Detection of ammonia and formaldehyde gas by sensors based on electrodeposited polyaniline conductive films

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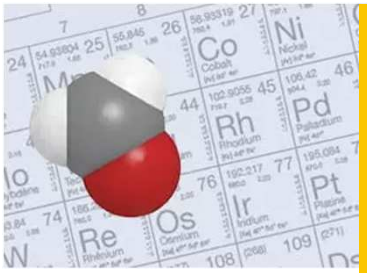
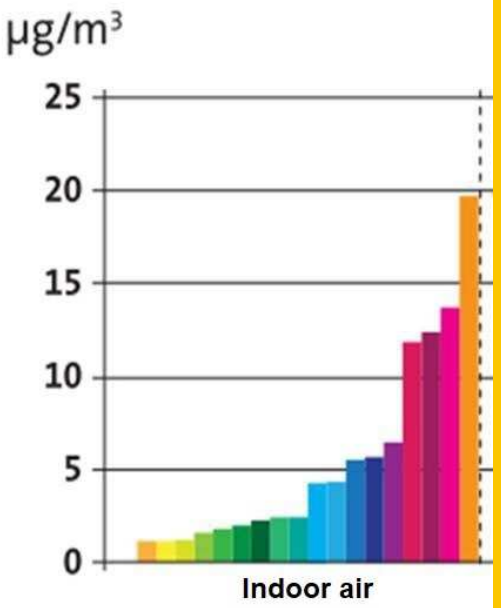
JEPO 2022, 49èmes Journées d'Etude des Polymères
Bussang, 3 Octobre 2022

General context





Observatoire de la Qualit

s CH_2O content

alth status and effects on man

inutes

rious lesions of the respiratory tract

erious pulmonary edema

t breathing difficulties

f the trachea and bronchi, cough

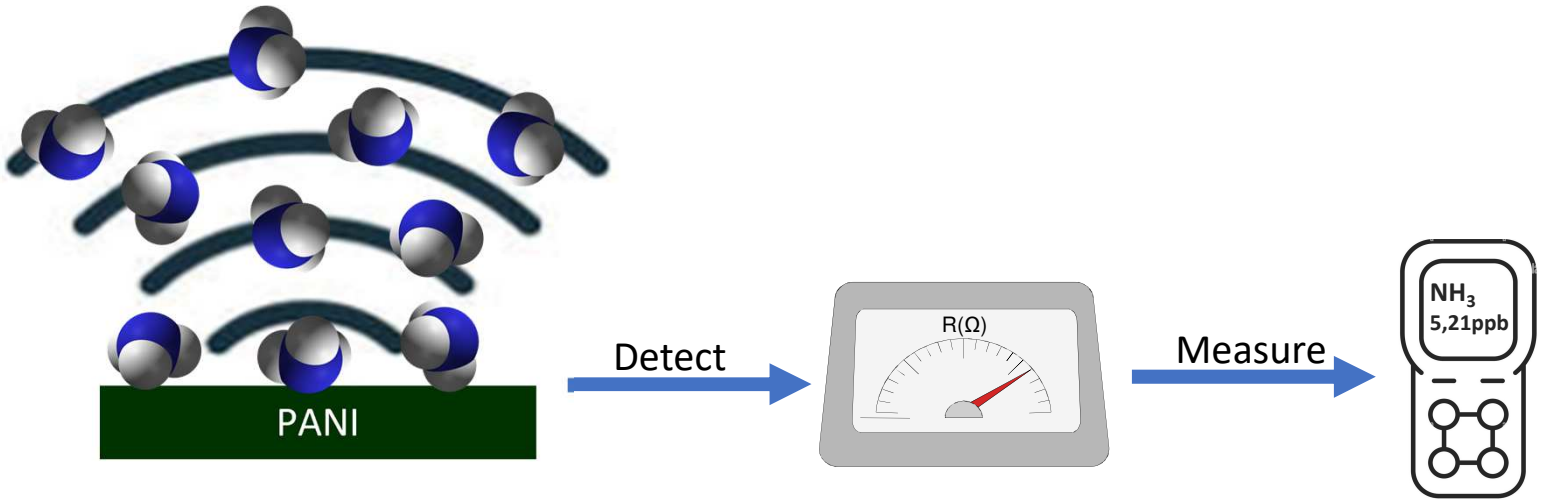
f the eyes and upper respiratory tract
oat)

ritation

Examples of existing CH_2O sensors

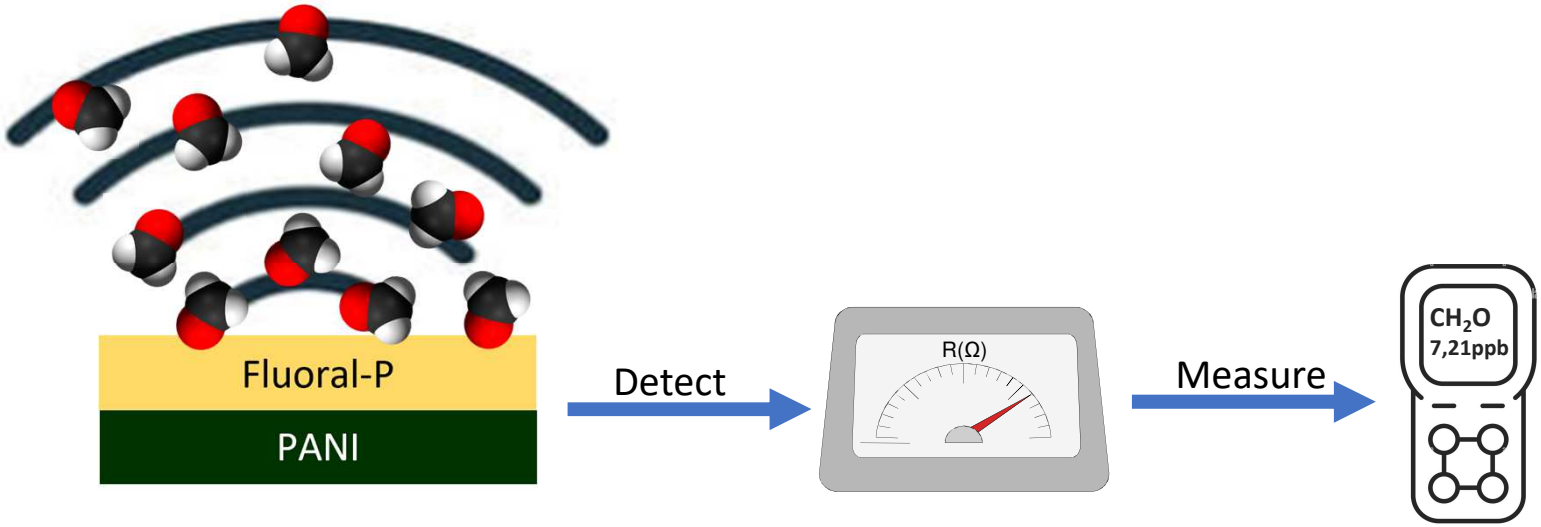
	low cost	good selectivity	low detection limit
	✗	✓	✗
	✓	✗	✗
	✗	✓	✓
	✗	✓	✓
	✗	✓	✗
	✓	✗	✗
	✗	✗	✓
	✓	✓	✗

1st Step of my PhD thesis (Detection of NH_3)



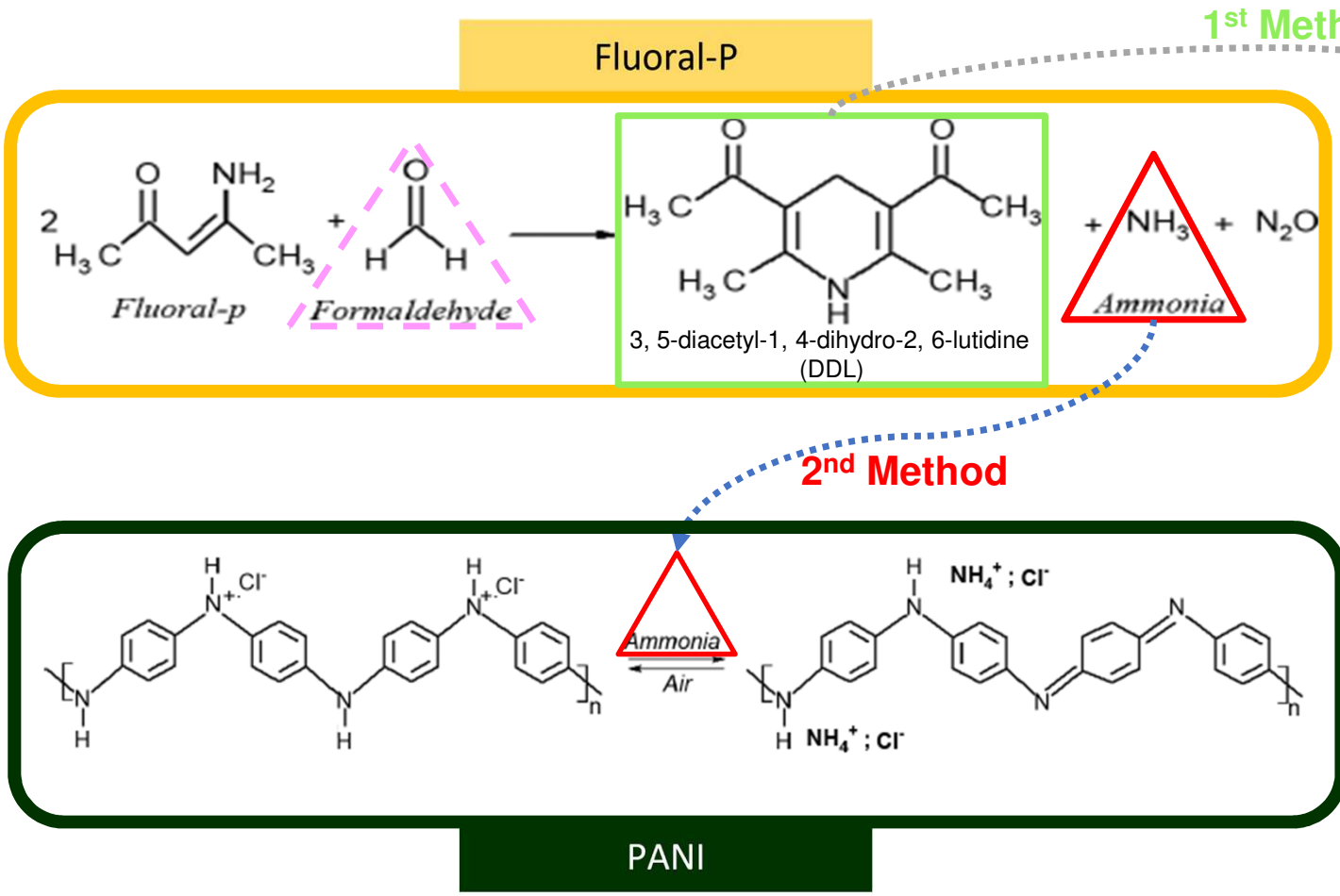
low cost	good selectivity	low detection limit
✓	✓	✓

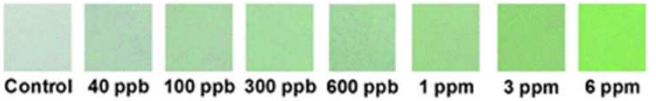
2nd Step of my PhD thesis (Detection of CH_2O)



low cost	good selectivity	low detection limit
✓	✓	✓

How does it work?



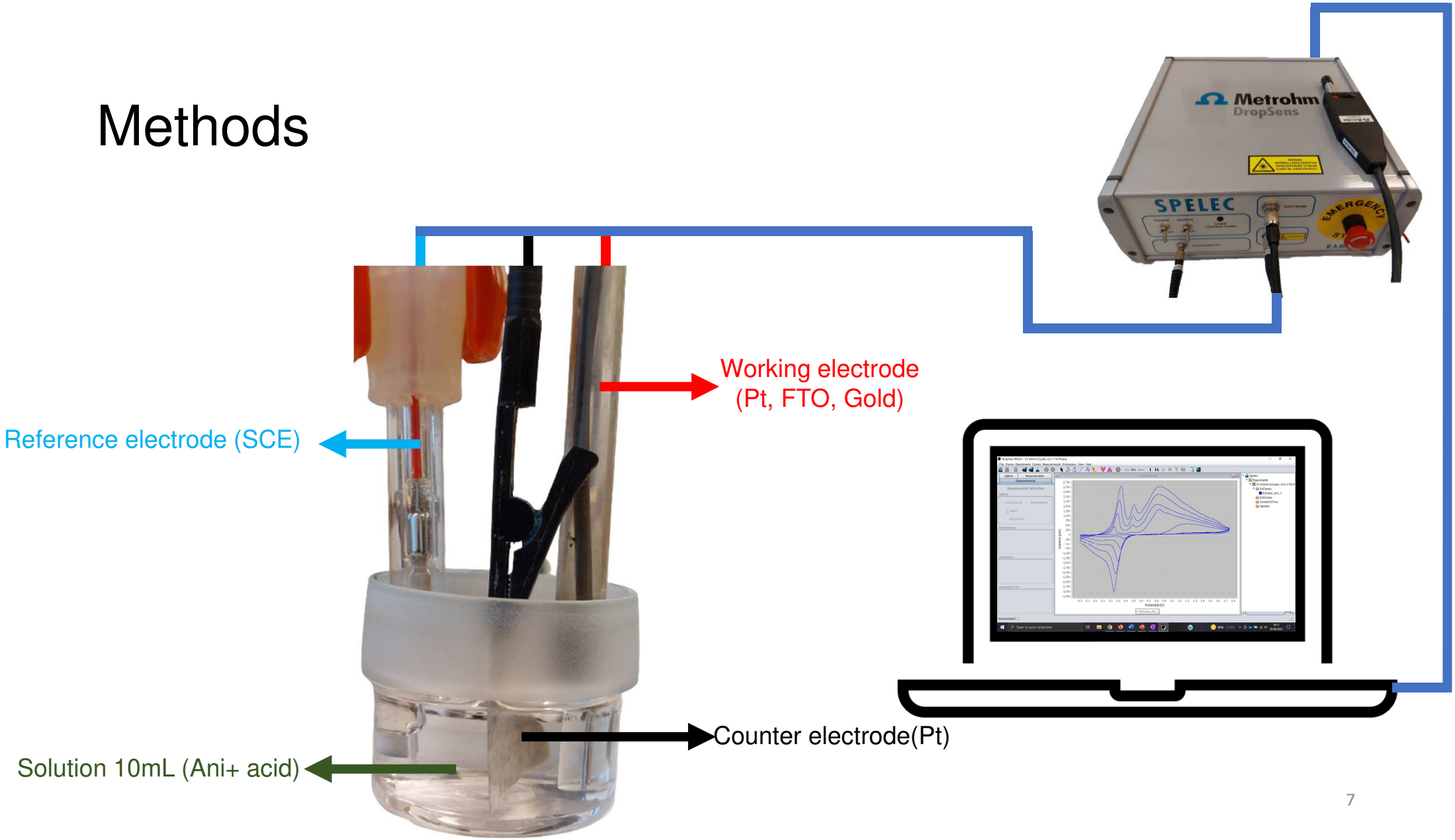


Choice of polymer :

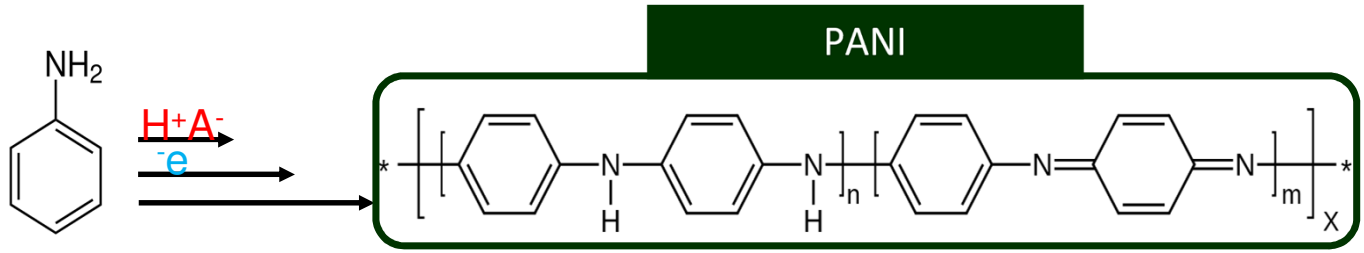
- tunable morphology
- environmental stability
- reversible redox chemistry
- easily synthesized at low cost
- change in PANI resistance as a function of NH_3 concentration

IEEE SENSORS JOURNAL, VOL. 12, NO. 5, MAY 2012

Methods


Metrohm
DropSens
SPELEC
Working electrode
(Pt, FTO, Gold)
Reference electrode (SCE)
Counter electrode(Pt)
Solution 10mL (Ani+ acid)

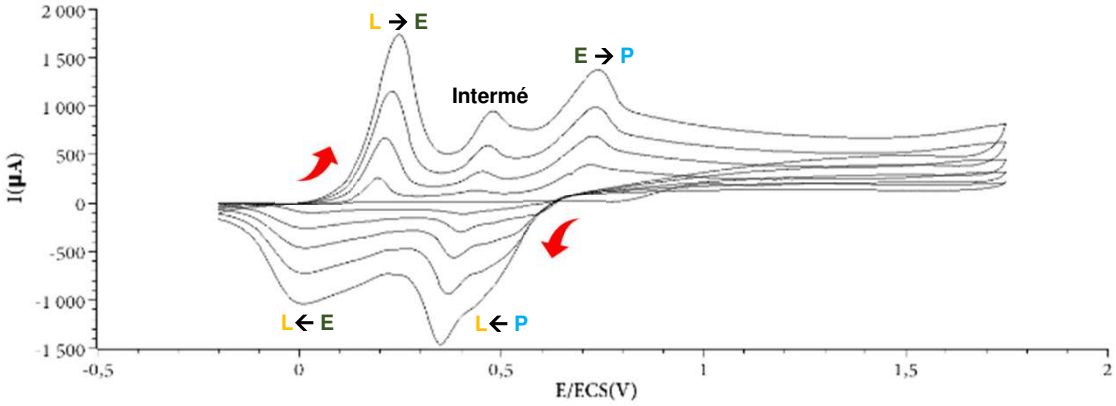
Synthesis of PANI by electrochemistry



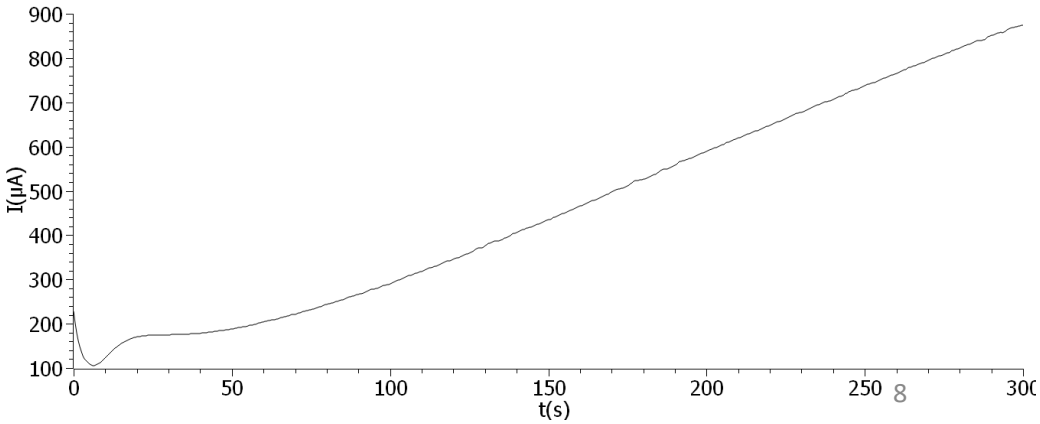
1. Oxidation of aniline
2. Formation of the radical cation then coupling
3. Polymerization of PANI
4. Doping of the PANI film

(m ; n) = (0 ; 1) Leucoemeraldine (L)
(m ; n) = (0,5 ; 0,5) Emeraldine (E)
(m ; n) = (1 ; 0) Pernigraniline (P)

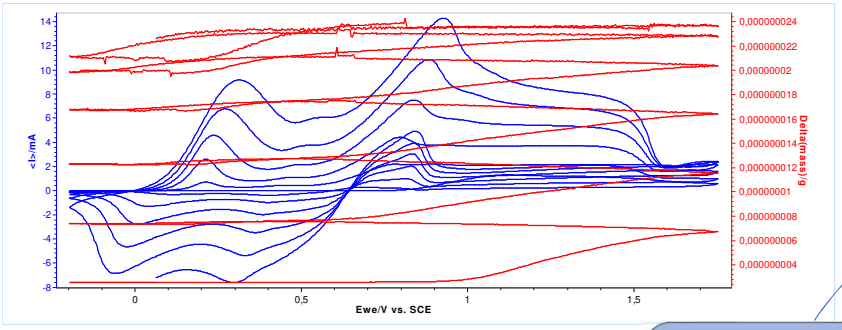
Cyclic voltammetry

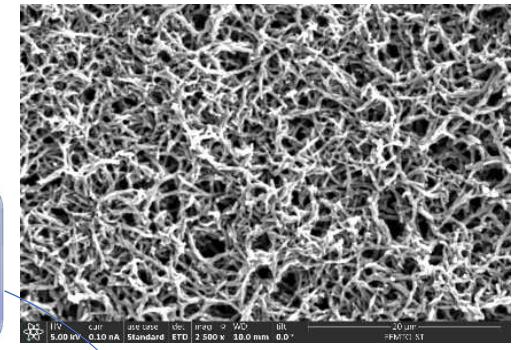


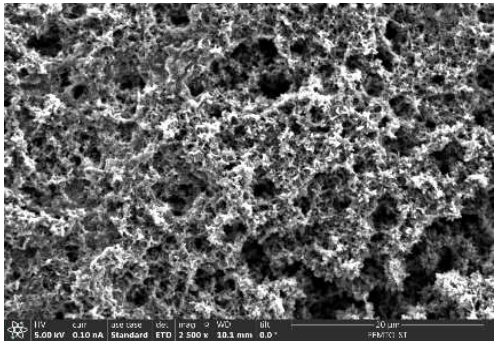
Chronoamperometry



Methods of characterization

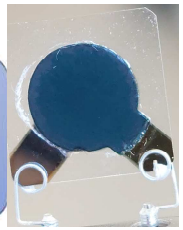




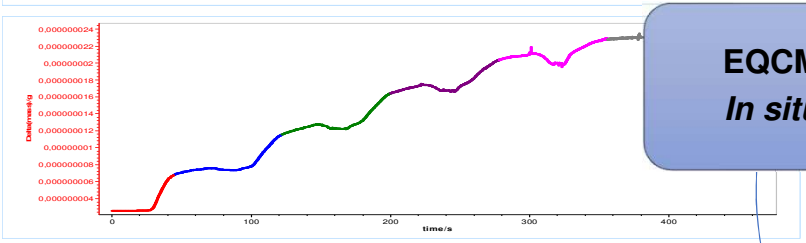


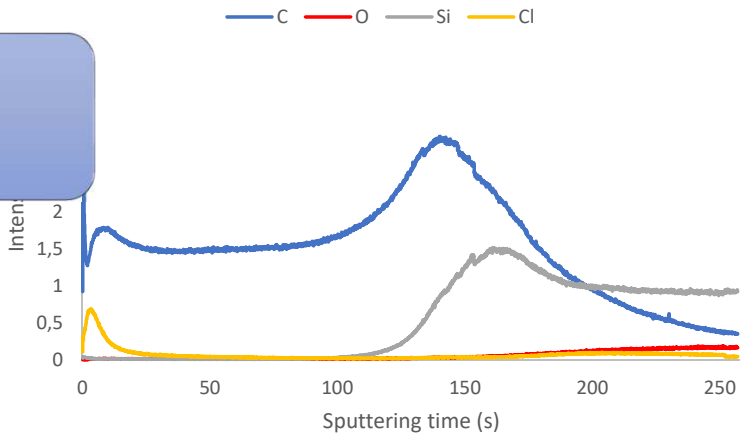
SEM

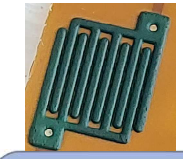
EQCM
In situ



SDL

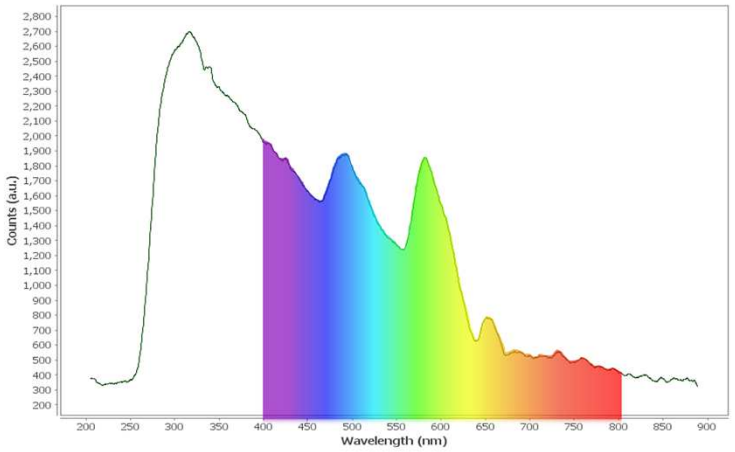


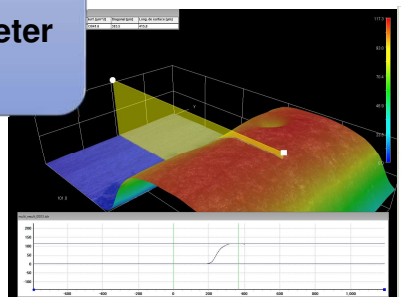


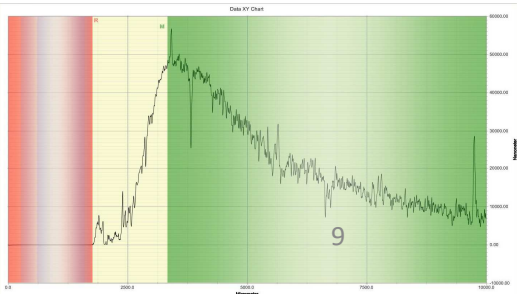


UV-Vis
In situ

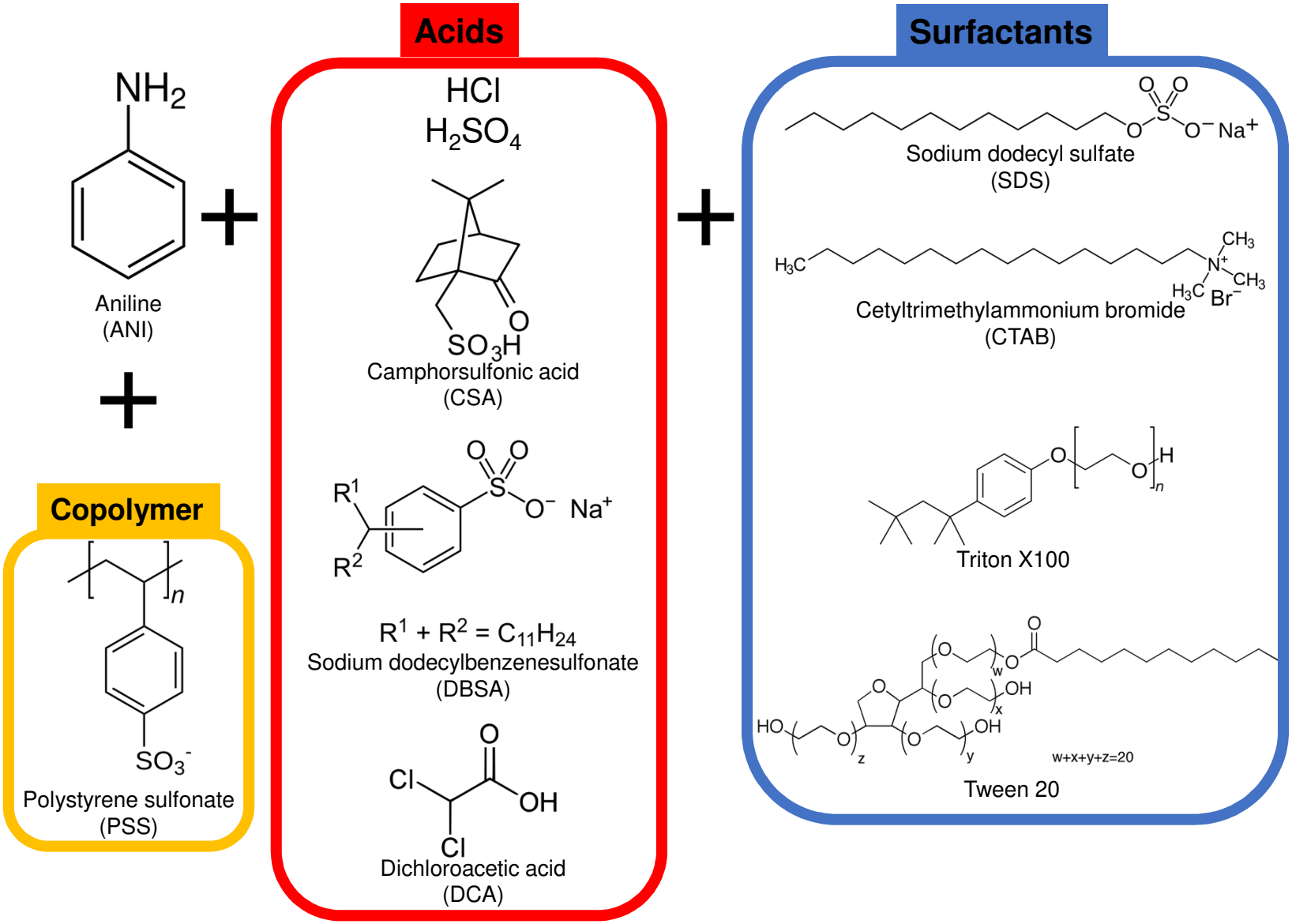
Profilometer



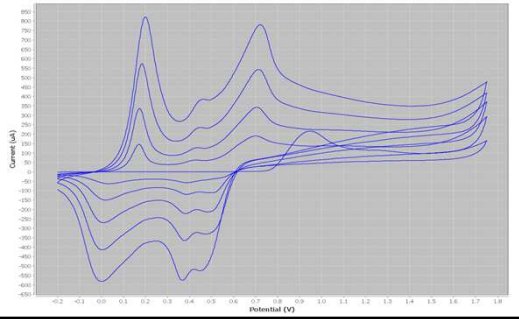
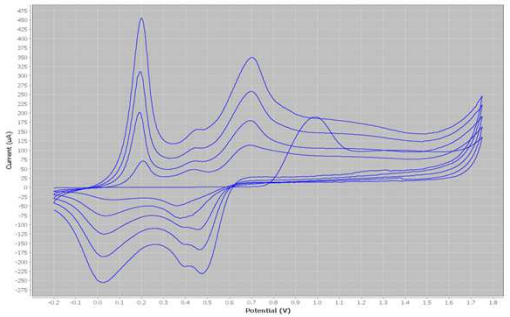
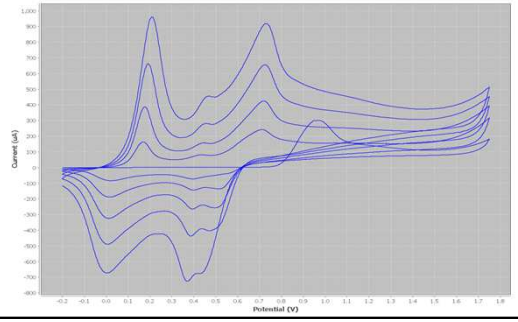
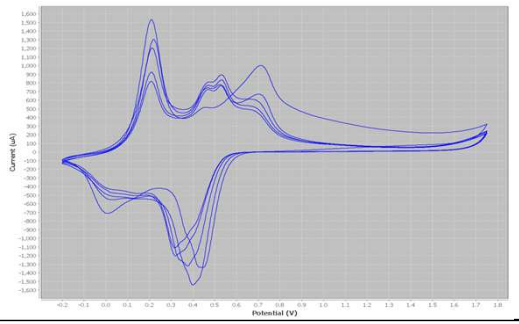
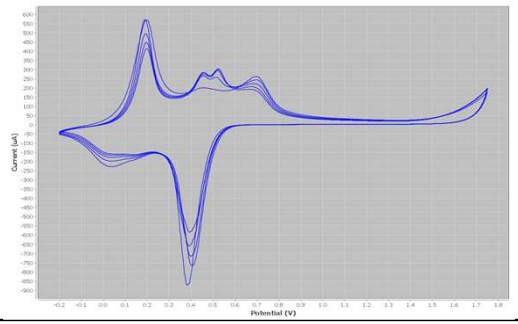
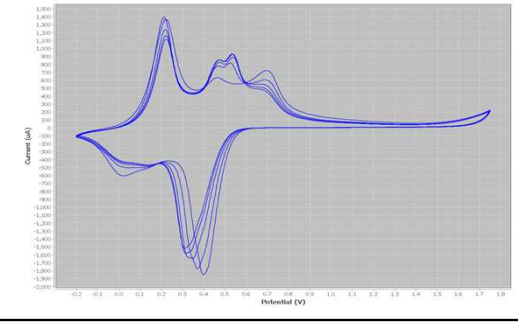
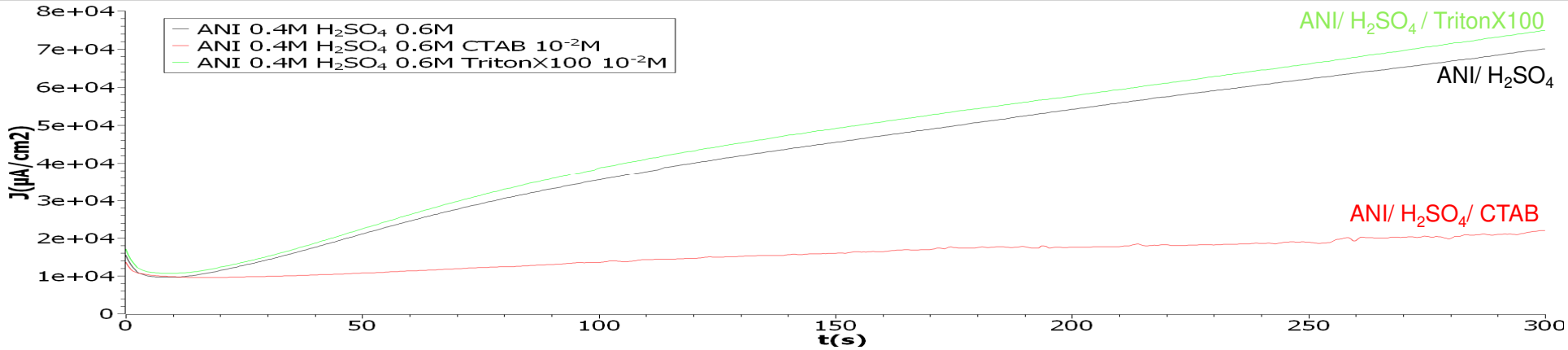




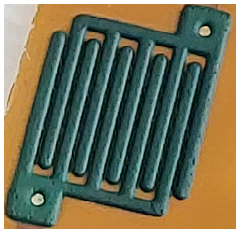
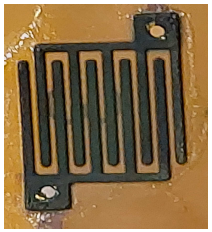
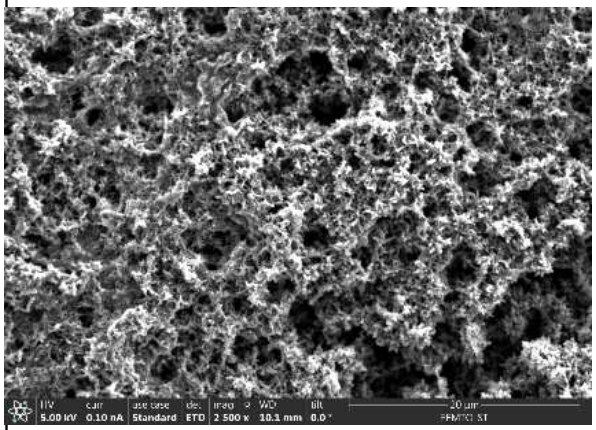
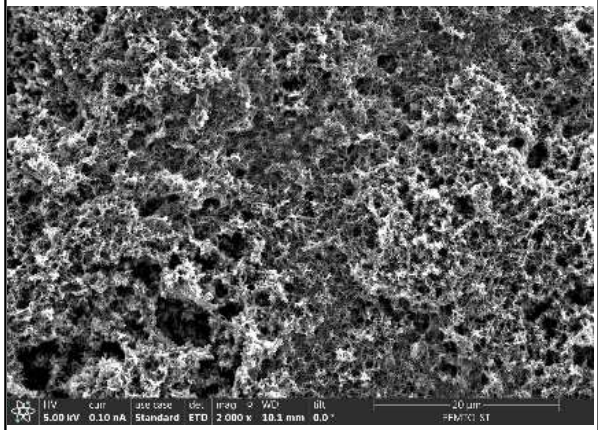
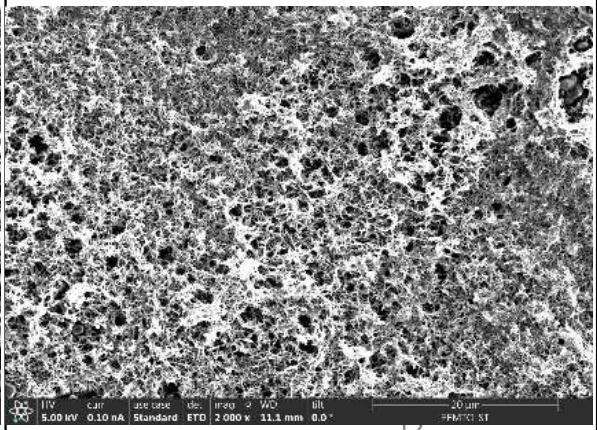
Results


Acids
Surfactants
Copolymer
NH2
Aniline
(ANI)
HCl
H2SO4
SO3H
Camphorsulfonic acid
(CSA)
R1
R2
O
S
O−
Na+
R1 + R2 = C11H24
Sodium dodecylbenzenesulfonate
(DBSA)
Cl
OH
Cl
Dichloroacetic acid
(DCA)
Sodium dodecyl sulfate
(SDS)
H3C
CH3
N+
H3C
Br−
Cetyltrimethylammonium bromide
(CTAB)
Triton X100
HO
OH
OH
w+x+y+z=20
Tween 20
SO3-
Polystyrene sulfonate
(PSS)

Results

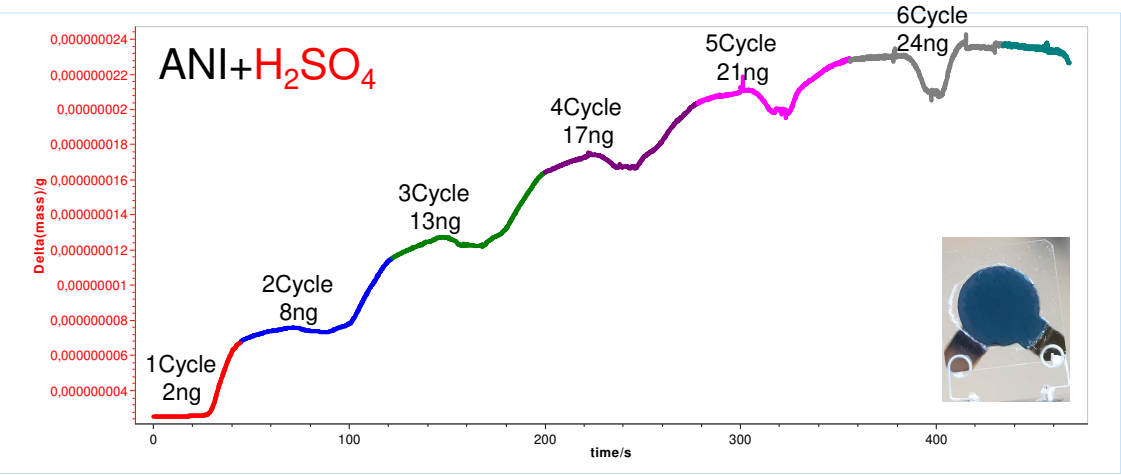
Pt	ANI+H_2SO_4	ANI+H_2SO_4+CTAB	ANI+H_2SO_4+TritonX100
CV			
Activity			
CA			

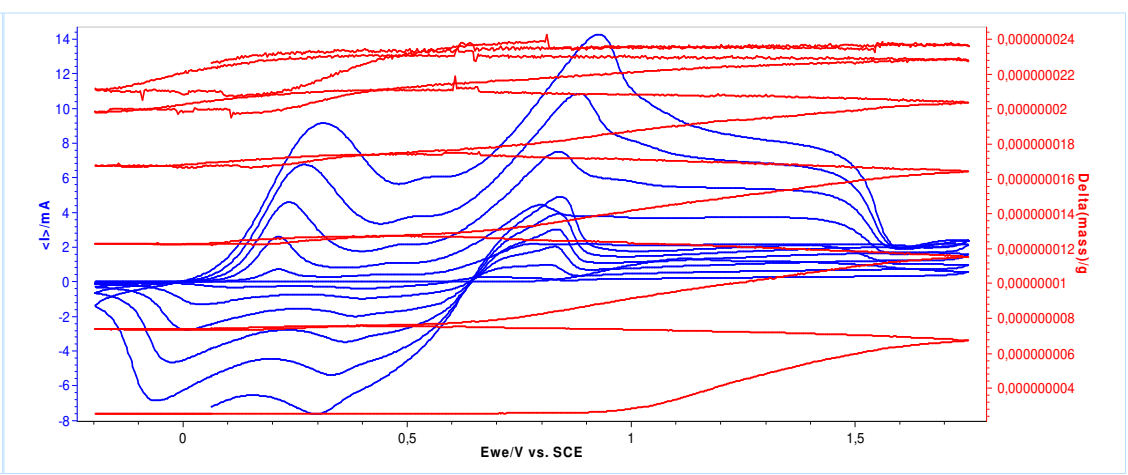
Results

	ANI+H_2SO_4	ANI+H_2SO_4+CTAB	ANI+H_2SO_4+TritonX100
Thickness/Roughness	31282nm/980nm	41700nm/1272nm	45337nm/1200nm
FTO/Gold	 	 	 
SEM X2000			

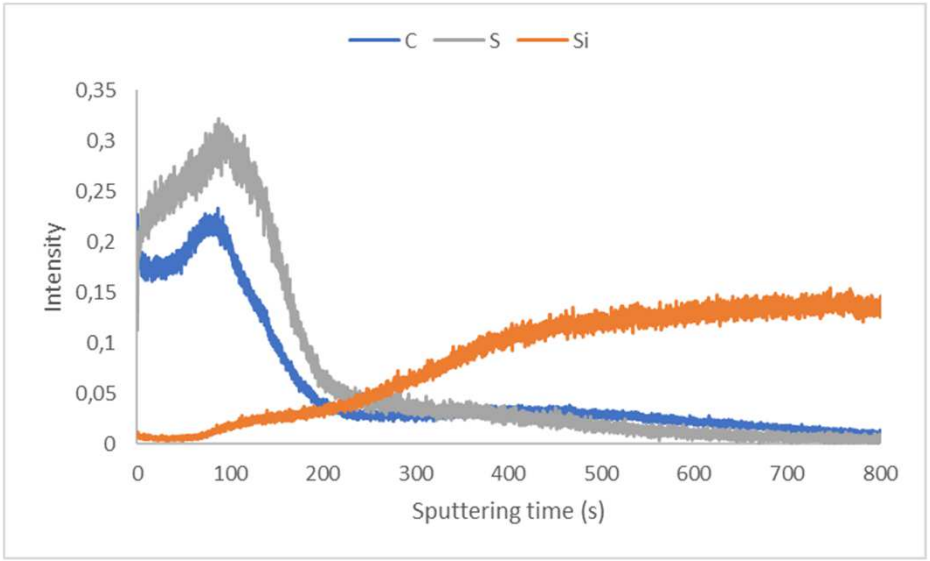
Results

Quartz microbalance

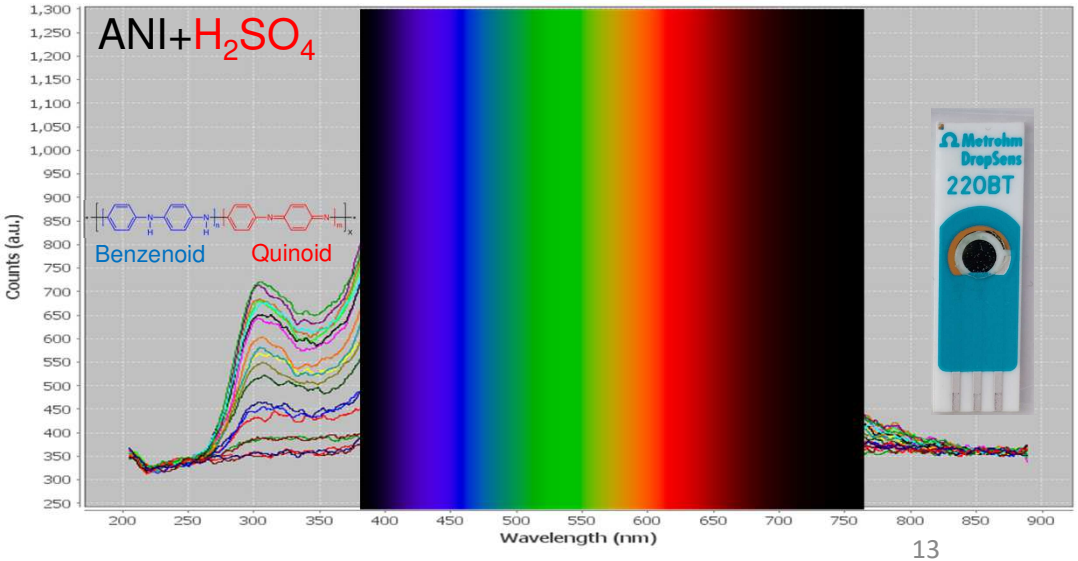




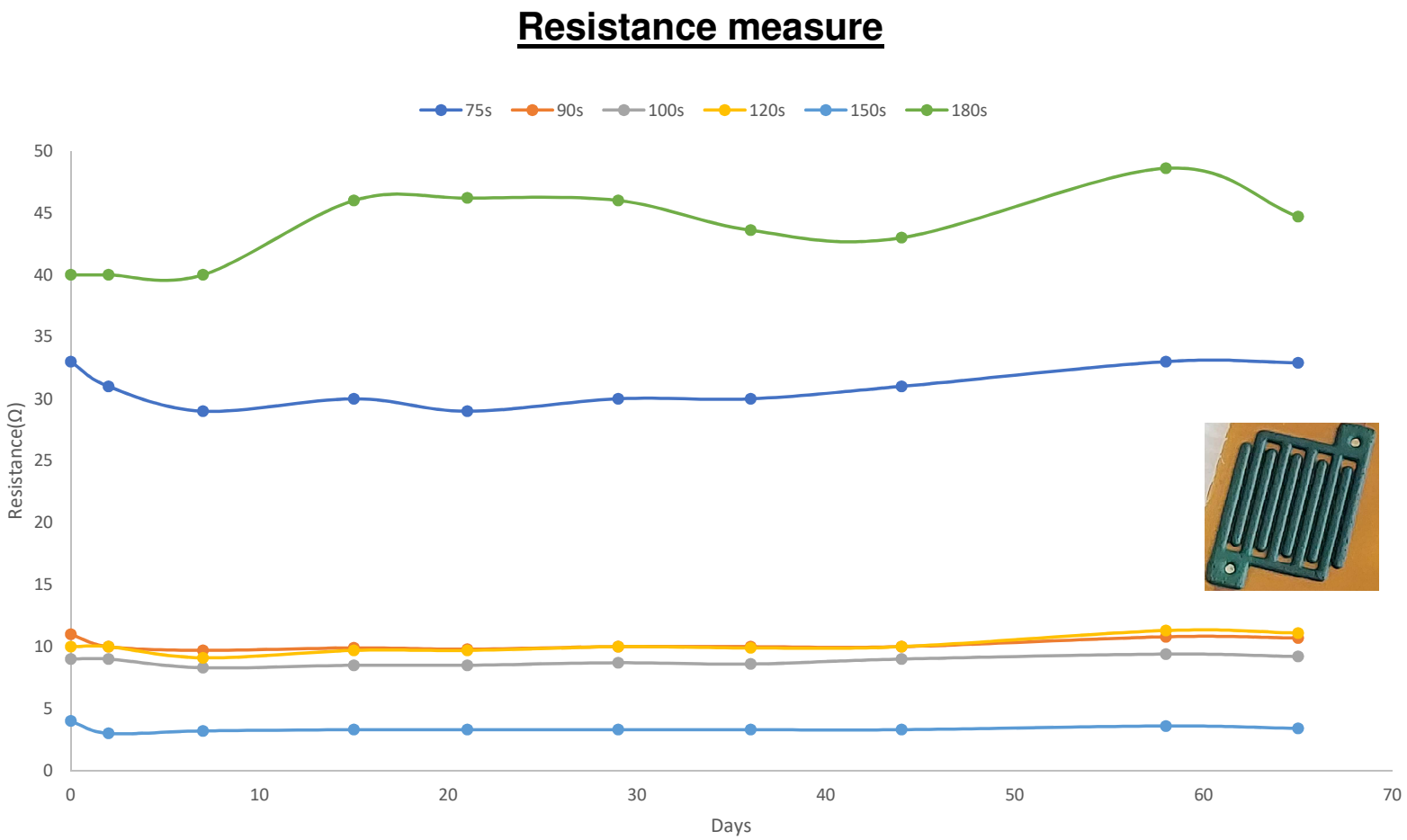
SDL

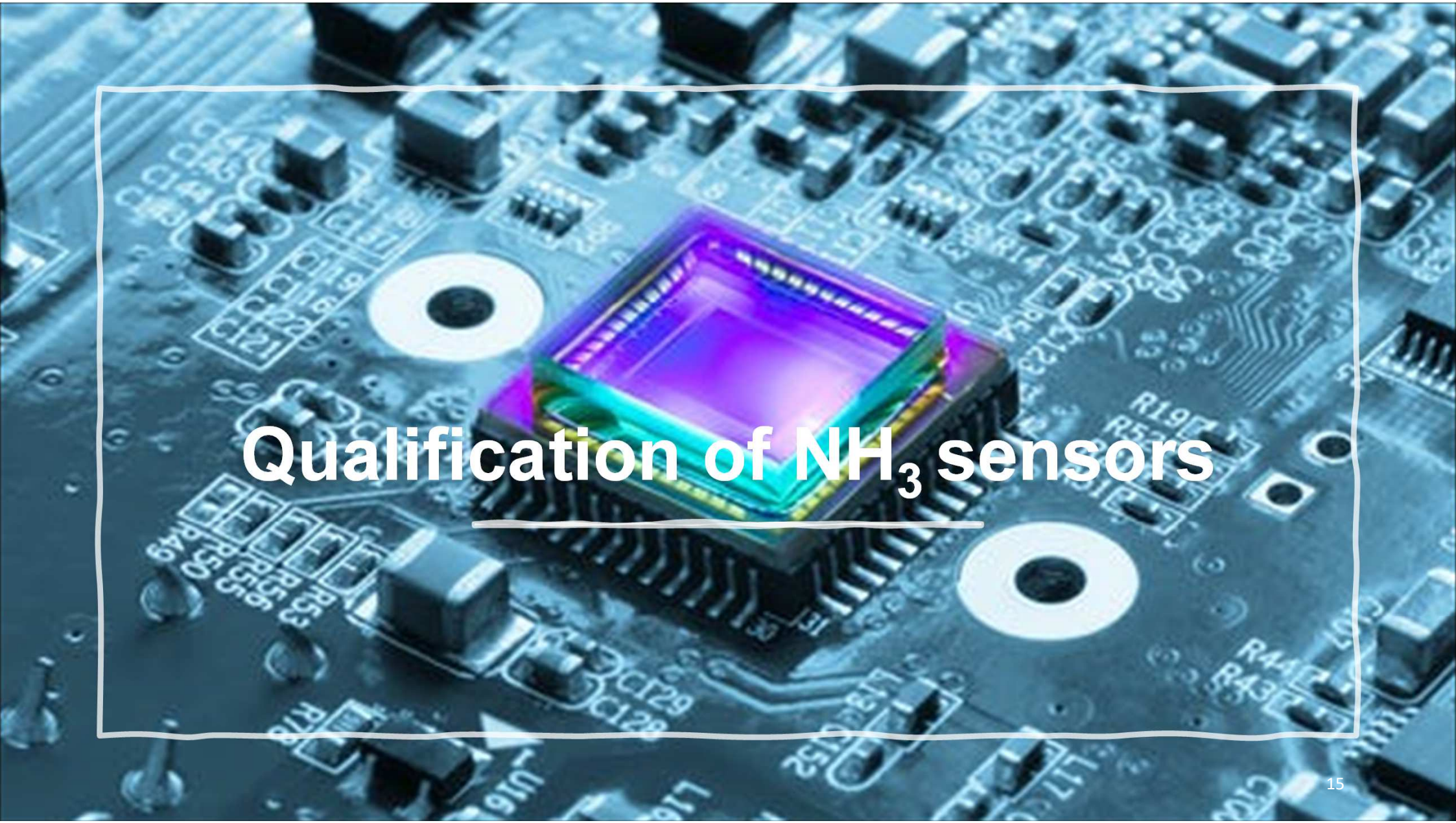


UV/Visible *in situ*



Results

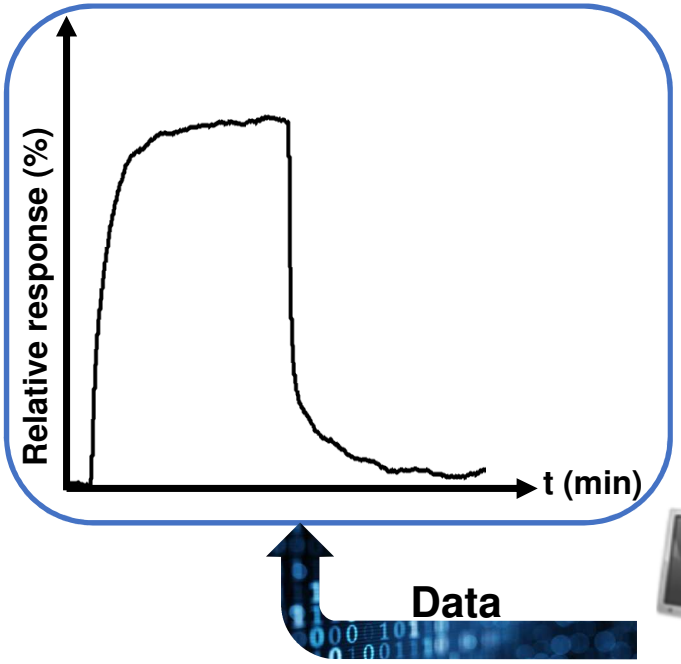

Resistance measure
75s
90s
100s
120s
150s
180s
Resistance(Ω)
Days
0
5
10
15
20
25
30
35
40
45
50
0
10
20
30
40
50
60
70

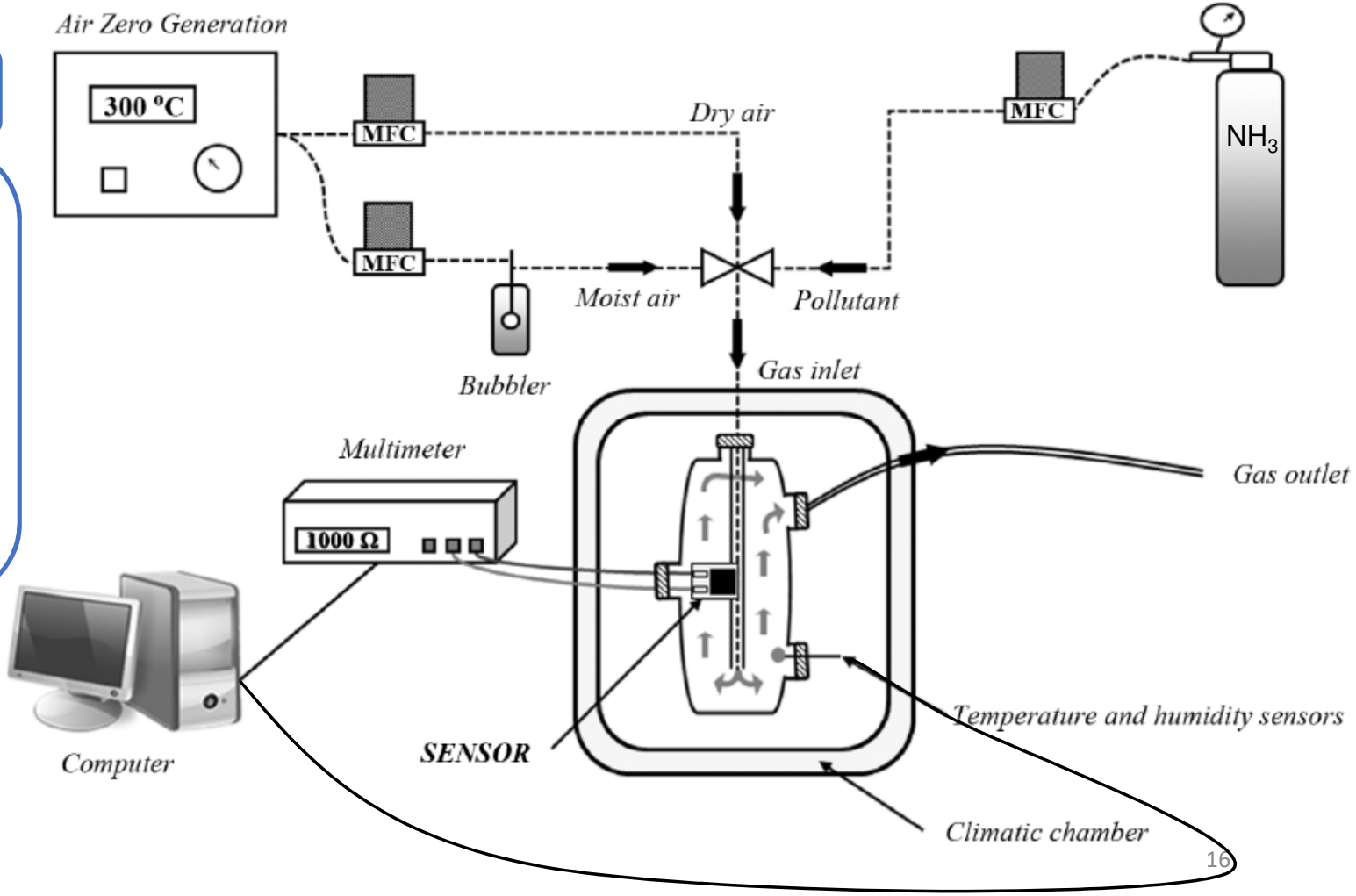


Qualification of NH_3 sensors

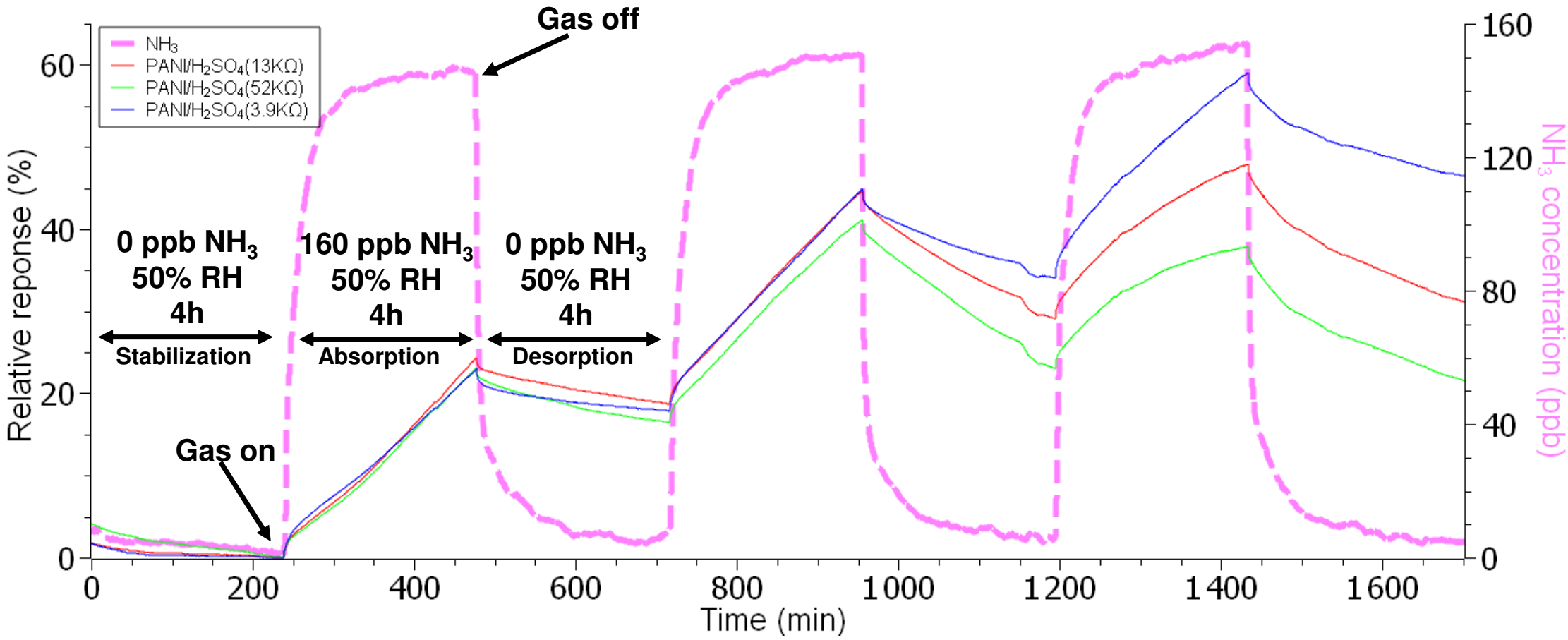
Chamber of exposure

$$\text{Relative reponse (\%)} = \frac{R(t) - R_0}{R_0} \times 100$$



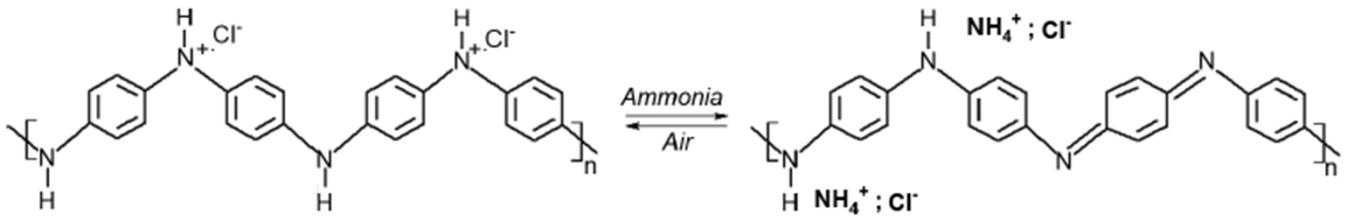


Results

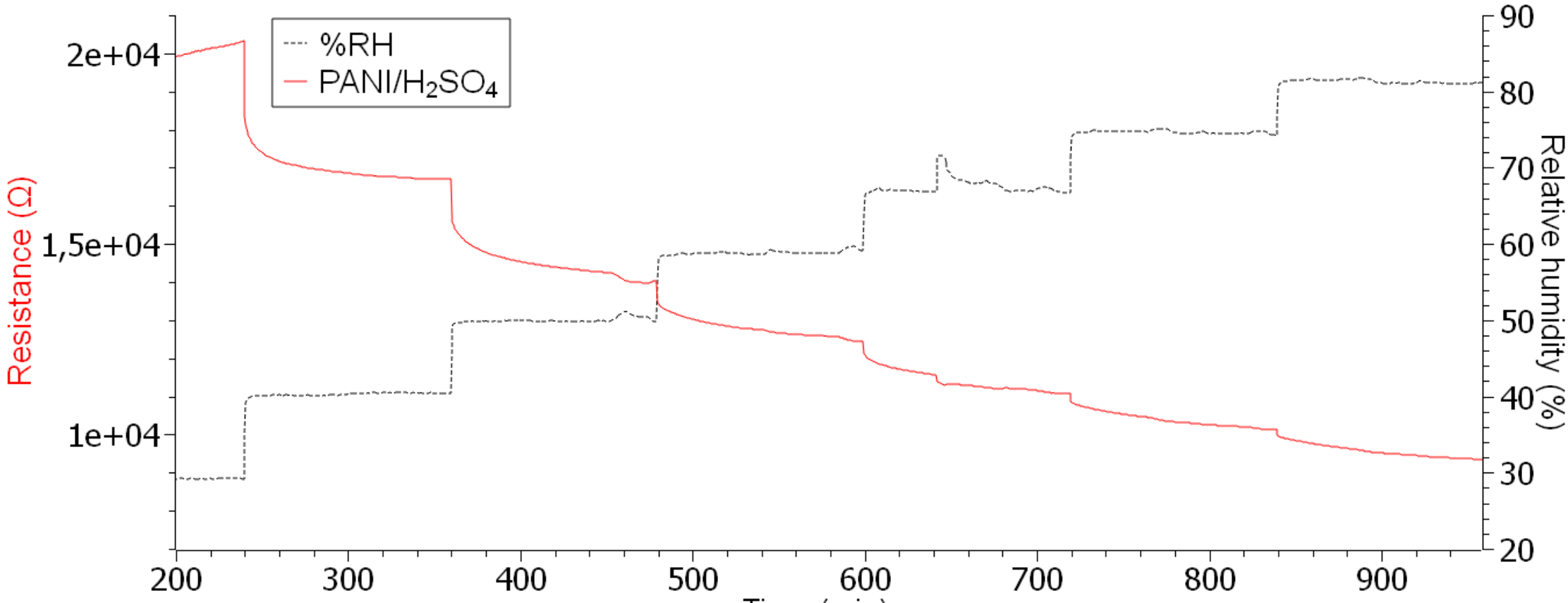


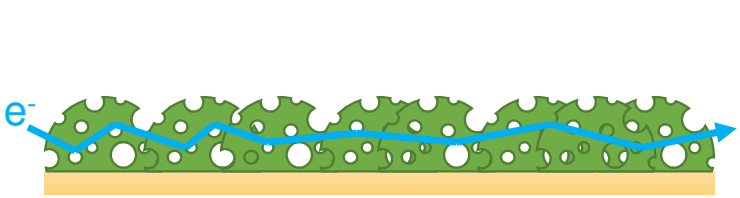
Morphology

Thickness

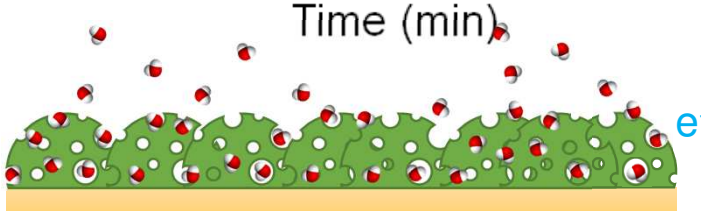


Results

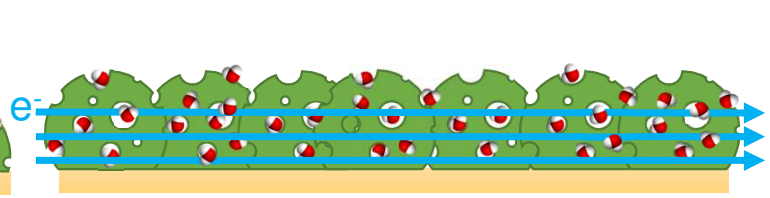




PANI/H_2SO_4

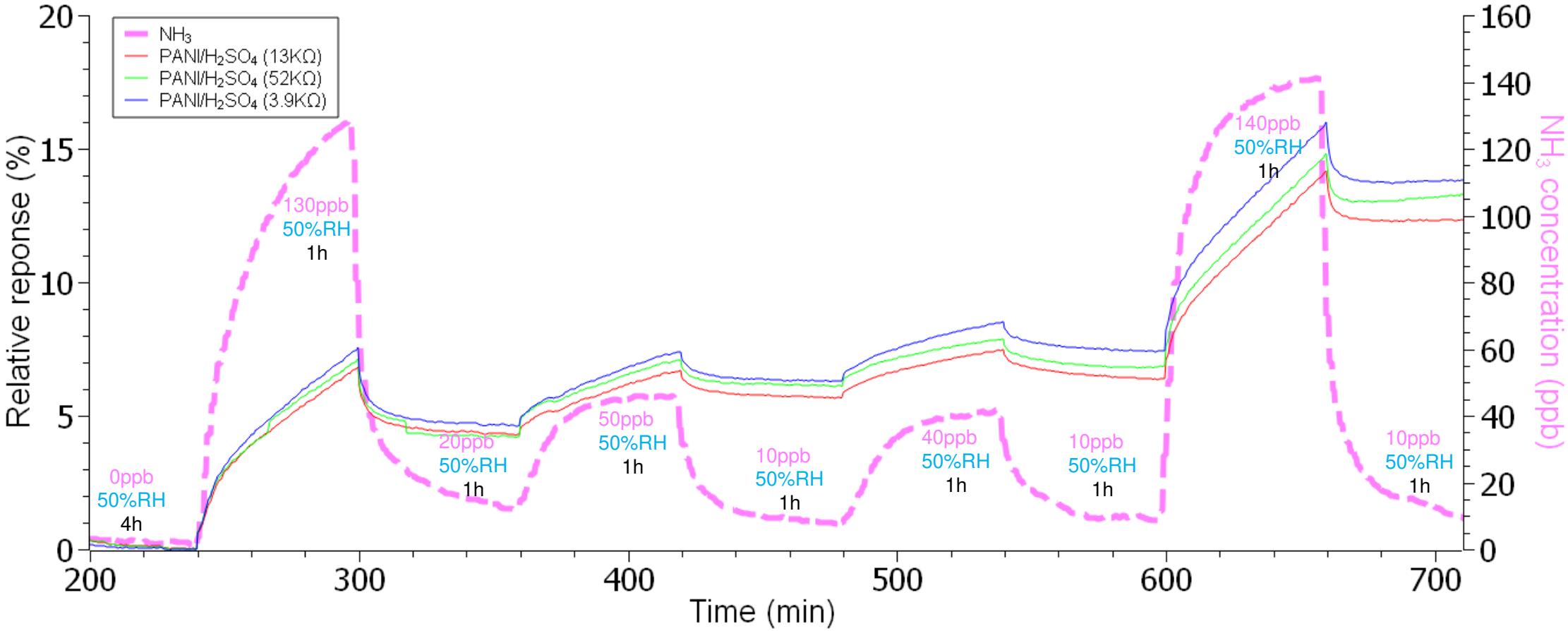


PANI/H_2SO_4 +%RH



PANI/H_2SO_4 Swollen

Results


NH3
PANI/H2SO4 (13KΩ)
PANI/H2SO4 (52KΩ)
PANI/H2SO4 (3.9KΩ)
Relative reponse (%)
NH3 concentration (ppb)
Time (min)
0ppb 50%RH 4h
130ppb 50%RH 1h
20ppb 50%RH 1h
50ppb 50%RH 1h
10ppb 50%RH 1h
40ppb 50%RH 1h
10ppb 50%RH 1h
140ppb 50%RH 1h
10ppb 50%RH 1h

Conclusion

Electrochemistry on FTO and Pt for optimization

Tests carried out with:

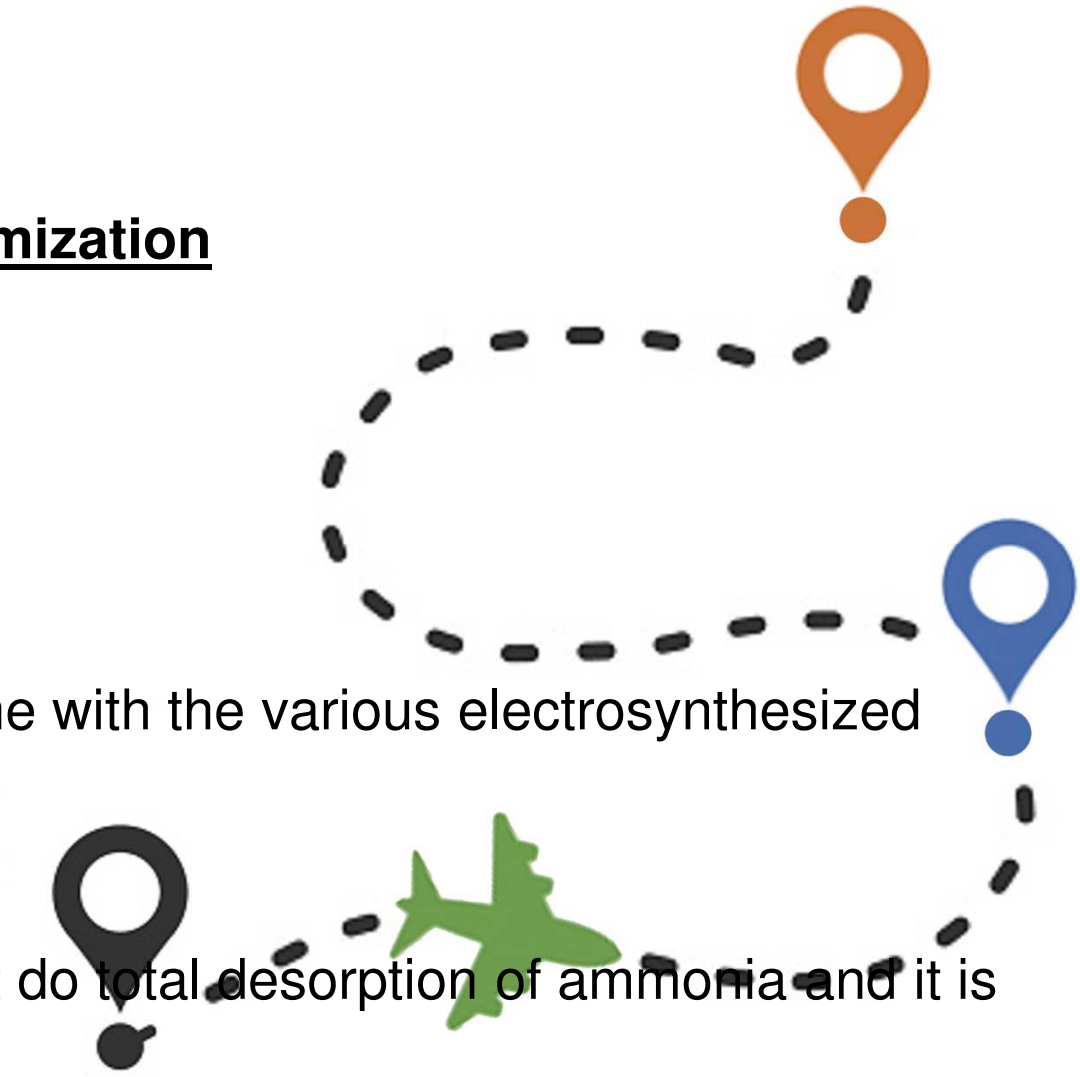
- many inorganic and organic acids
- anionic, cationic and neutral surfactants
- Copolymerization with a polyelectrolyte

Polymerization on gold sensors

Monitoring of resistance as a function of time with the various electrosynthesized polymers

Qualification of sensors for NH_3

PANI/H_2SO_4 can respond to NH_3 but it can't do total desorption of ammonia and it is sensitive to humidity



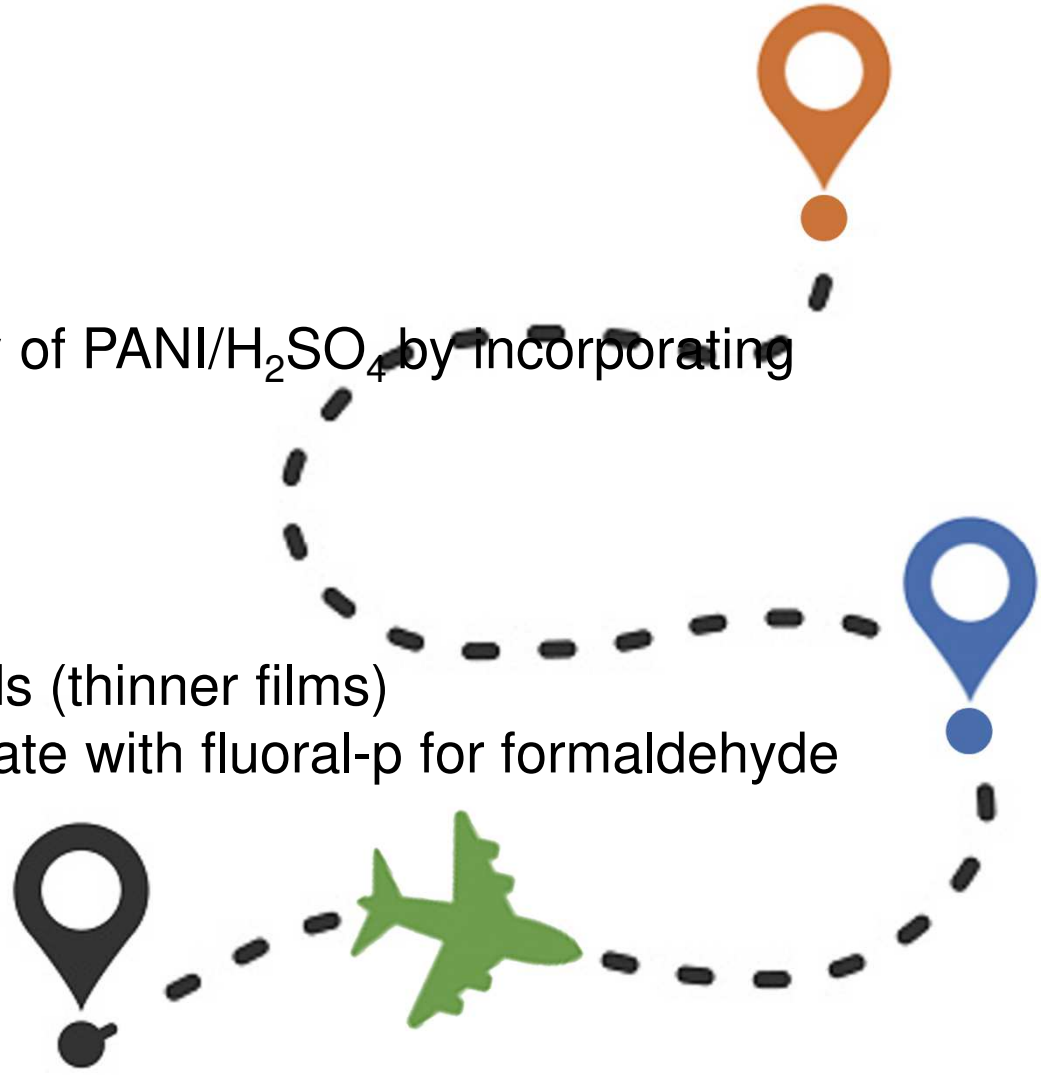
In progress:

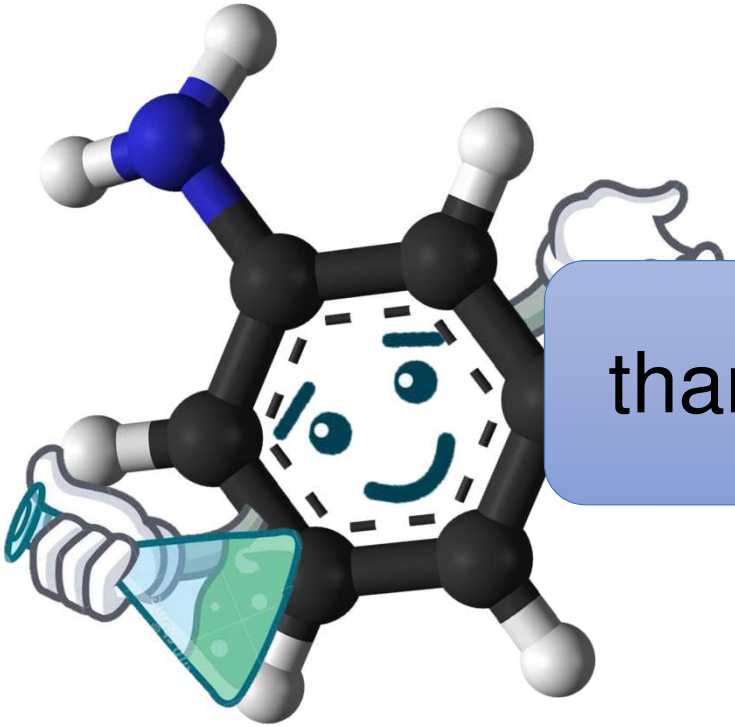
PANI/H_2SO_4/ TPU

It is necessary to increase the hydrophobicity of PANI/H_2SO_4 by incorporating polyurethane

Upcoming test

- Qualification of sensors for NH_3 : PANI/ Acids (thinner films)
- Use the best ammonia sensor and incorporate with fluoral-p for formaldehyde detection





thank you for your attention