Elaboration de capteurs chimiques à base de polymères

Journée Capteurs OSU THETA - DIPEE BFC

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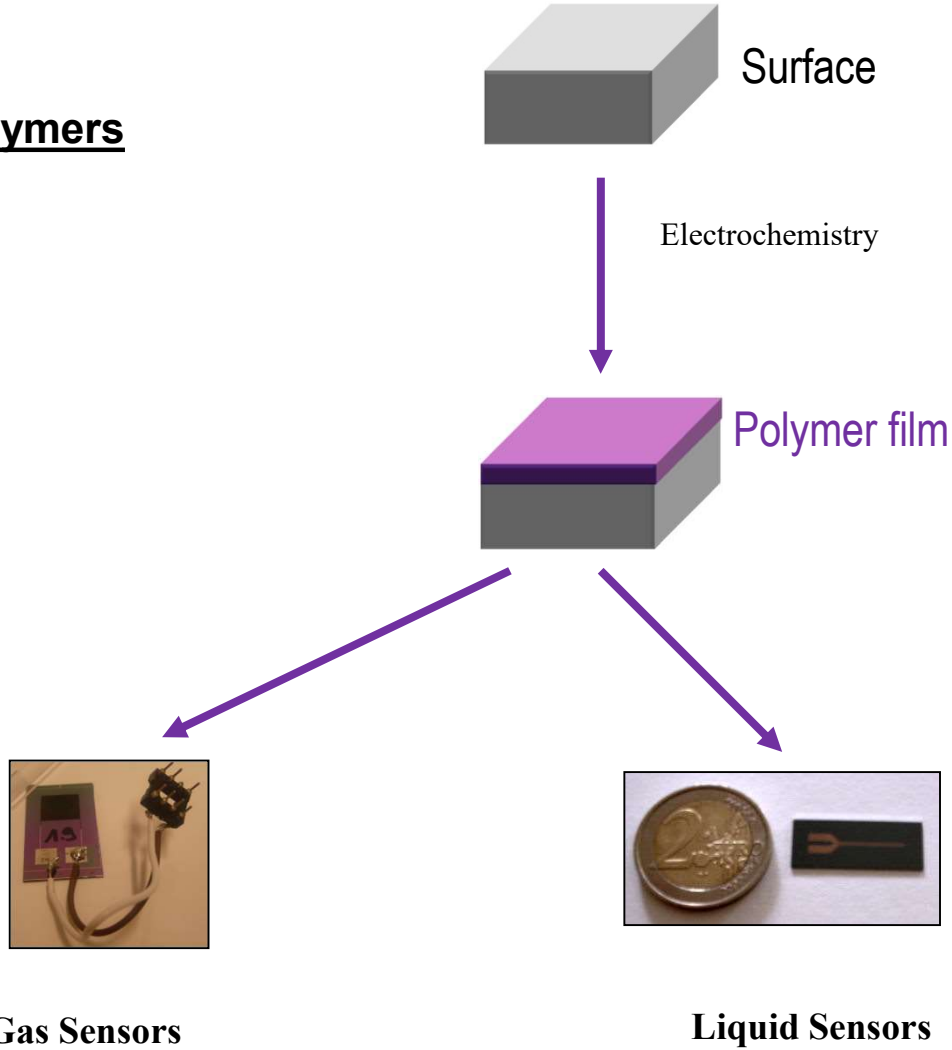
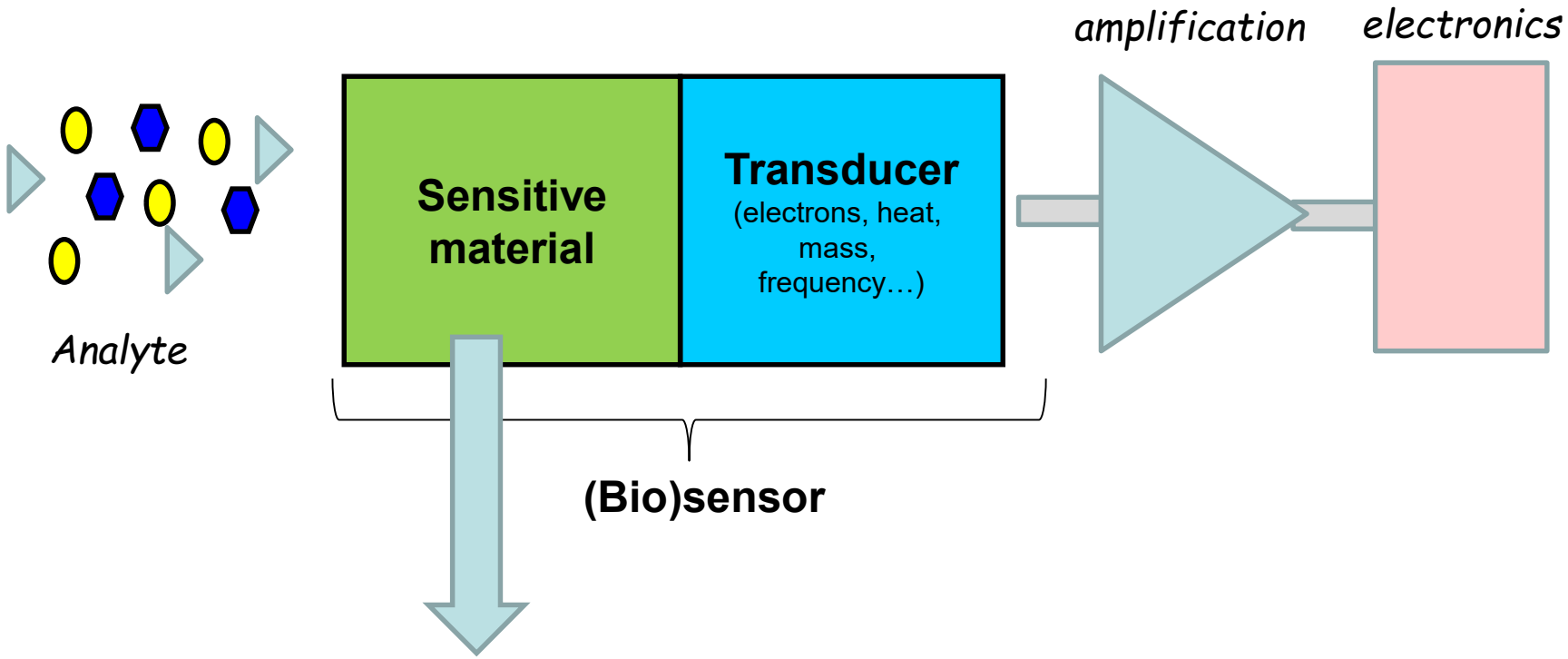
Overview:

1. **Electrodeposition of conducting polymers**
2. Development of **gas sensors**
3. Development of **liquid sensors**

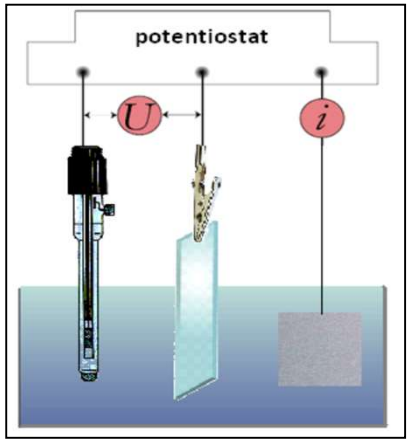


Chemical sensing:

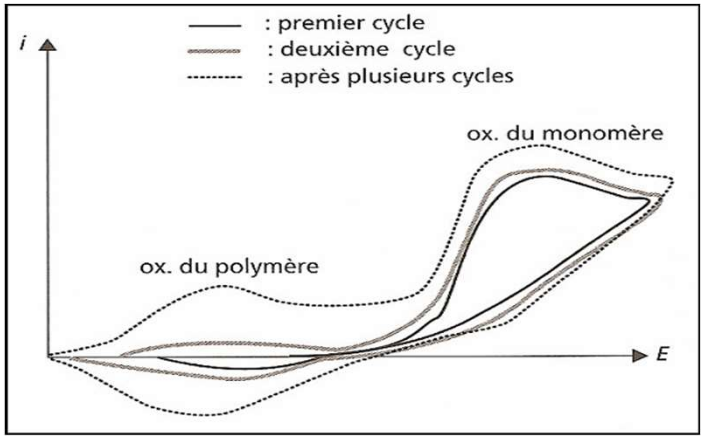


A large number of sensitive materials exist: oxide particles, carbon materials (graphene, CNT), organic materials, polymers (electrodeposited, self-assembled, molecular imprinted)

Electrodeposition of conducting polymer films:



Electrolyte:
Monomer + solvent (+supporting salt)



Potentiodynamic or potentiostatic electropolymerization

Conducting polymers - Introduction:

History:

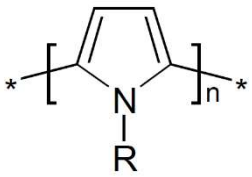
In 1977, A.J. Heeger, A. MacDiarmid and H. Shirakawa reported high conductivity of polyacetylene. For this research, they were awarded the 2000 Nobel Prize in Chemistry.


Alan J. Heeger

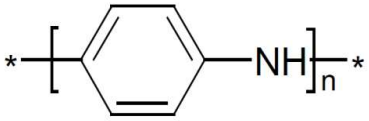

Alan G. MacDiarmid


Hideki Shirakawa

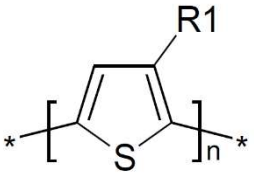
The most studied classes of conducting polymers:



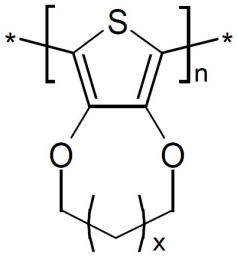
Polypyrroles



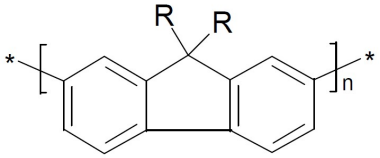
Polyanilines



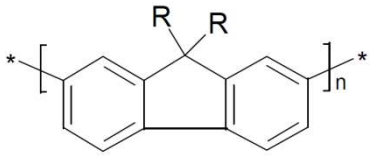
Polythiophènes



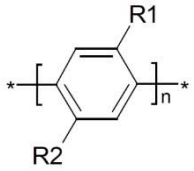
Poly(3,4-alkylènedioxythiophènes)



Polycarbazoles



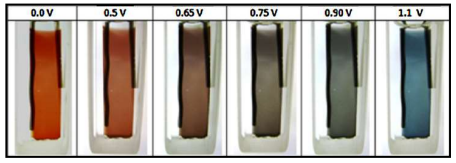
Polyfluorène



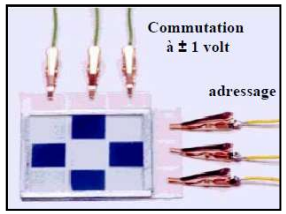
Polyparaphénylènes

Conducting polymers - Applications:

- Electrochromism:



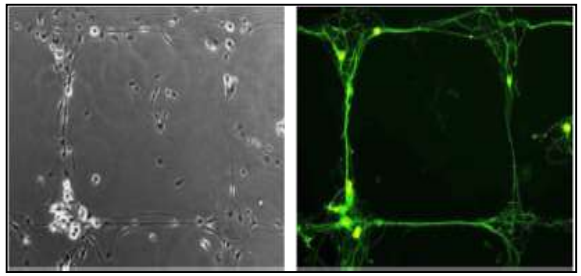
Films obtained from 2,5-di(2-thienyl)-1H-pyrrole *(Rende, Electrochimica Acta)*



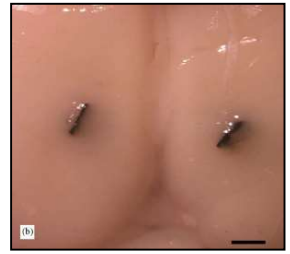
- Biomedical:

- Used as a support for cell culture

-*in* vivo (catheters, implants,…) to modify electrical and mechanical properties



Song, Biomaterials

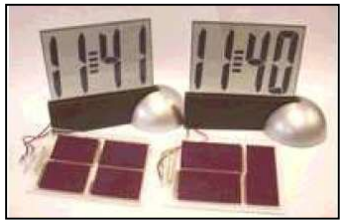


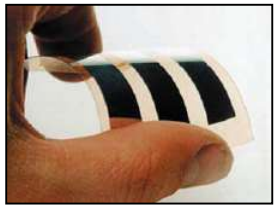
George, Biomaterials

- Organic photovoltaics:

Use of PEDOT:PSS derivatives (anode)

or P3HT (sensitive layer)





- Sensors

- OLED (Organic Light-Emitting Diodes) :

Use of polyphenylenevinylene and

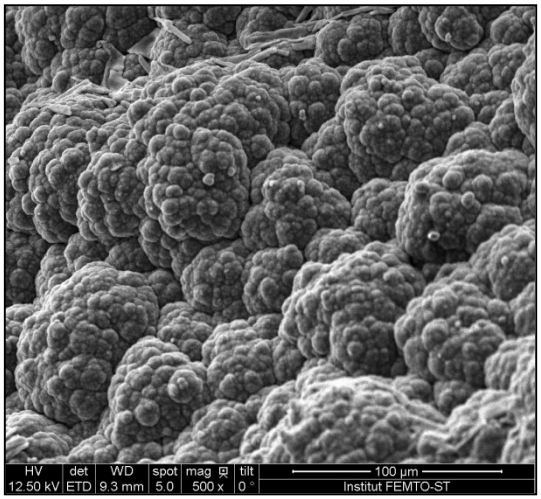
polyfluorene derivatives as luminophores

In our lab:

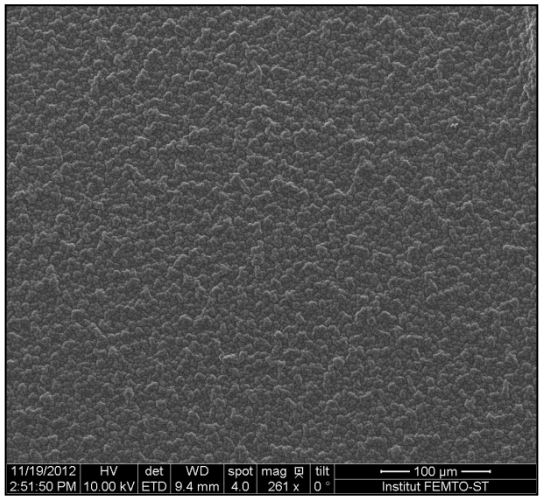
✓ **Synthesis of polymers and control of their properties:**

Possibility to control the thickness, conductivity, morphology, roughness, porosity of the polymer films by choosing appropriate electrodeposition parameters: electrodeposition potential, time deposition, monomer concentration, nature of the dopant, solvent,…

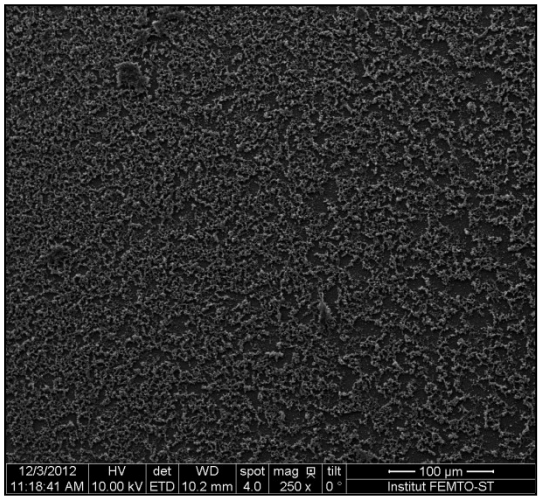
Example: influence of the solvent on the morphology of polypyrrole films:



Electrodeposition in water



in acetonitrile

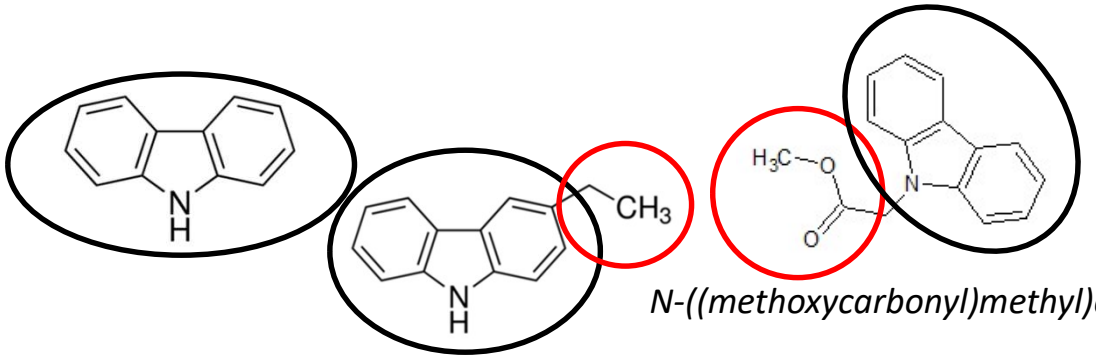


in bmimPF_6 (ionic liquid)

Electrodeposition of conducting polymer films

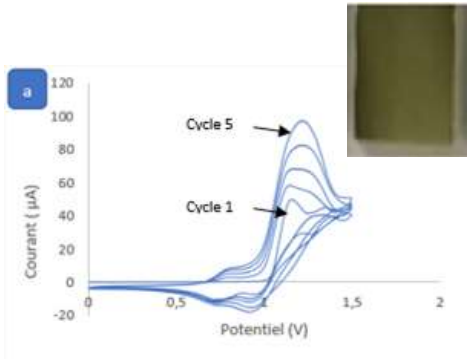
✓ Synthesis of original monomers by organic chemistry and their electropolymerization:

- Grafting of an carboxyl, hydroxyl, ester, alkyl groups to a carbazole monomer:



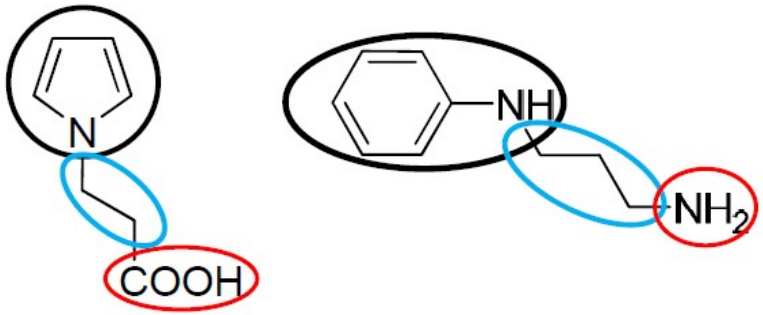
3-ethylcarbazole

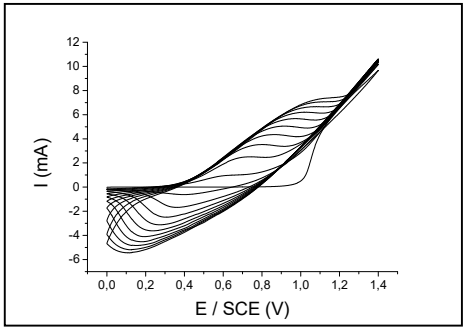
N-((methoxycarbonyl)methyl)carbazole



Electrodeposition of carbazole

- Functionalization of pyrrole and aniline monomers by alkyl chains terminated by $–NH_2$ and –COOH groups:



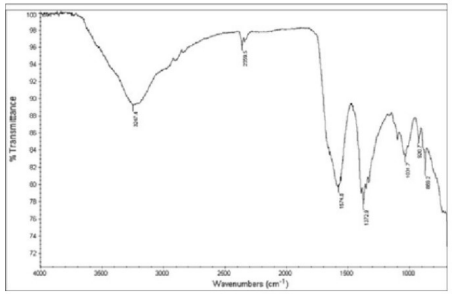


Electrodeposition of poly(N-pyrrolylundecanoïc acid)

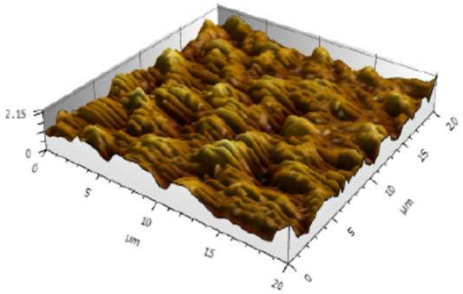
Electrodeposition of conducting polymer films

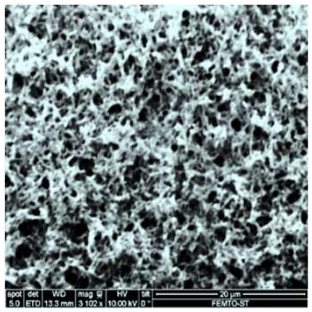
✓ Characterization of the electrodeposited polymer films:

Chemical structure

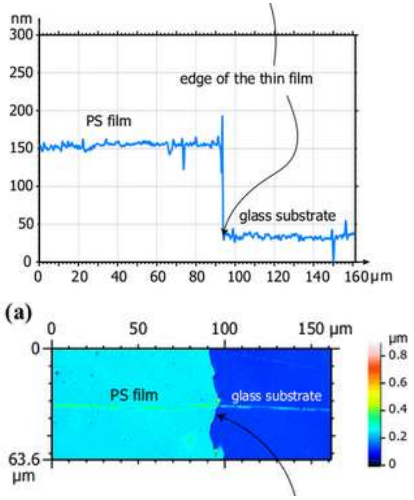


Morphology



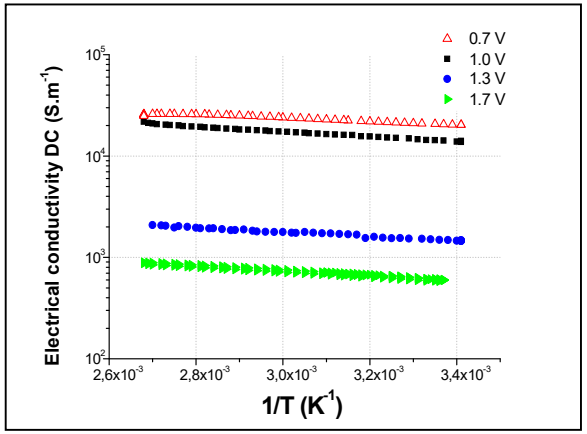


Thickness, roughness



Wettability

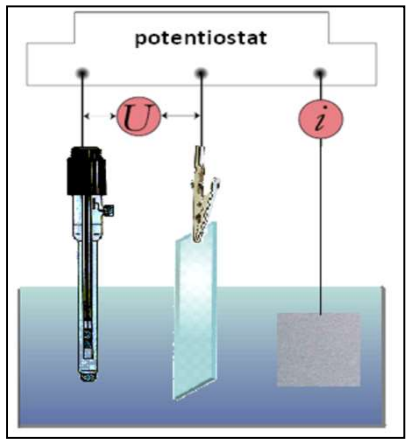
Conductivity



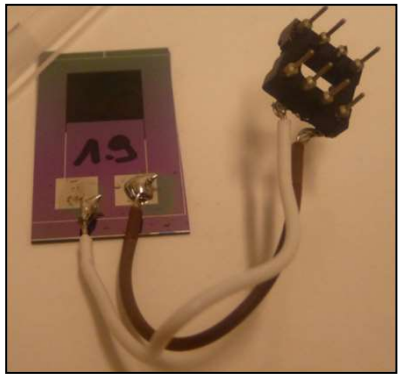
Development of gas sensors

based on electrodeposited polymers

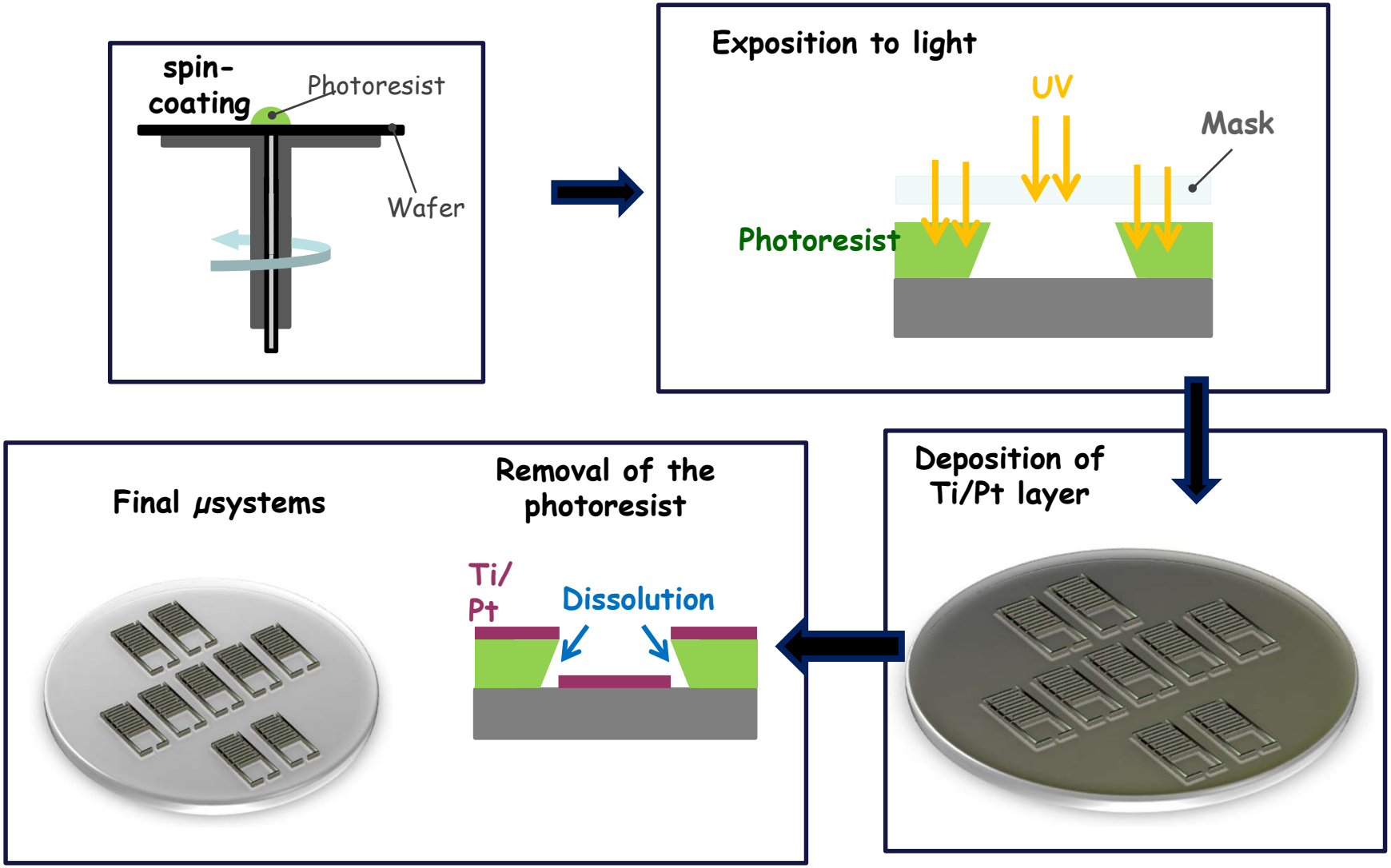
Electrochemistry



Sensors

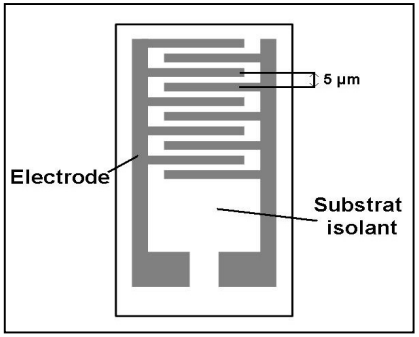


Fabrication of the microsystems by photolithography:



Development of gas sensors based on electrodeposited polymers

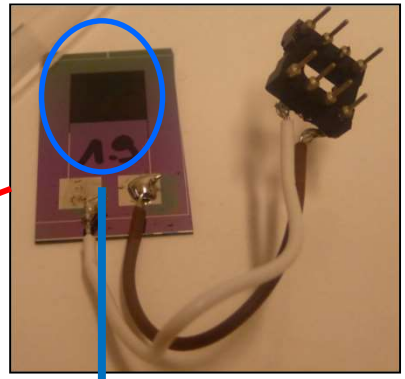
Application to the development of ammonia gas sensors using either polypyrrole or polypyrrole+phtalocyanine as sensitive layer:

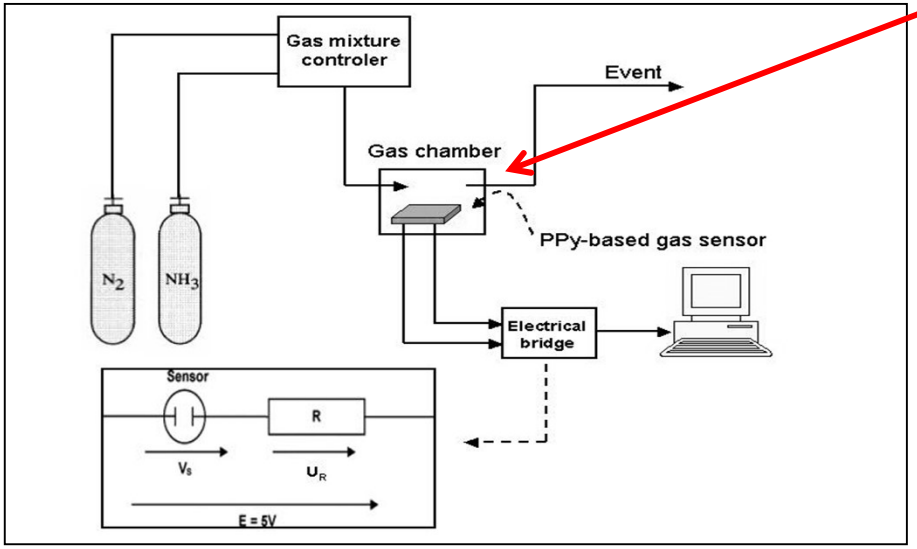


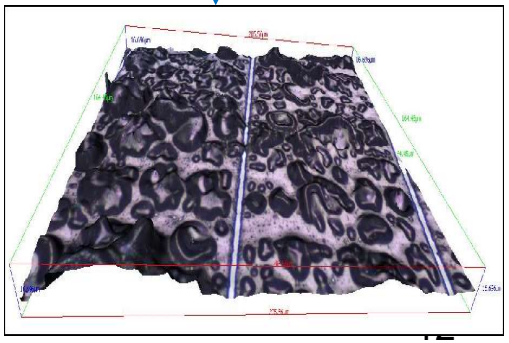
Dépôt Ppy

200 nm

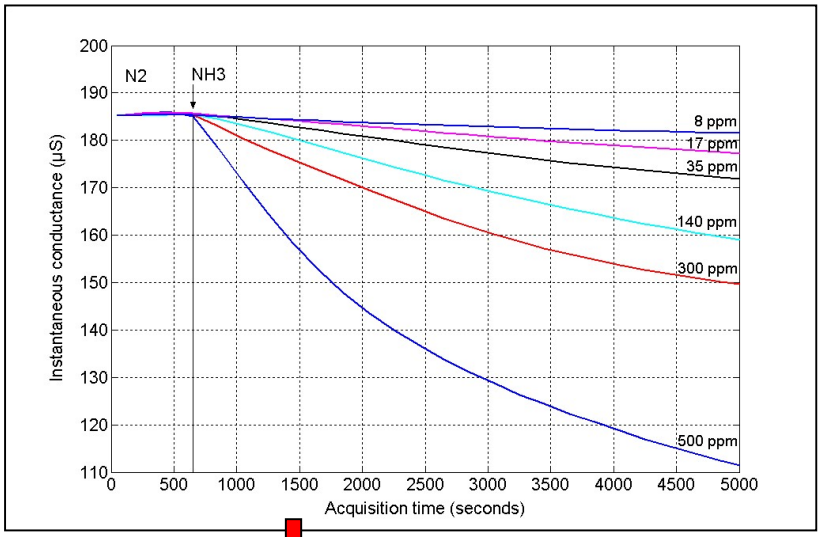
microsystème + PPy

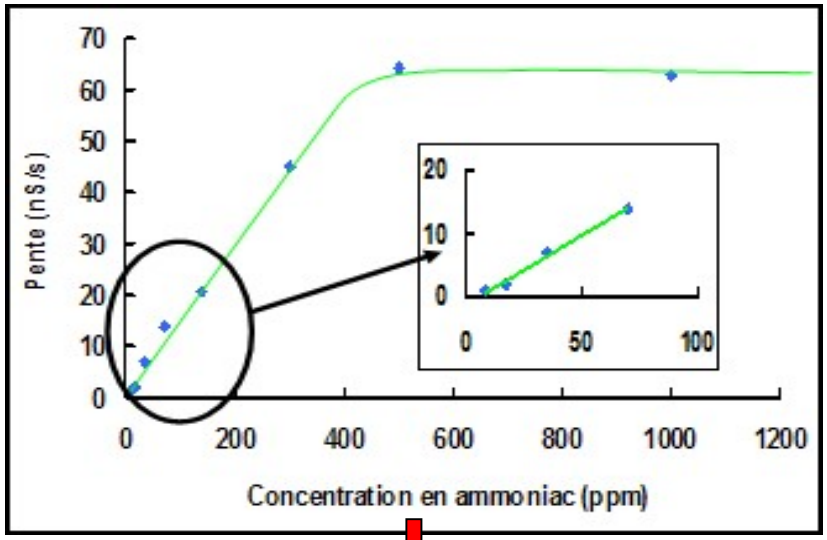






Influence of the NH_3 concentration on the response of the sensor:





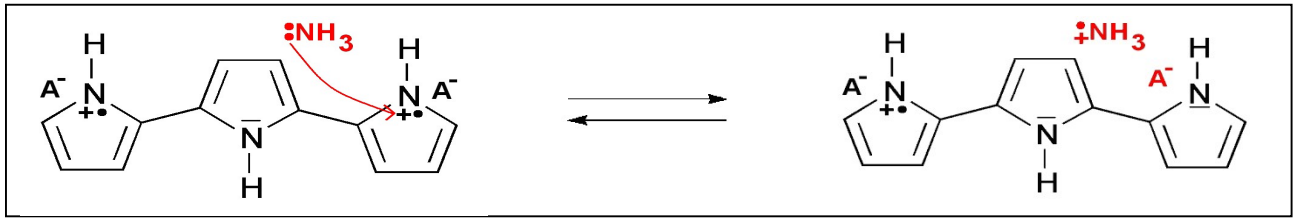
Slope↓ when $[NH_3]$ ↑

Linear responses for $[NH_3]$ varying from 8 to 500 ppm

Saturation of the response for $[NH_3]$ > 500 ppm

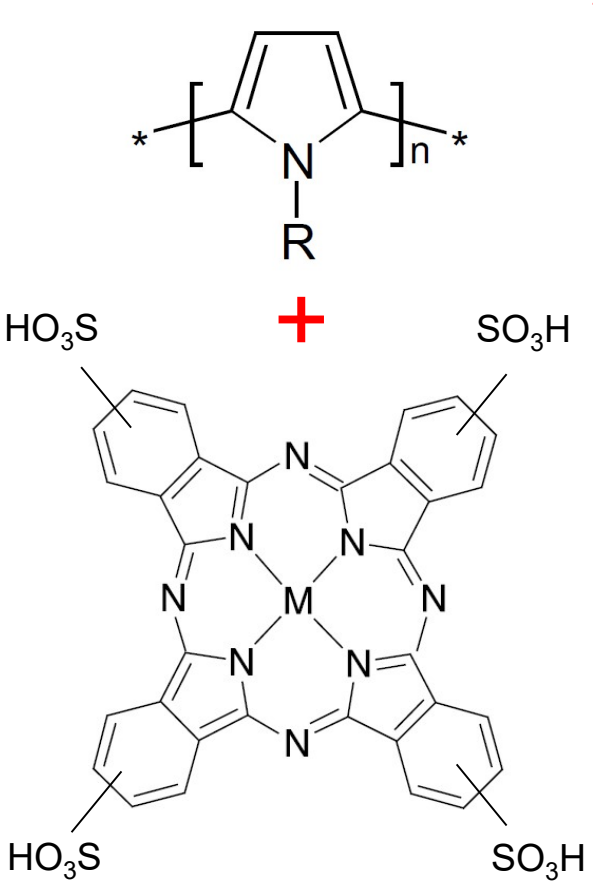
Limit of detection: 8 ppm

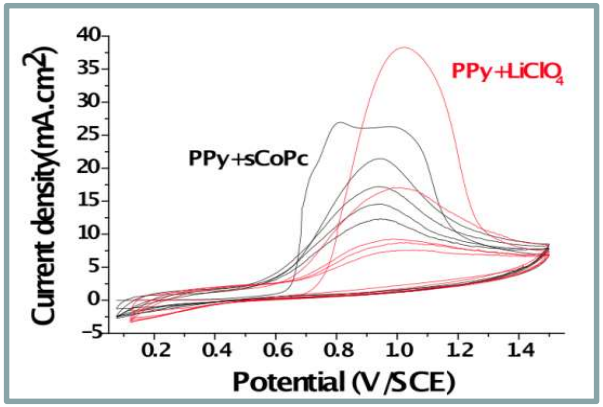
Response mechanism:

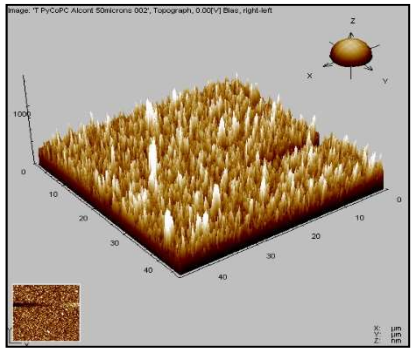


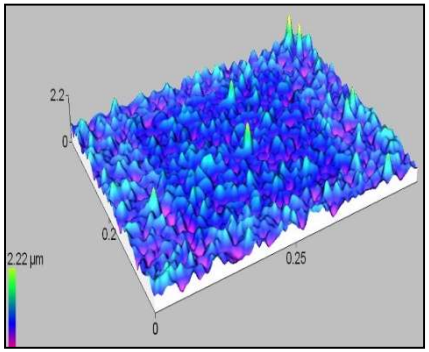
✓ Preparation of an hybrid material by electropolymerization to improve the sensor (coll. ICMUB Dijon – M. Bouvet, R. Meunier-Prest):

- Synthesis of hybrid materials by electrodeposition of solutions containg { polypyrrole + sulfonated cobalt phthalocyanines } and {polypyrrole + sulfonated copper porphyrines}:

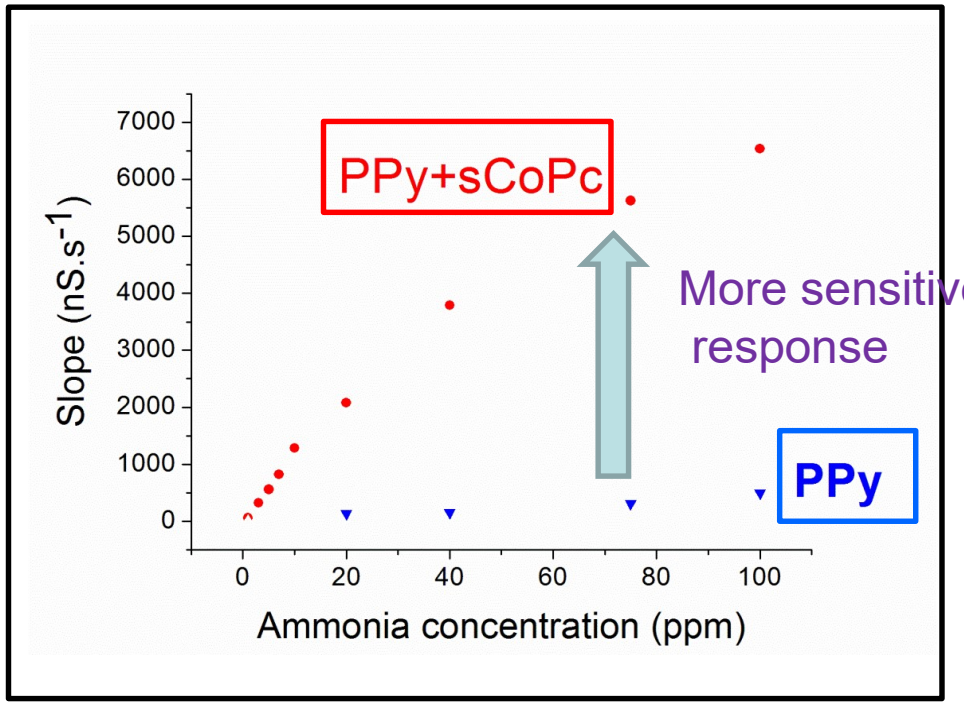


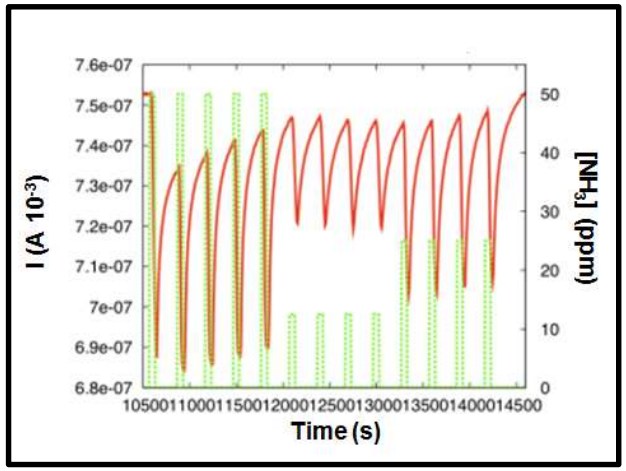






Development of gas sensors based on electrodeposited polymers





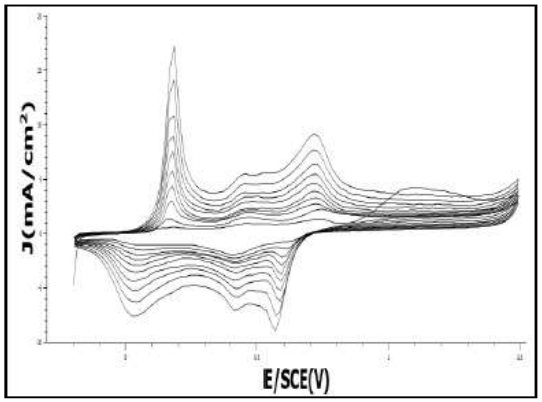
Reproducible responses

Hybrid material:

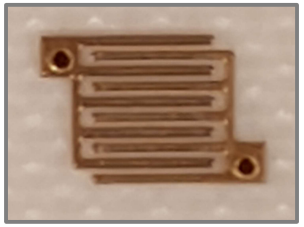
Very good sensibility – Very good limit of detection (1 ppm) – Working at 25°C

Other gas sensors (coll. IMT Lille Douai – N. Reddon, C. Duc):

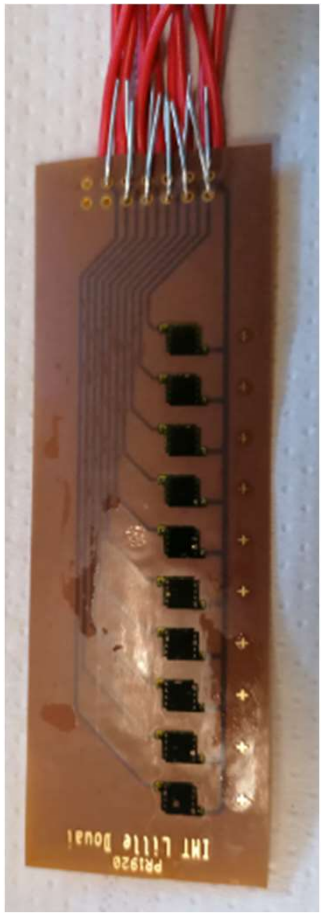
Electropolymeization of polyaniline films:

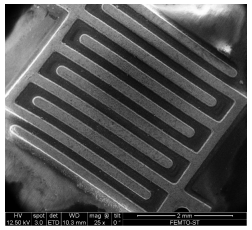


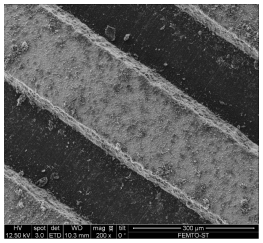
Arrays of sensors:

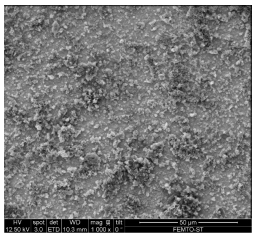


Development of gas sensors based on electrodeposited polymers

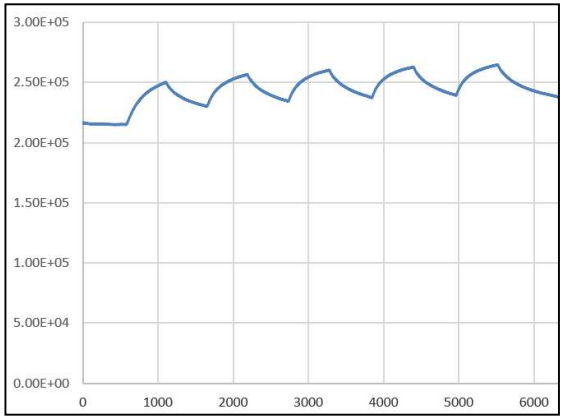








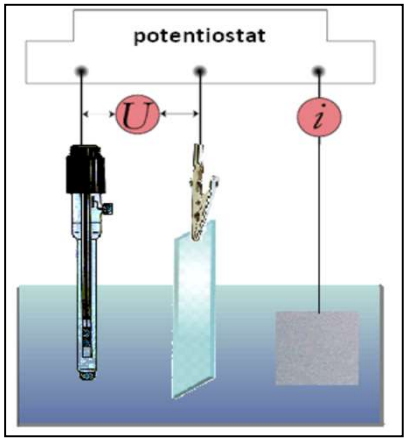
Response of a sensor to ammonia (50 ppm):



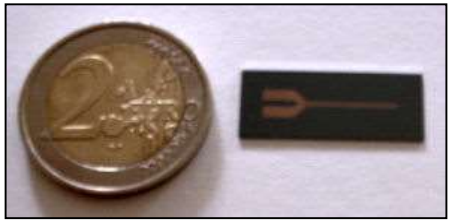
Development of liquid sensors

based on electrodeposited polymers

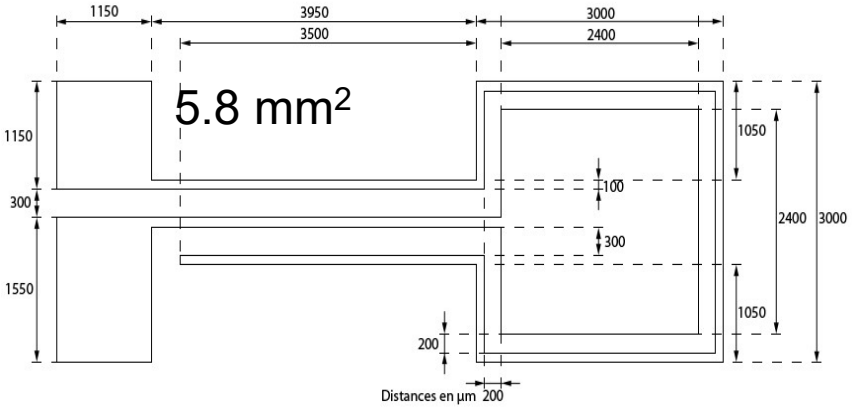
Electrochemistry

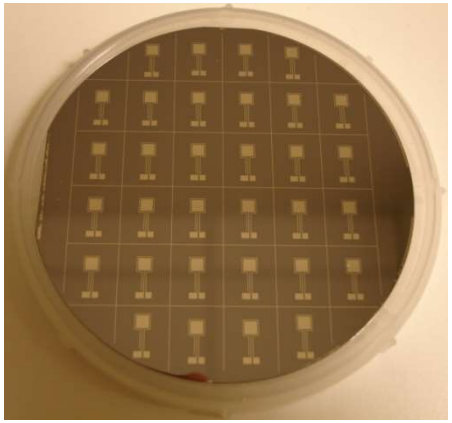


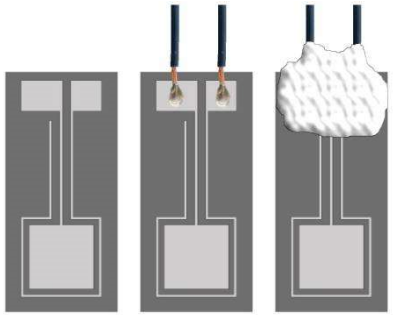
Sensors



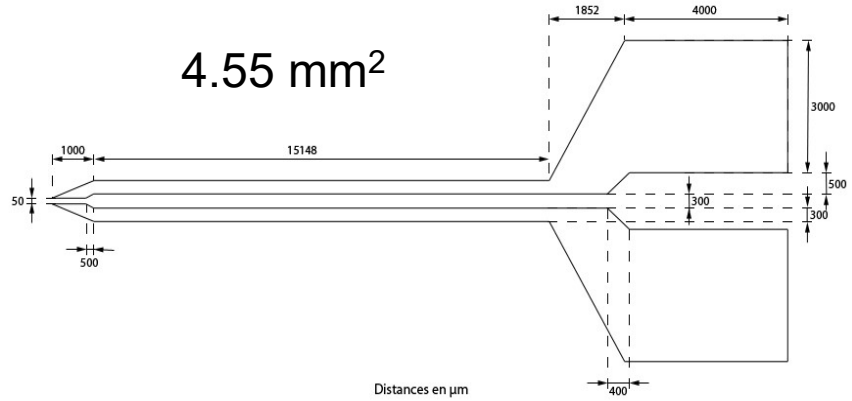
Fabrication of µsystems:

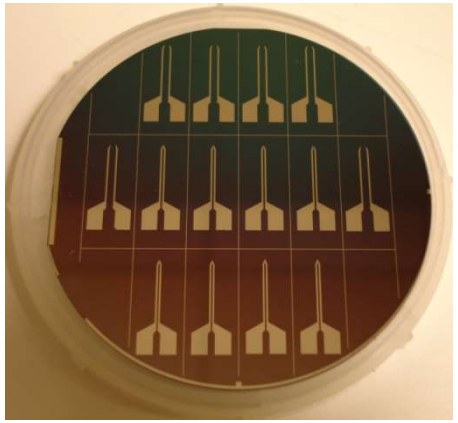


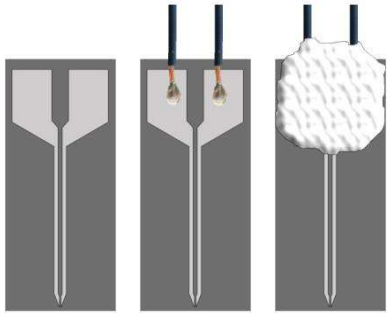




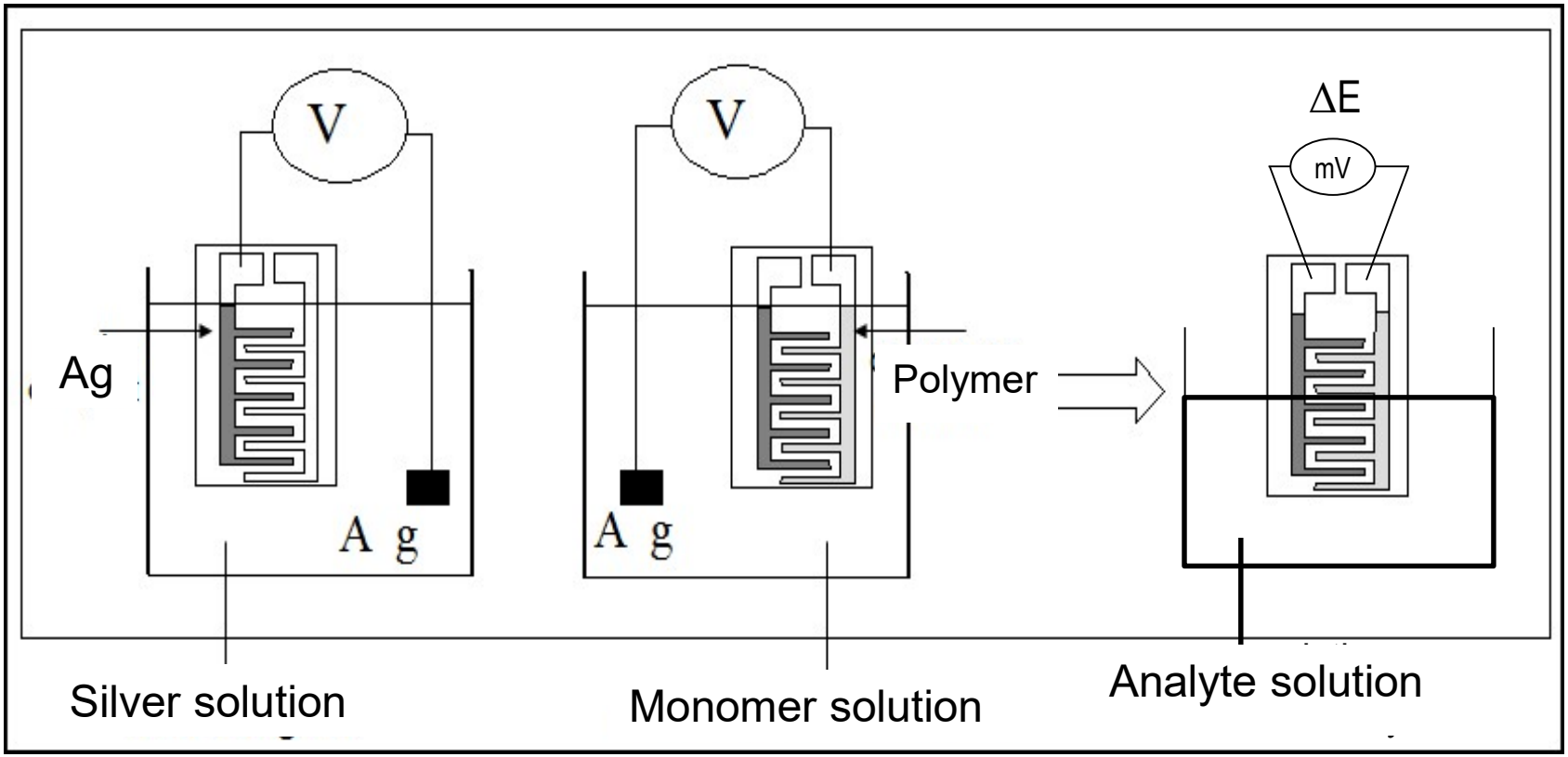
3'' wafers





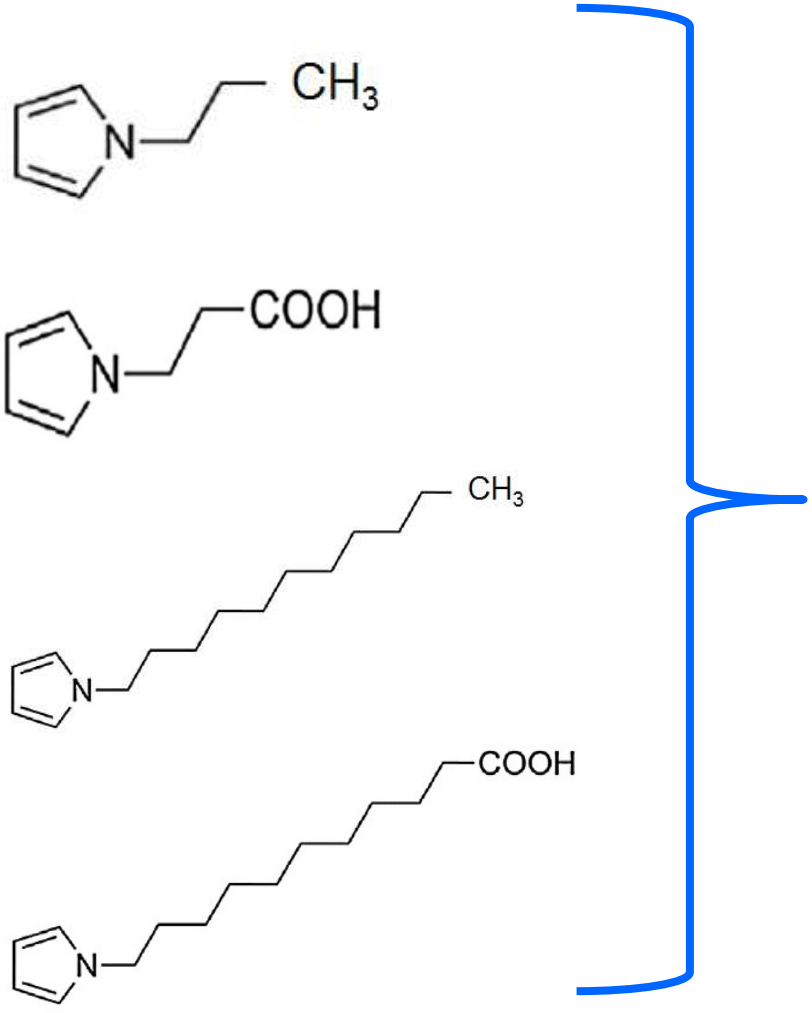


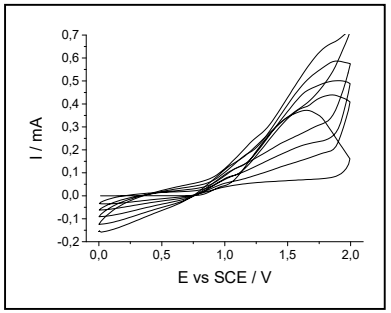
Electrodeposition of Polymer films and Ag films



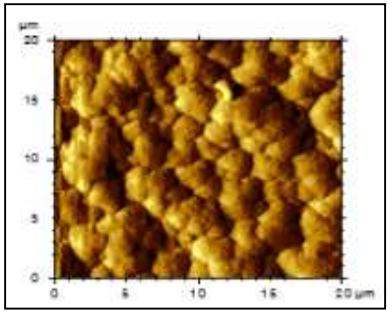
Development of liquid sensors based on electrodeposited polymers

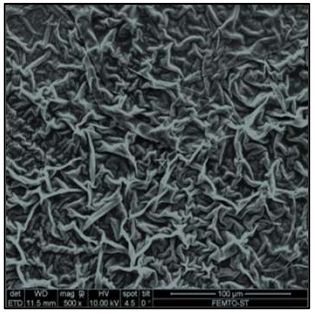
✓ **Synthesis of monomers containing carboxyl groups to be used as pH sensitive materials:**





Electrodeposition



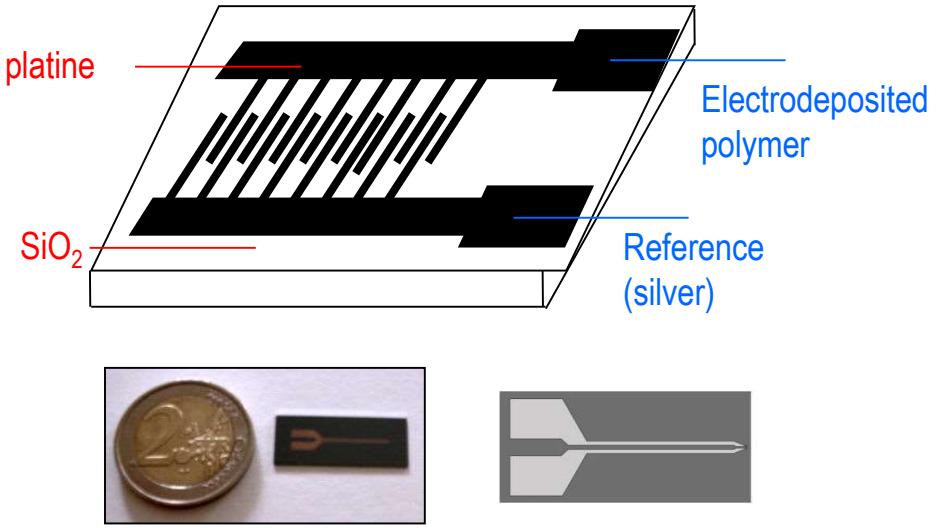


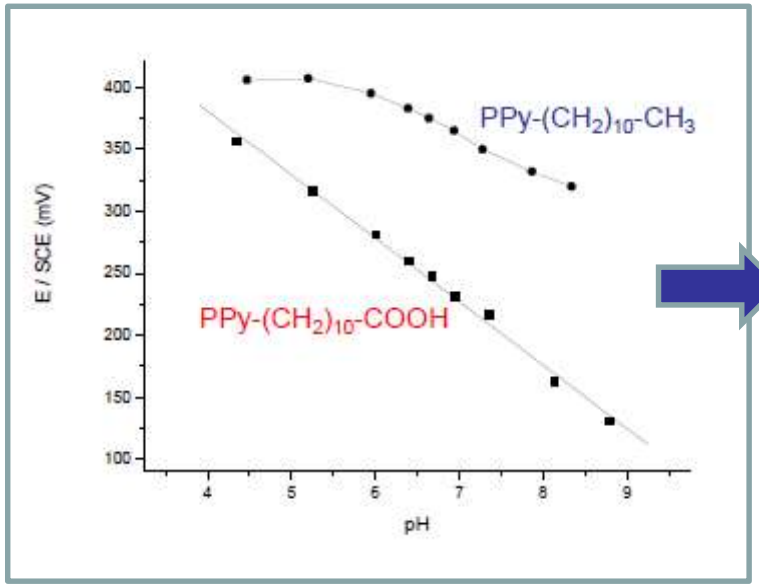
Characterization

Development of liquid sensors based on electrodeposited polymers

pH sensors:

Preparation of a monomer by organic chemistry to serve as sensitive material



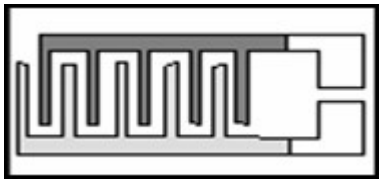


- Films PPy-$(CH_2)_{10}$-COOH
- Potentiometric responses of the sensors:

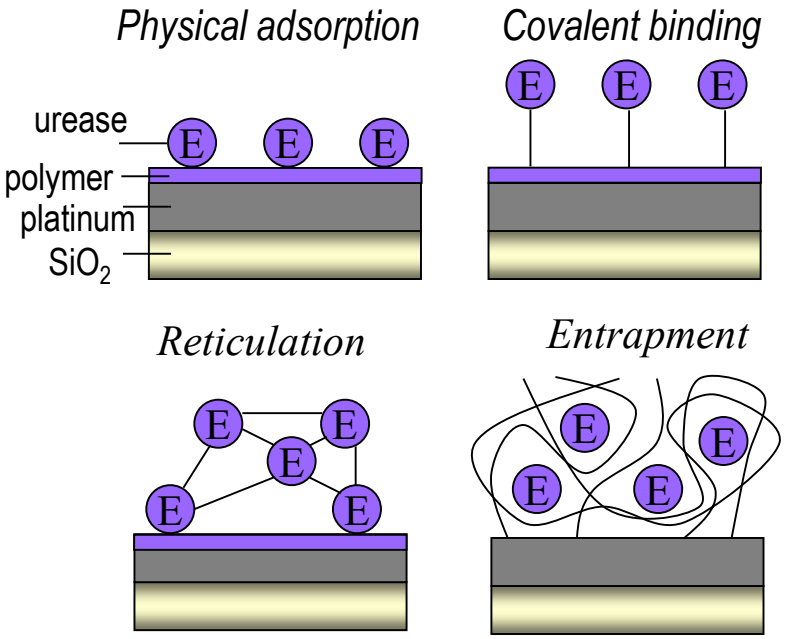
- linear from pH 4 to pH 9,
- good stability in time (> 30 days),
- reproducibility, repetability, reversibility, short response time
- good sensibility (50 - 60 mV/pH unit).

Development of liquid sensors based on electrodeposited polymers

Electrochemical enzymatic sensors for the detection of urea:

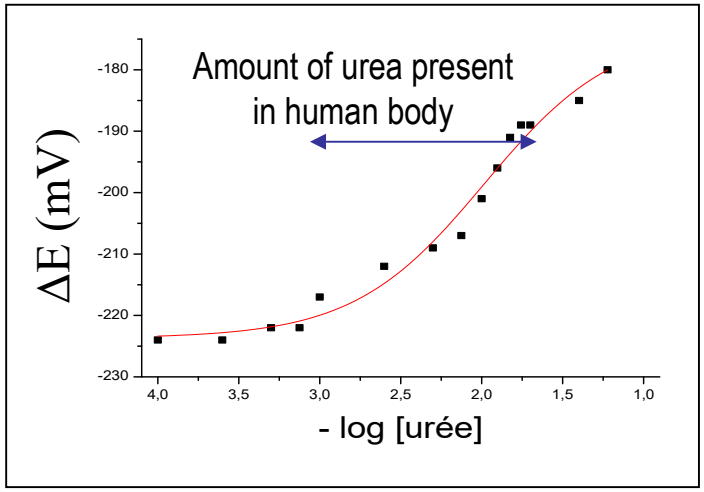


Principle: similar to the one used for pH sensors but necessity to immobilize an enzyme catalyzing urea hydrolysis to induce pH changes



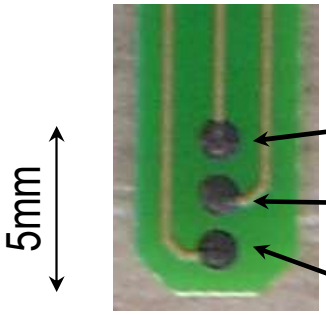
Results:

- Sigmoidal and reproducible potentiometric responses,
- Reticulation = best way to immobilize urease (best analytical results)



Polymer used: polyethylenimine

✓ **Deposition of these films on a home-made « potentiostat »** (fabricated by S. Yunus et al., UCLouvain, Belgium):



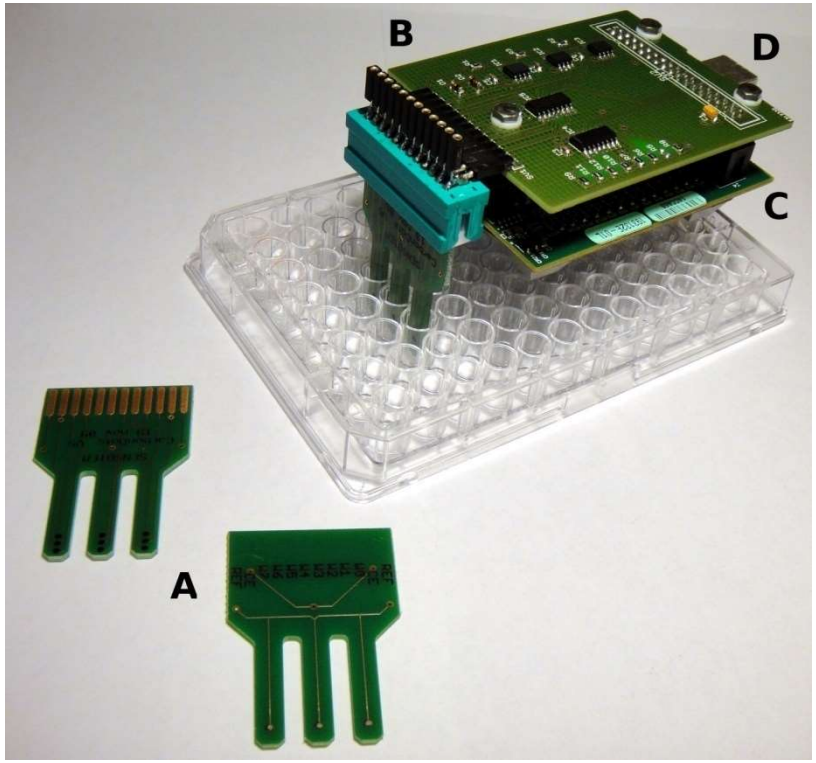
3 electrodes set-up:

Working electrode

Counter-electrode

Working electrode

=> Reference electrode: Ag/AgCl

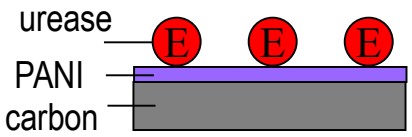


Advantages:

- Fast
- Repetability: 6 simultaneous experiments
- Portable

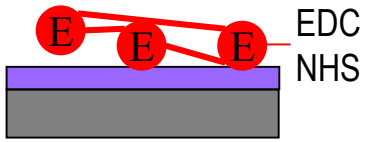
Elaboration of biosensors (using a sensitive layer made of electrodeposited polyaniline, self-assembled polyelectrolytes and urease):

PANI-Urs



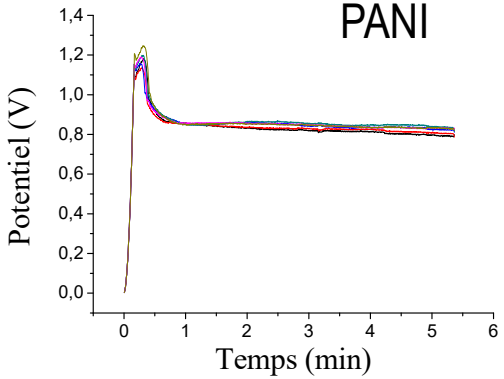
Physical adsorption

PANI-EN-Urs

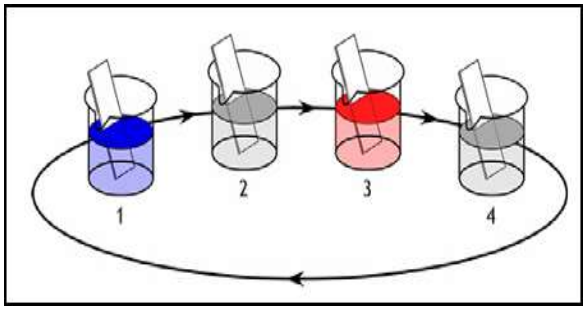


Reticulation

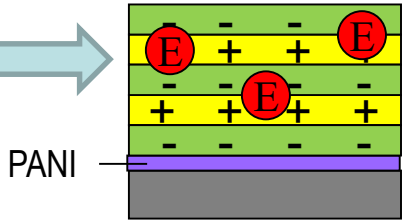
PANI



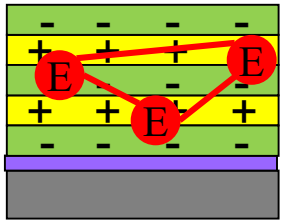
Multilayered polymer film
(obtained by alternated deposition of polycation and polyanion)



PANI-(+/-)$_n$-Urs

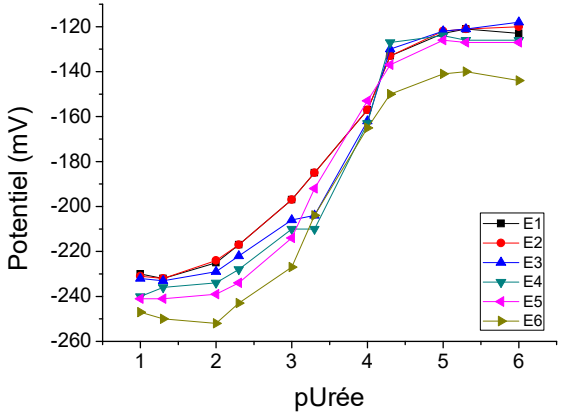


PANI-(+/-)$_n$-EN-Urs



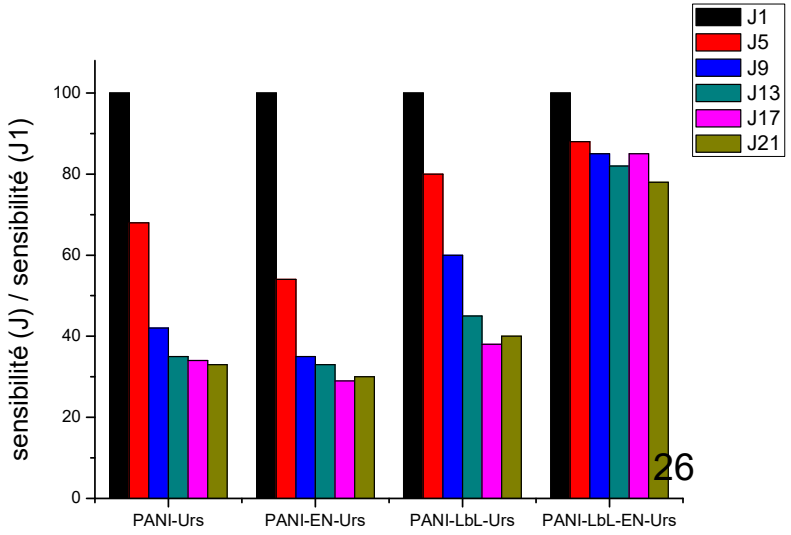
Addition of the LbL film

Results: Potential = f(-log[urea]): sigmoid, fast response time (10 s), reproducible, sensitive.

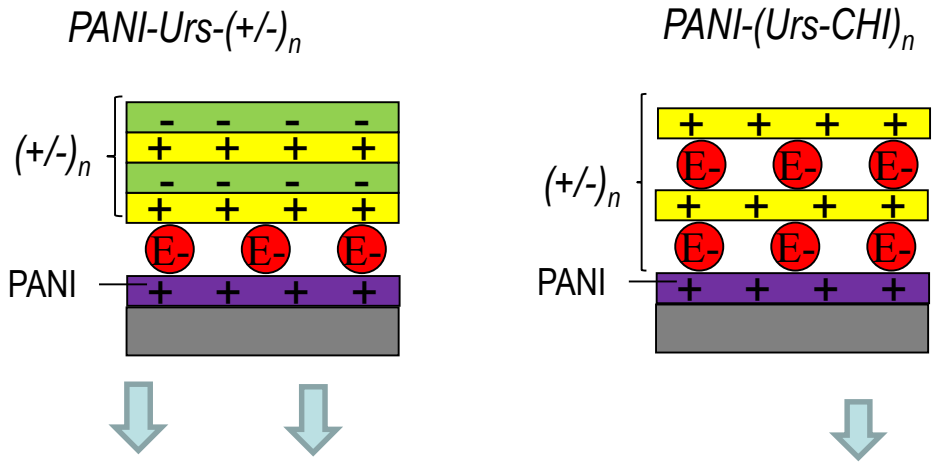


Influence of the enzyme immobilization method on the sensitivity and stability in time of the biosensor.

sensor	sensitivity
PANI / Urs	250 mv
PANI / EN / Urs	260 mV
PANI / $(+/-)_n$/ Urs	190 mV
PANI / $(+/-)_n$/ EN / Urs	115 mV



Test of other original configurations

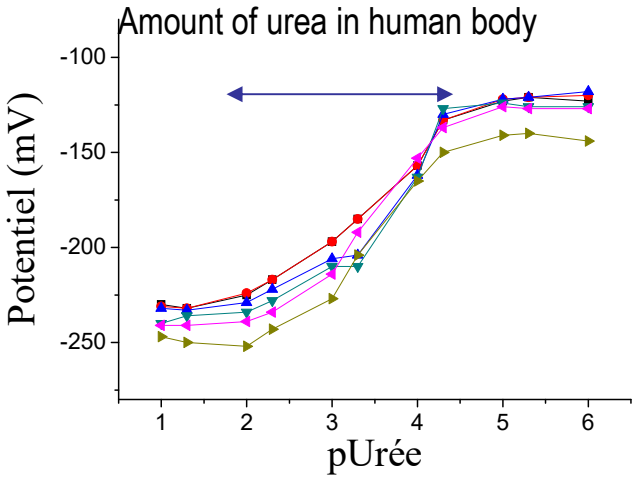


	PANI-Urs	PANI-$(+/-)_n$-En-Urs	PANI-Urs-$(+/-)_n$	PANI-$(Urs\text{-}CHI)_5$
D1	240 mV	110 mV	106 mV	231 mV
D5	68% J1	82% J1	98% J1	90% J1
D15	35% J1	80% J1	93% J1	82% J1
D25	33% J1	78% J1	94% J1	81% J1

Good sensitivity and stability in time of the sensitive layers combining polyaniline, polyelectrolytes and enzyme.

Perspectives: biomedical applications

- Sensitive range corresponds to the amount of urease in human body



- Tests performed on synthetic urine:

Good results, underestimation of the urea amount by 10% due to numerous interferents in urine

-Next step: trying with real samples

Other strategies…

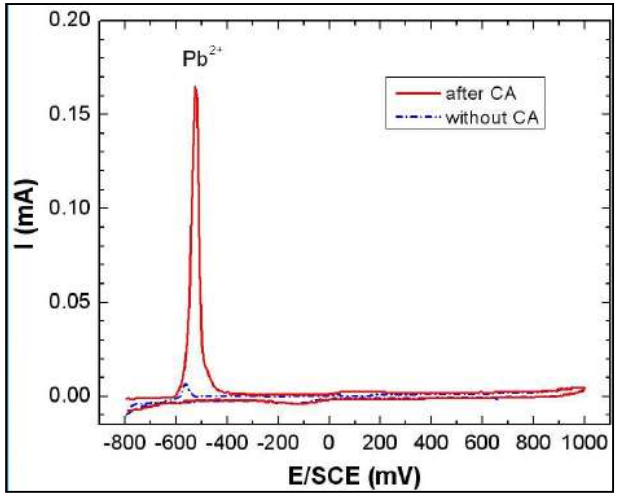
Development of environmental liquid sensors

based on polymers

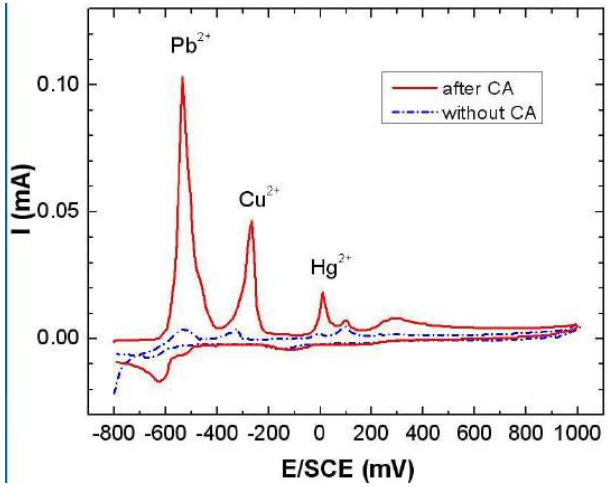
Anodic Stripping Voltammetry:

1) Chronoamperometry at a potential allowing to reduce Pb(II) in $Pb_{(s)}$ at the electrode: here at -800 mV.

2) Cyclic voltammetry between -800 and +1000 mV at low scan speed in a potental range allowing the oxidation of Pb into Pb(II).

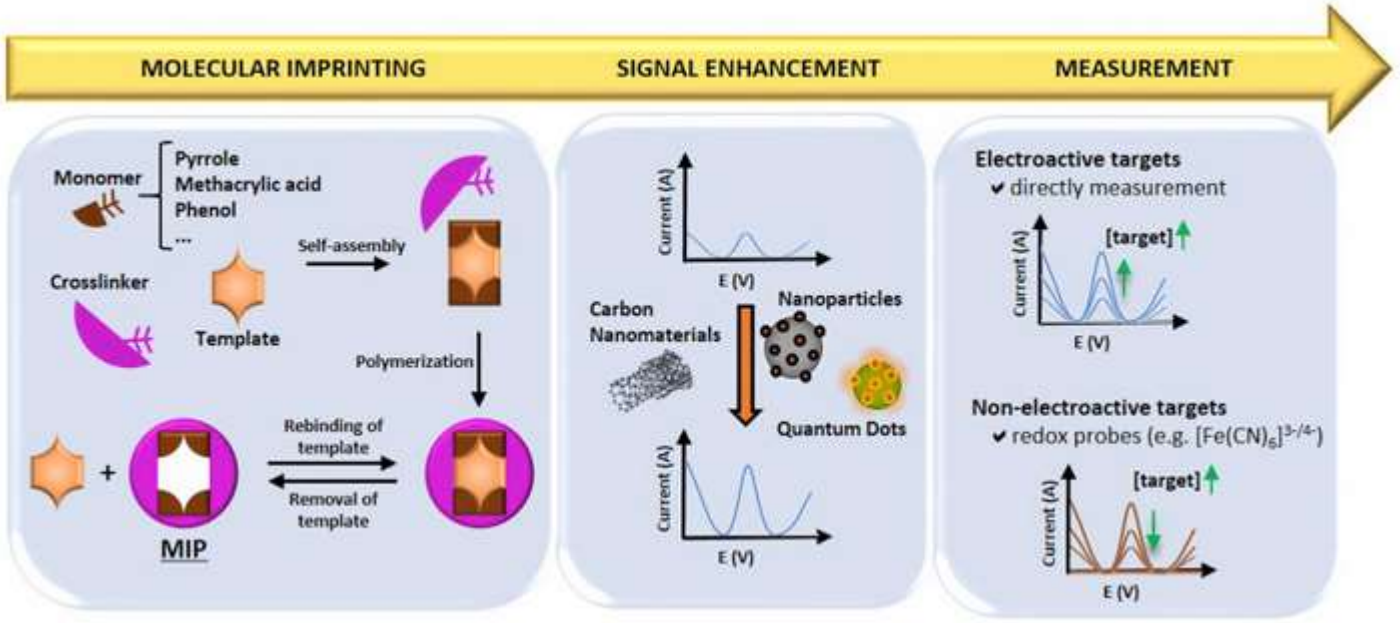


Quantification of Pb(II)
in a monometallic solution



Quantification of Pb(II), Cu(II) and Hg(II)
in a polymetallic solution

Molecularly Imprinted Polymers:



Contaminants pouvant être détectés:

- Produits pharmaceutiques comme des antibiotiques ou des hormones (Sulfamethoxazole, Erythromycin, 17-β-estradiol…),
- Pesticides dont insecticides ou herbicides (Glyphosate, Atrazine, Parathion…)
- Métaux lourds
- Autres(bisphenol A, trinitrotoluène…)

P. Rebelo et al., Molecularly imprinted polymer-based electrochemical sensors for environmental analysis (review), Biosensors and Bioelectronics, 172 (2021) 112719.

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Mulhouse (V. Roucoules, F. Bailly)

Elaboration de capteurs chimiques à base de polymères

Journée Capteurs OSU THETA - DIPEE BFC

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