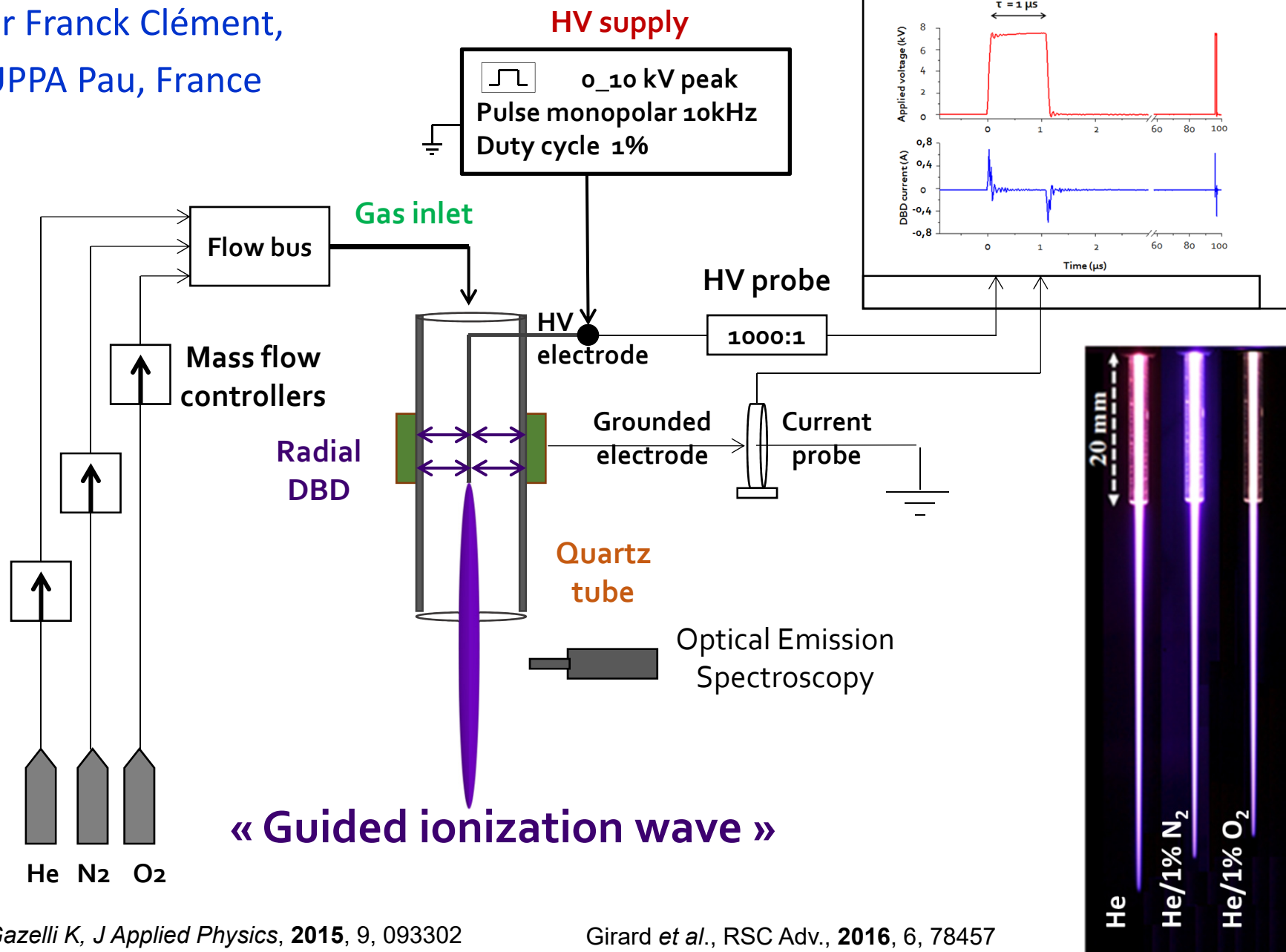
Commercial systems :

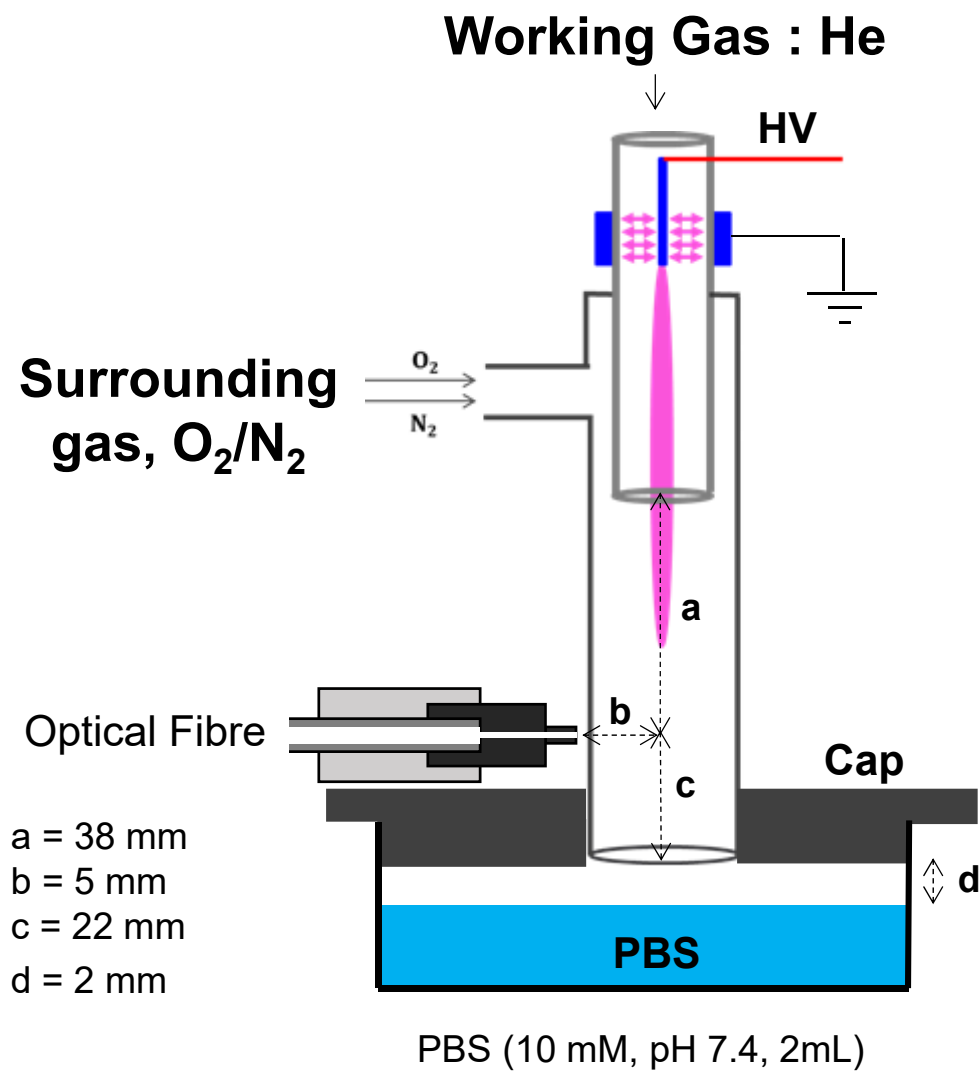


Research plasma setup:

Pr Franck Clément,

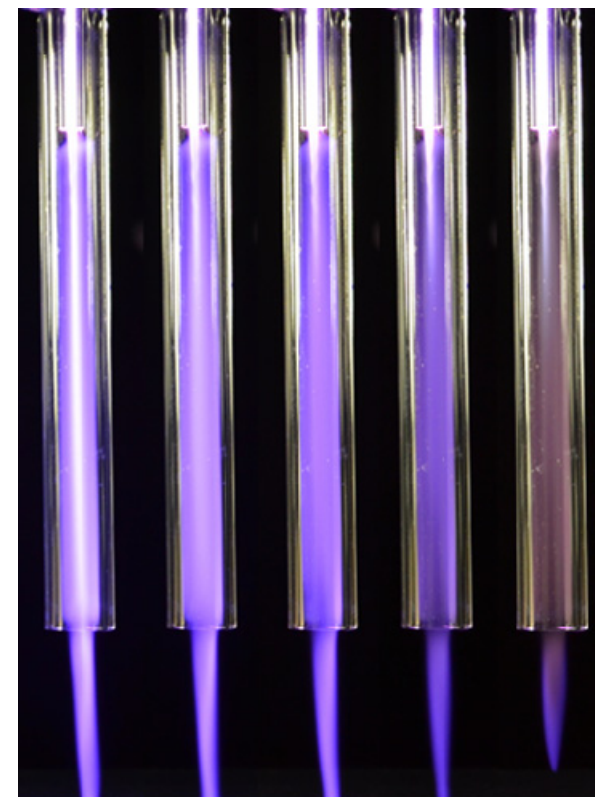
UPPA Pau, France





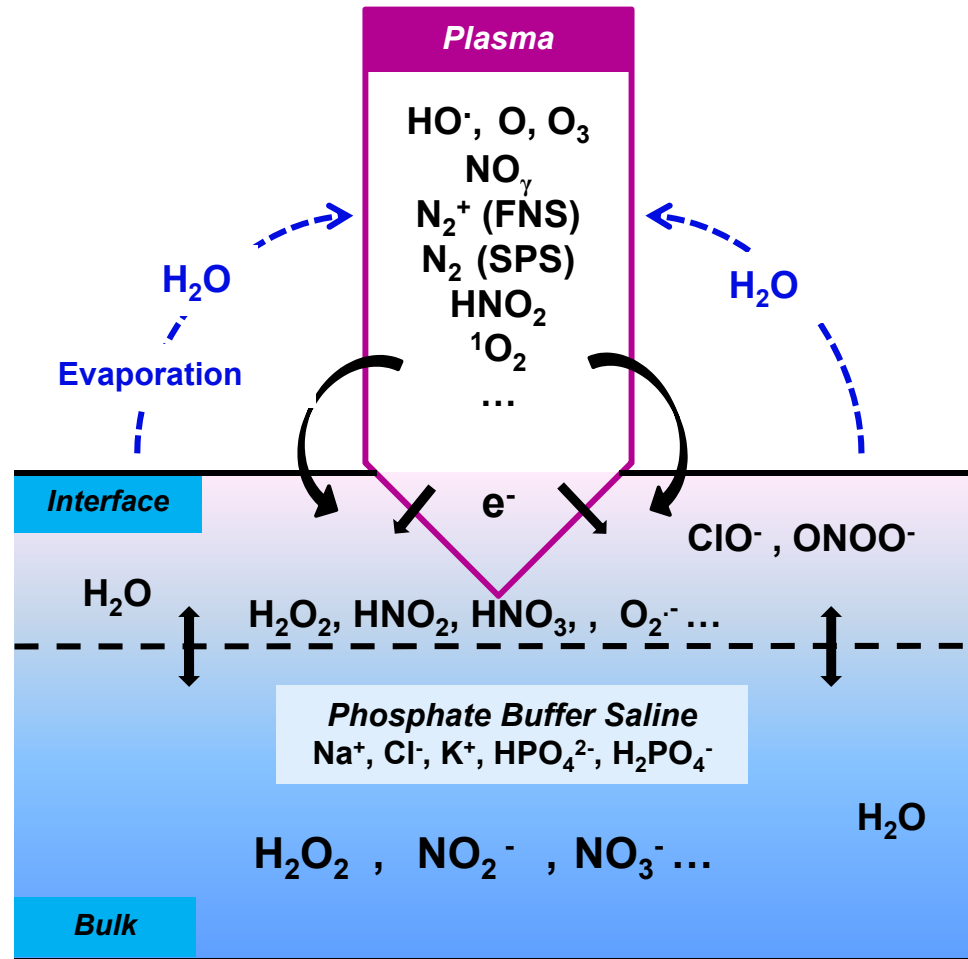
**Treatment of cells in culture or
tissue surface (skin explants)**

Diffusive Plasmas



100% N₂
20% O₂/80%N₂
50% O₂/50%N₂
80% O₂/20%N₂
100% O₂

Understanding the interface between plasma and an aqueous solution



Links between chemical species in the plasma and induced chemistry in liquid ?

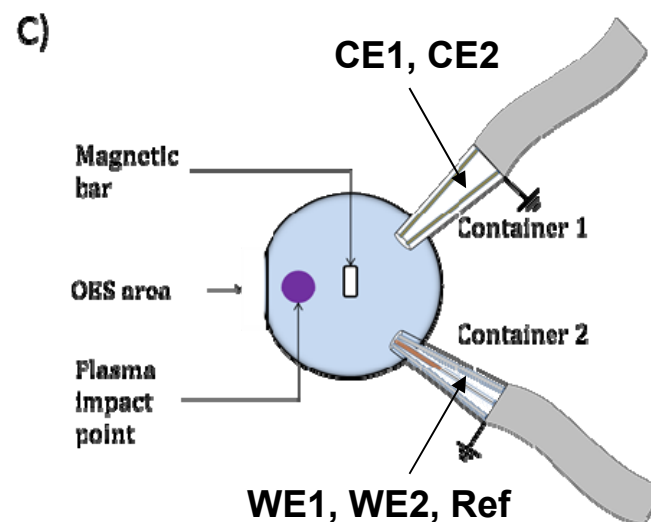
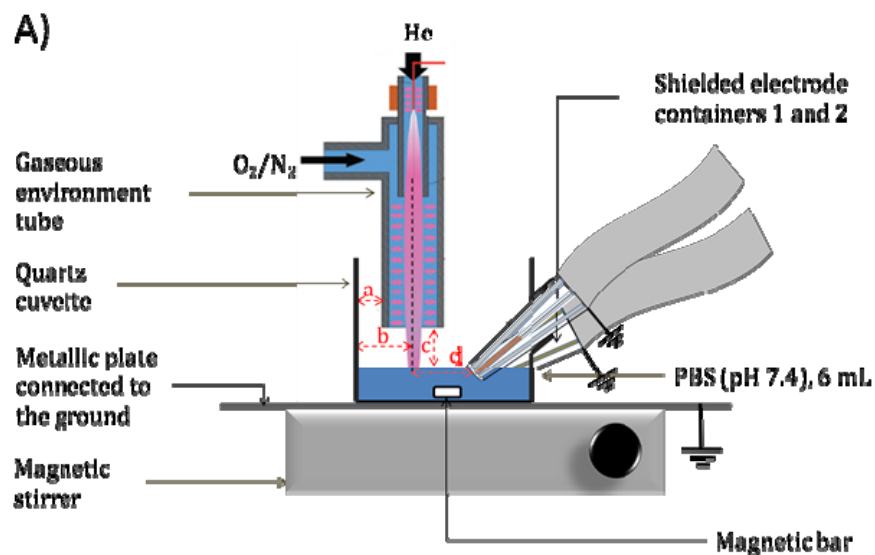
Girard *et al.*, RSC Adv., **2016**, 6, 78457

Dezest M *et al.*, PLoS ONE, **2017**, 12 (3), pp.e0173618

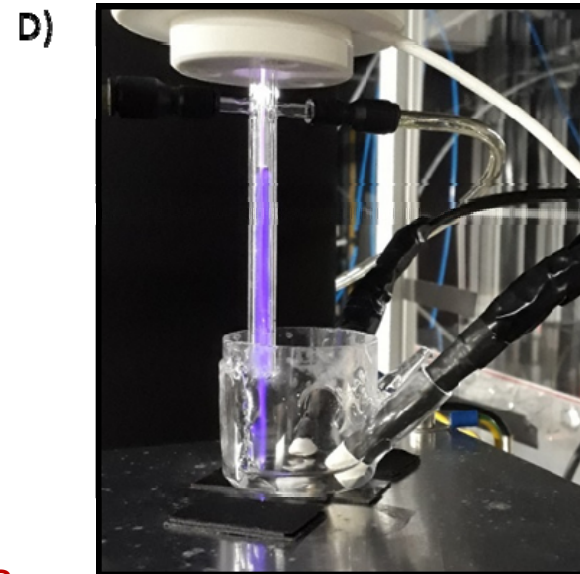
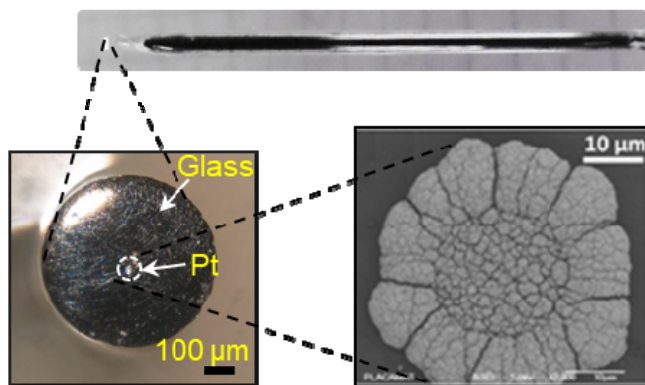
Girard F *et al.*, Phys. Chem. Chem. Phys., **2018**, 20, 9198-9210

Dezest M *et al.*, Scientific Reports, **2017**, 7, 41167

In situ monitoring of ROS-RNS generated by plasmas in aqueous solution



B) **Black Pt-modified microelectrode**

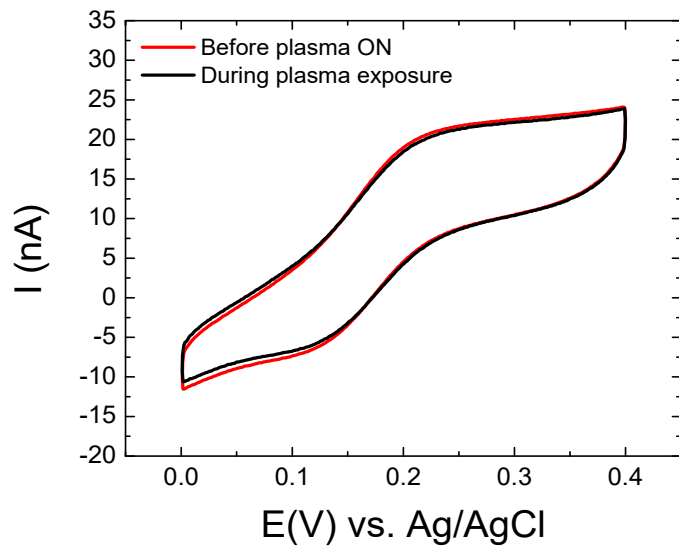


Question addressed : is sensitive electroanalysis possible next to a plasma stream ?

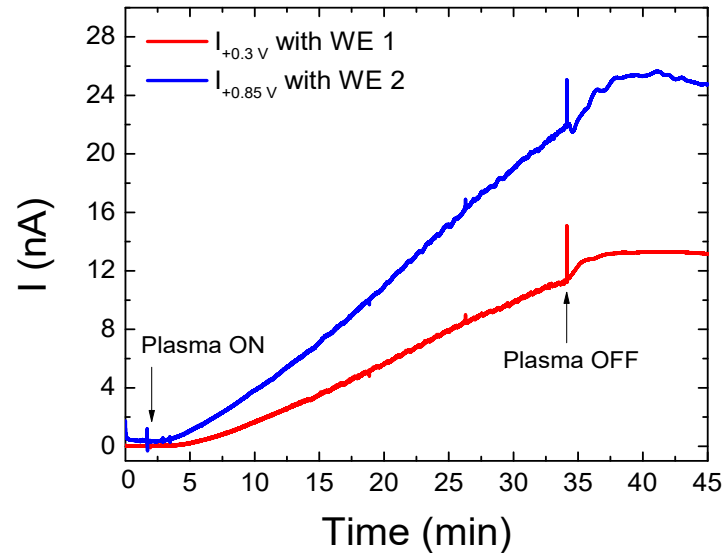
Pulsed local E field : 10 kV/cm, A peak currents

In situ monitoring of ROS-RNS generated by plasmas in aqueous solution

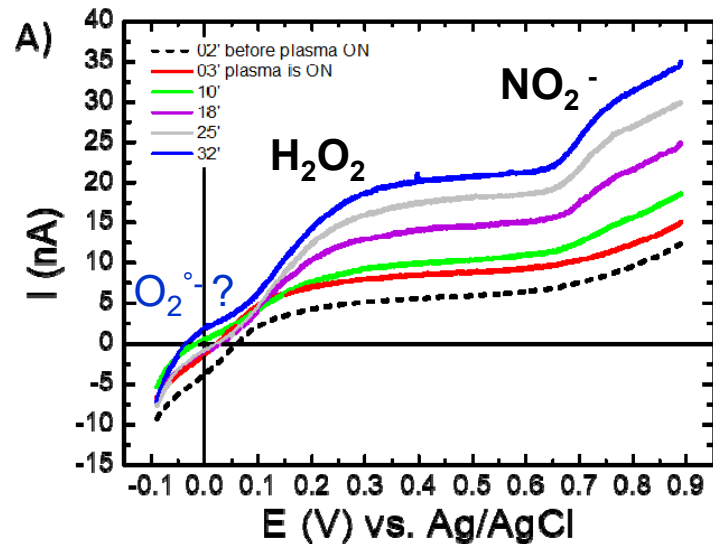
Cyclic voltammetry of $\text{Fe}(\text{CN})_6\text{K}_4$



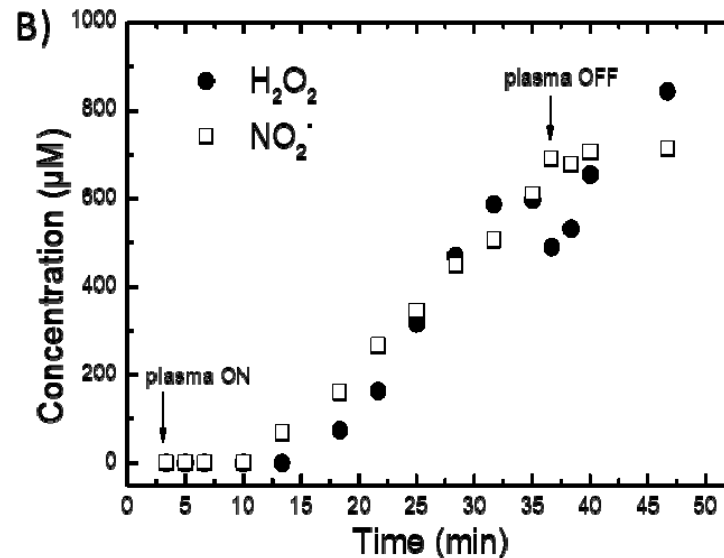
Chronoamperometry at 2 electrodes (2 distinct E)



Cyclic voltammetry in PBS during plasma



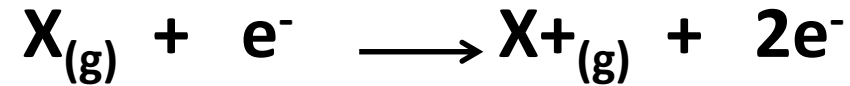
Species produced



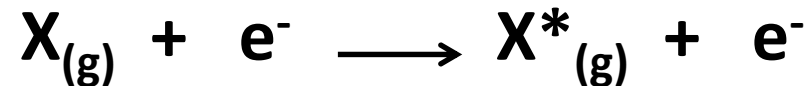
Answer to Question: YES !

Basic reactions in a plasma :

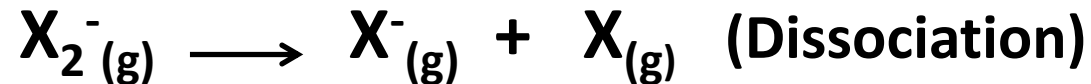
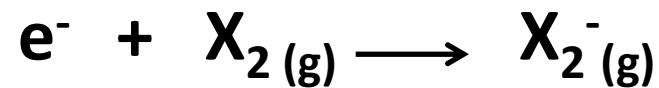
Electronic ionization



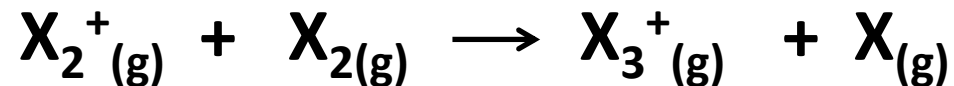
Electronic excitation



Electronic attachment

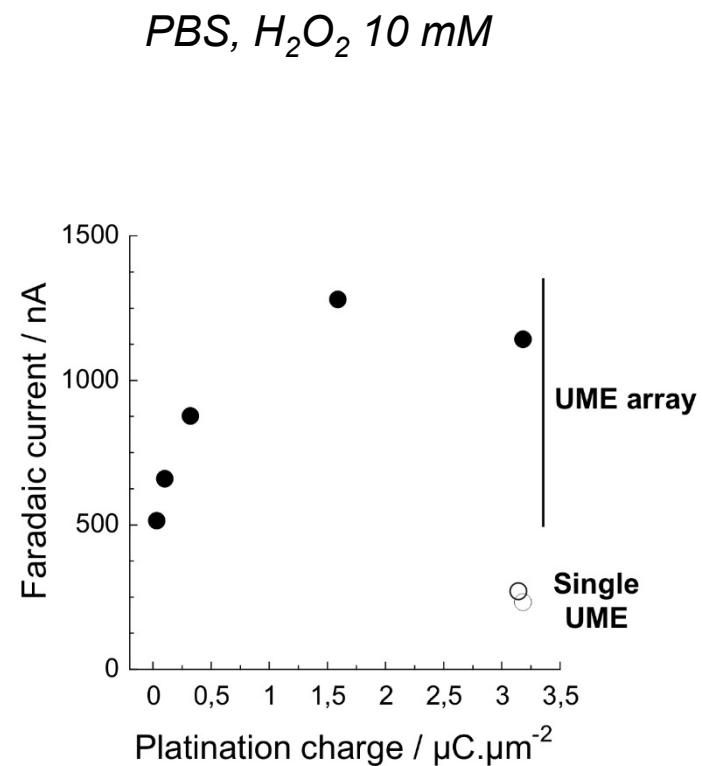
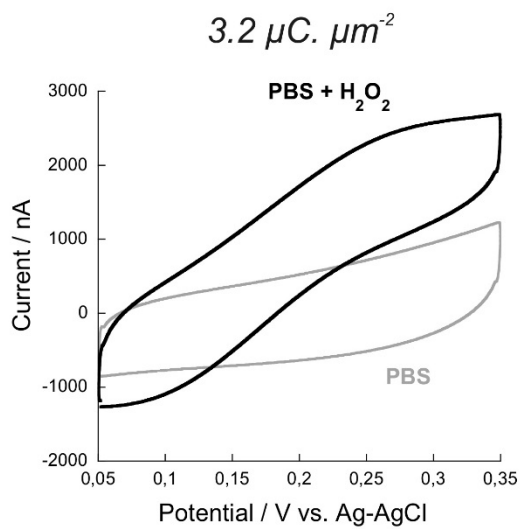
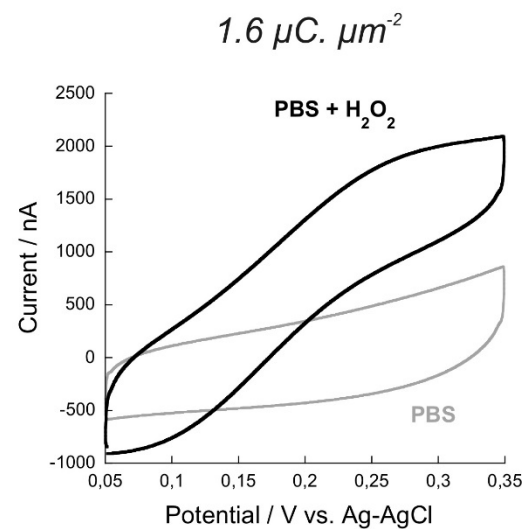
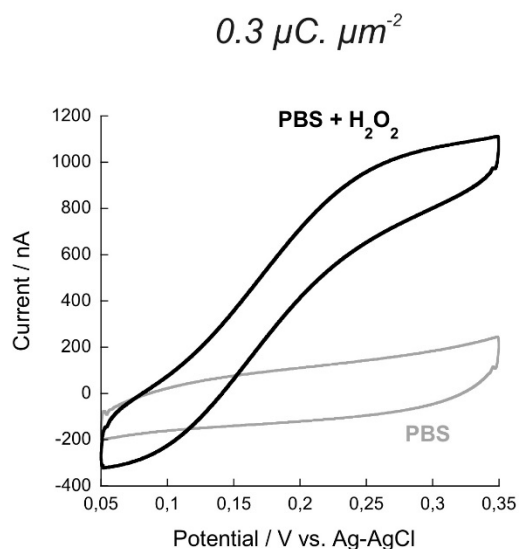
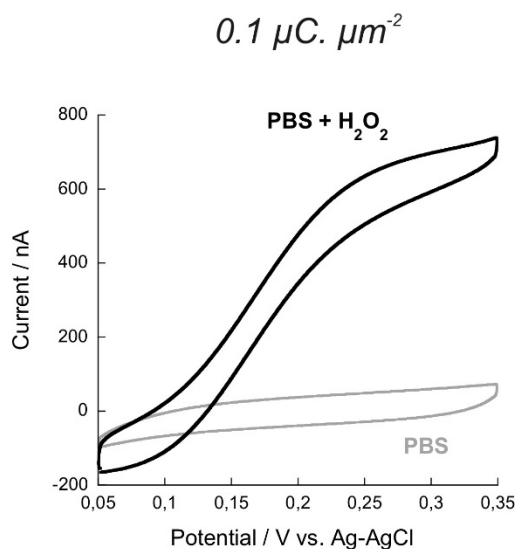


Ion-molecule collision



These charges generate a local electric field \vec{E}_l

Voltametric response as function of the platinization charge :



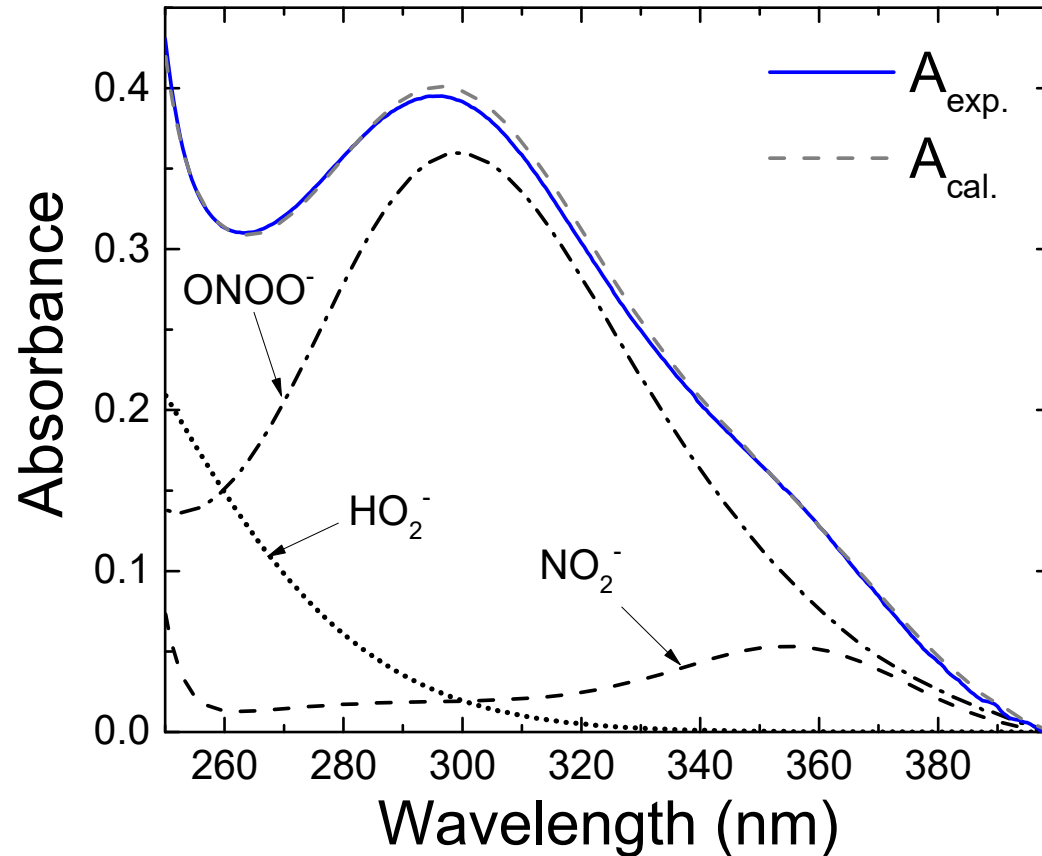
Plasma-liquid interactions

7.5 kV
10 kHz
duty cycle = 1 %

He/1%N₂



UV-visible absorption spectroscopy

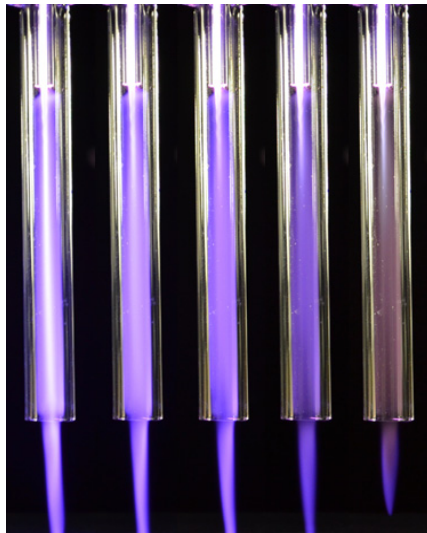


- ✓ $ONOO^-$: hypothesis validated
- ✓ $[ONOO^-] \approx 50 \mu M$ (10 minutes of treatment)
- ✓ Stabilized at pH 12 but probably also exists at pH 7.4

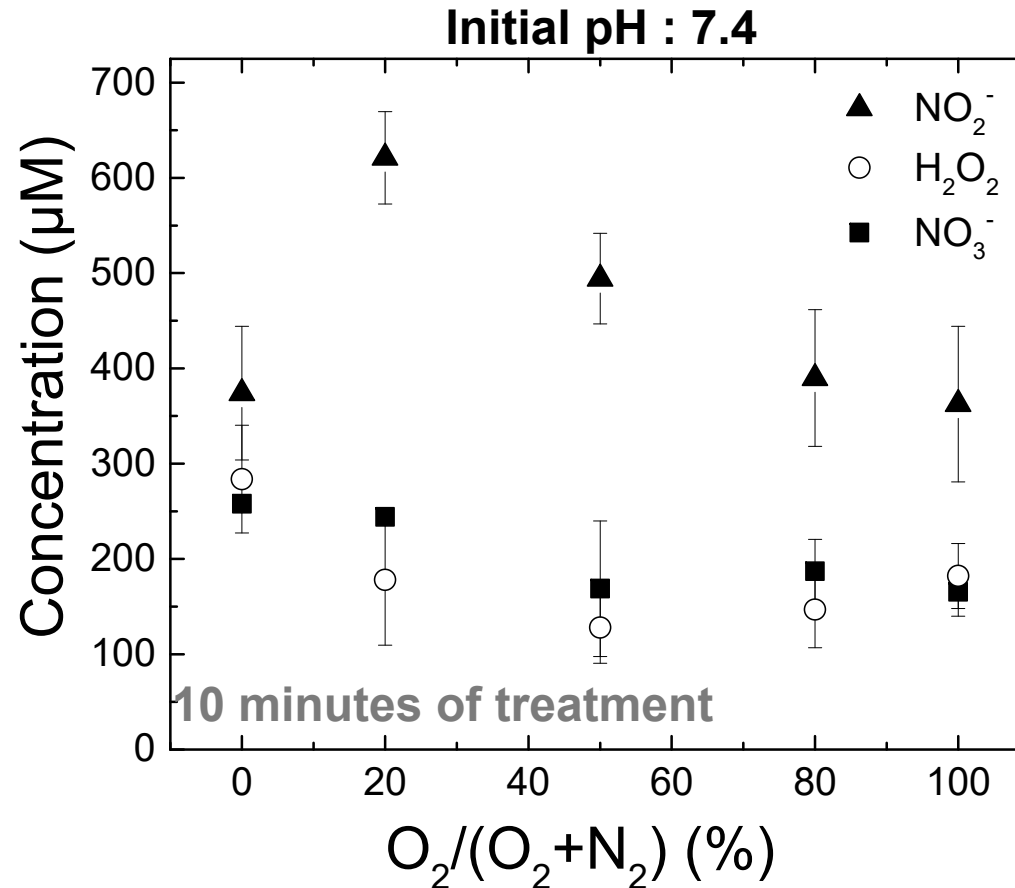
Plasma-liquid interactions

7.5 kV
10 kHz
duty cycle = 1 %

NO_2^- , H_2O_2 and NO_3^- quantification



100% N_2
80% N_2 /20% O_2
50% N_2 /50% O_2
20% N_2 /80% O_2
100% O_2



- ✓ $[\text{NO}_2^-]_{\text{max}}$ for the “air shielding” (20% O_2 /80% N_2)
- ✓ $[\text{H}_2\text{O}_2]_{\text{max}}$ and $[\text{NO}_3^-]_{\text{max}}$ for 100% N_2 in the shielding gas

Importance of the N_2 and air shielding gases, already observed by
H. Tresp, M. U. Hammer, K.-D. Weltmann and S. Reuter, *Plasma Med.*, 2013, 3.