CARBON NANOTUBES-BASED GAS SENSORS FOR POLLUTANTS: ELABORATION METHODS FOR NO2 AND BTX DETECTION

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In the Framework of COST- Action TD1105 hosted by the SGS 2012 Workshop
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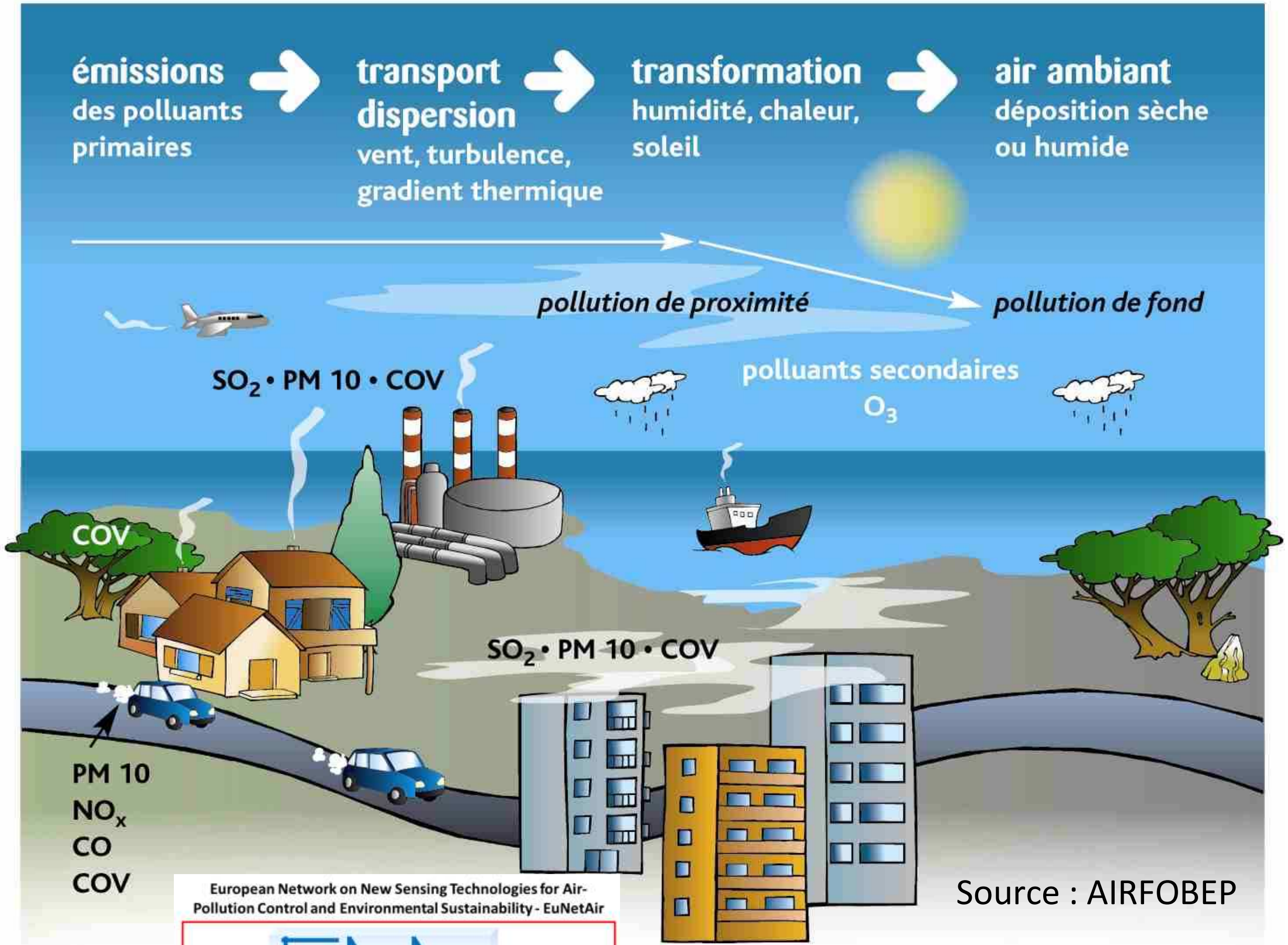
Overview



European Network on New Sensing Technologies for Air-Pollution Control and Environmental Sustainability - EuNetAir

EuNetAir
European Network on New Sensing Technologies for Air-Pollution Control and Environmental Sustainability

Pollution: ... ity induced by
the prese... or pa...
which ca... effec...
dependin... ion

COST
EUROPEAN COOPERATION
IN SCIENCE AND TECHNOLOGY

Climat change,
Increasing desease
(disquieting effects)

Needs for developping
Sensors
dedicated to pollutants

COST – Action TD1105

Plan

1 - Pollutants: introductory view

2 - CNTs-based sensors: Sensors elaboration for NO_2 and O_3 Detection

- → Dispersion route using a surfactant
- → Characterisation of the CNTs-based sensors
- → Sensor development and experimental results towards NO_2 and O_3

3 - CNTs-based sensors: Sensors elaboration for BTX Detection:

- → Noncovalent functionalisation method
- → Characterisation of the CNTs-MCs hybrid materials
- → Sensor development and experimental results towards toluene

4 - Conclusion and perspectives

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1- Pollutants: introductory view

Major Pollutants: NO_2/NO_x , O_3

❖ NO_2 and O_3: Similarities

- → Strong oxidising gases
- → Alike molecular masses
- → Chemical reactivities
- → Similar interactions with materials

❖ NO_2 and O_3: relationship (in the atmosphere)

→These two gases are linked by a chemical reaction:

$$NO + O_3 \rightarrow NO_2 + O_2 + h\nu$$

$$NO_2 \xrightarrow{h\nu} NO + O$$

$$O^* + O_2 \rightarrow O_3 + h\nu$$

❖ What about Health?

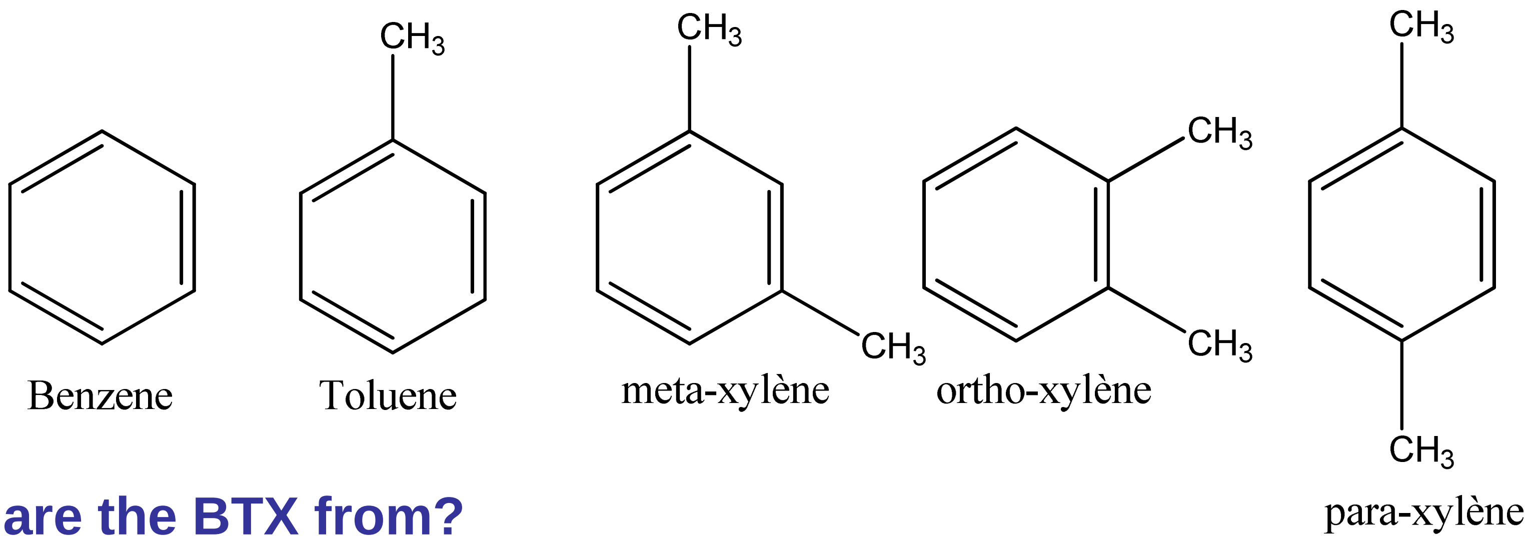
→ Carcinogenic, involved in respiratory deseases, etc.

1- Pollutants: introductory view

What are BTX?

→ **Benzene, Toluene and Xylenes:**

similar structures, physical properties and reactivities.



Where are the BTX from?

→ **Industries (catalytic reforming, steam cracking etc.), Car exhaust etc.**

What about Health?

→ **Carcinogenic, cause problems in the respiratory system, etc.**

NB: the terminology BTEX can be also found in the litterature: BTX + Ethylbenzene

1- Pollutants: introductory view

Gas sensors (literature):

Sensors based on Metal oxide (MOX) thin films:

→ SnO_2

(Lee *et. al*, Sens. and Actuators B, 77, 2001, 228)

Sensors based on porous adsorbent material :

→ Silicate

(Yuliarto *et. al*, Sens. and Actuators B, 138, 2009, 417;
Ueno *et. al*, Sens. and Actuators B, 95, 2003, 282)

Sensors based on conducting polymer :

→ Polypyrrole

(Wallace *et. al*, Sens. and Actuators B, 84, 2002, 252)

Methodology based on spectroscopic monitoring:

→ IR, GC-MS

Problems: portability, high cost, space

Sensors based on Nanomaterials:
→ CNTs

(Kong and Franklin, *et. al*, Science 287, 2000, 622;
Penza *et. al*, Sens. and Actuators B, 135, 2008, 289)

Problems:
- **→reproducibility**
- **→stability**
- **→selectivity**
- **→ etc.**

Plan

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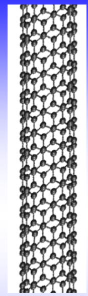
CNTs for gas sensors!

Why the CNTs?

CNTs: Properties

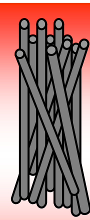


- mechanical properties
- optical properties
- electrical properties (semiconducting, metallic etc.)
- high surface area (SWNTs)

- surface sensitivity towards adsorbed species
- high number of adsorption sites

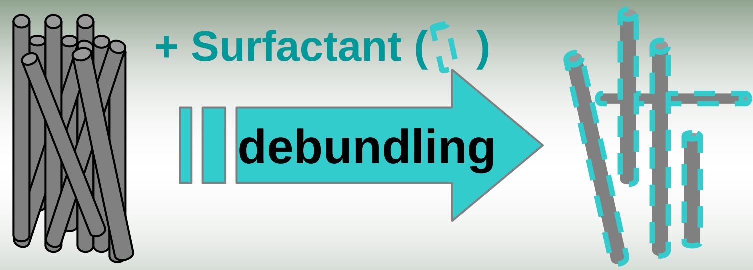
Why the dispersion route?

CNTs : Bundling effect



- high surface tension → bundling effect
- reducing the surface for adsorption

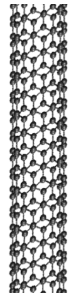
CNTs debundling (surfactant)



Bundle of CNTs Single CNTs

Surfactant: SDS, NaDDBS, etc.

CNTs for gas sensors: Dispersion route using a surfactant



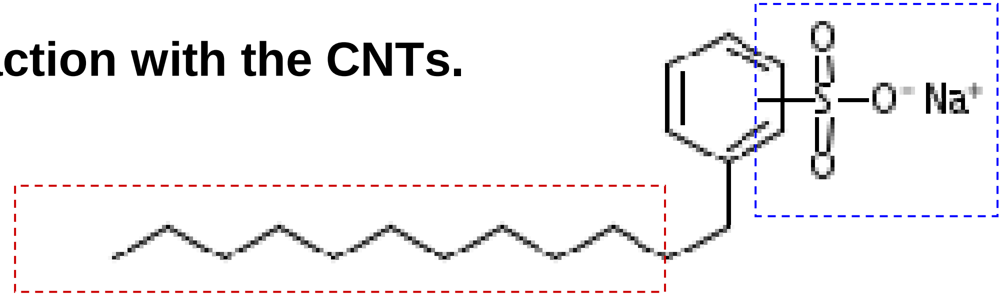
Surfactant method (assisted by sonication):

How does it work?

➢ **Hydrophobic and hydrophilic interaction** between **surfactant + nanotube + water**
→ **debundling;**
❖ **solubilisation / stabilisation in the aqueous phase.**

Choice of surfactant?

NaDDBS (Natrium dodecylbenzene sulfonate) seems to be advantageous over others ionic and non-ionic surfactants. (*)
Benzene ring → additional π–π interaction with the CNTs.



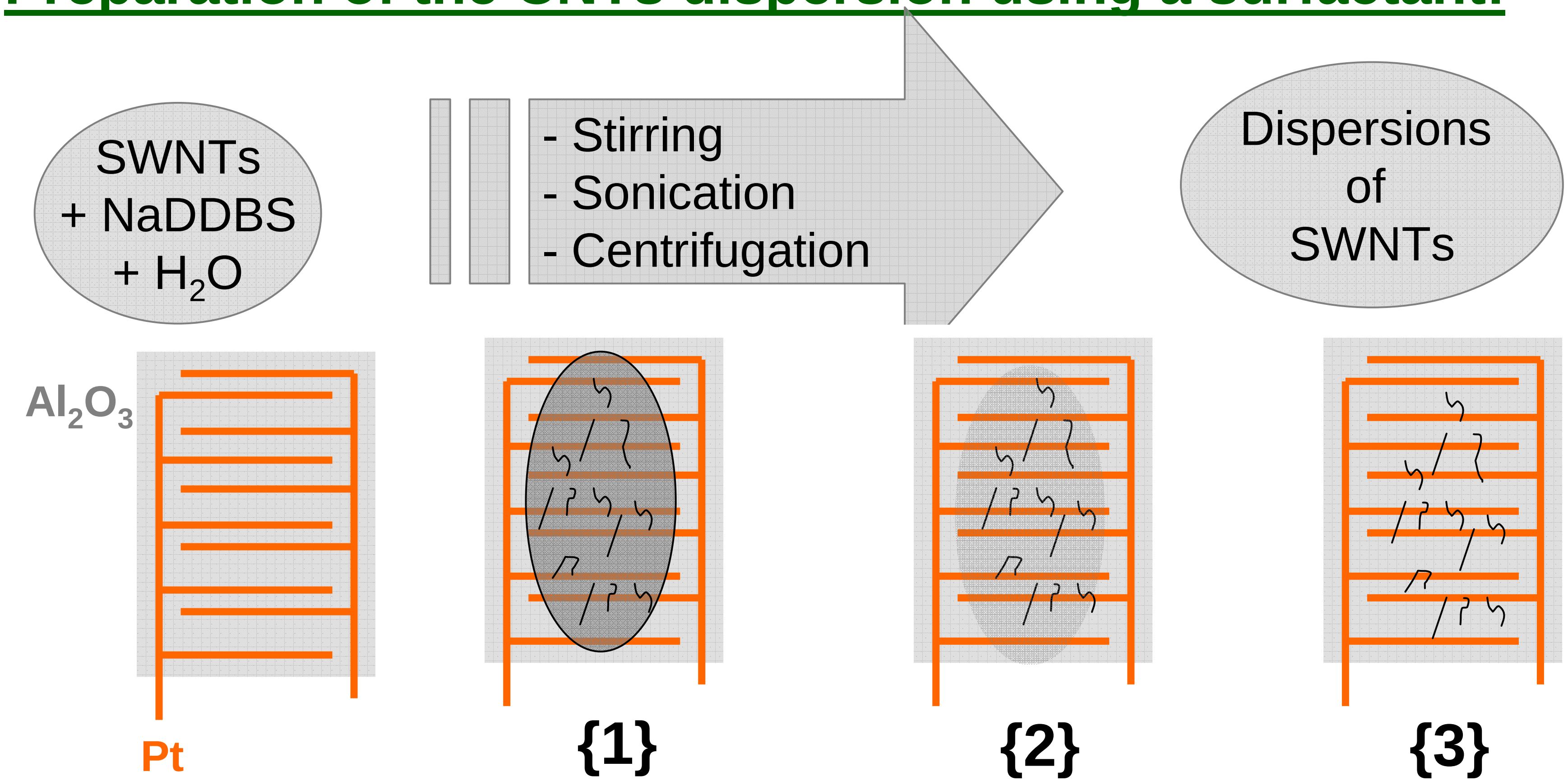
NaDDBs

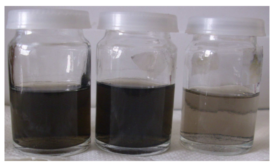
* Islam *et. al*, Nano Letters, 3, 2003, 269.
* Sun and Gao *et. al*, J. Alloys and Compds, 485, 2009, 456.

2- CNTs-based sensors: Sensors elaboration for NO_2 and O_3 Detection

CNTs for gas sensors: Dispersion route using a surfactant

<u>Preparation of the CNTs dispersion using a surfactant:</u>





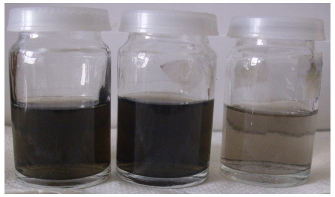
Drop-cast

Drying (110°C)

Annealing (150-300°C)

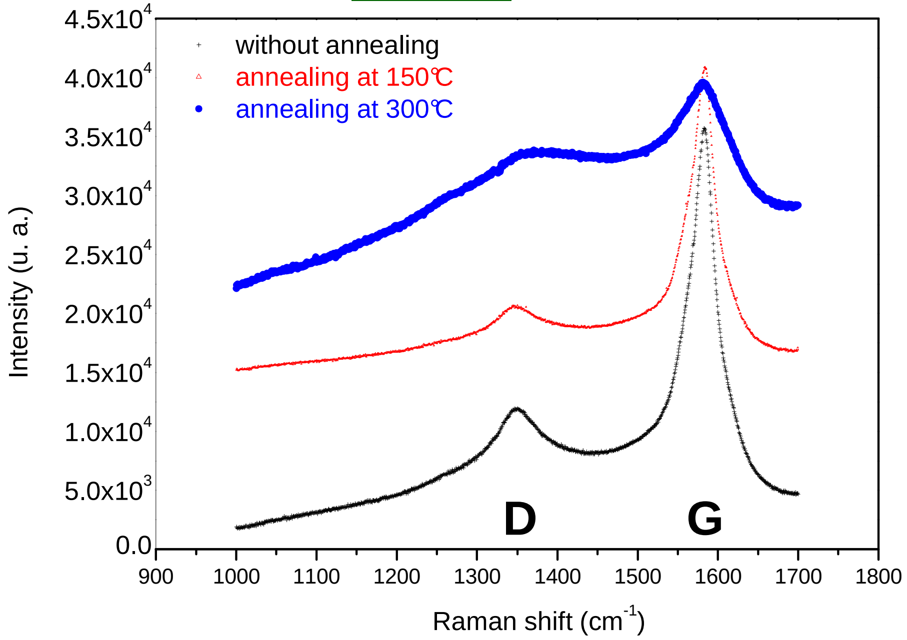
2- CNTs-based sensors: Sensors elaboration for NO_2 and O_3 Detection

CNTs for gas sensors: Dispersion route using a surfactant



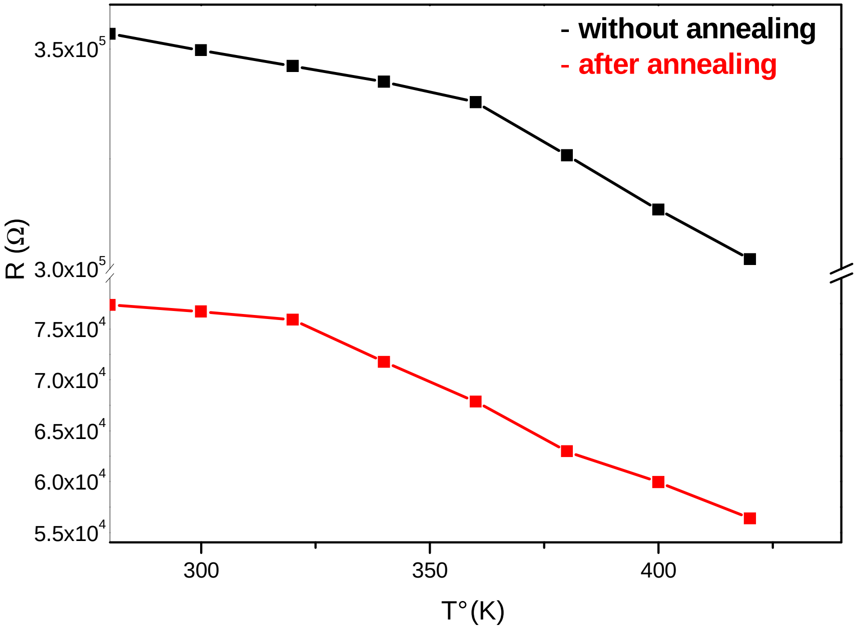
Characterisation of the CNTs dispersion :

Raman



D and G bands, before and after annealing.

I-V Characteristics



→Ohmic character (resistive sensors)

→Semiconducting behavior

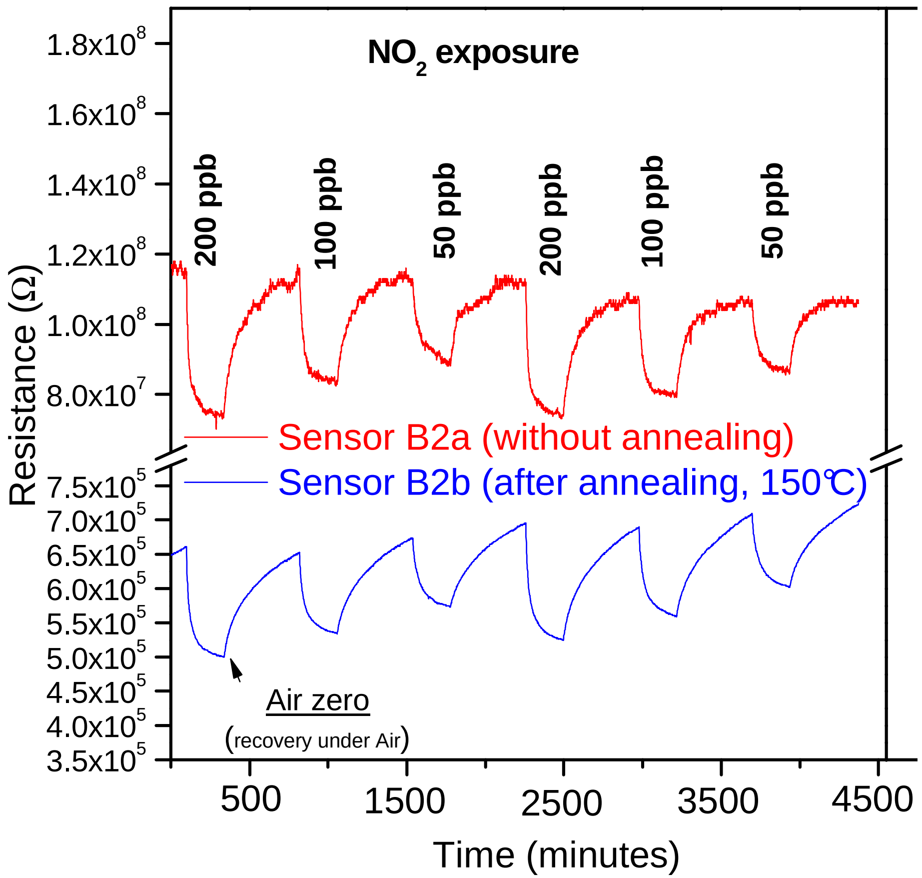
(CNTs batch of SC and metallic)

→No observable surfactant effect on the Semiconducting behavior

CNTs for gas sensors: Dispersion route using a surfactant

Sensor development and experimental results towards NO_2 :

Sensor response (70℃)

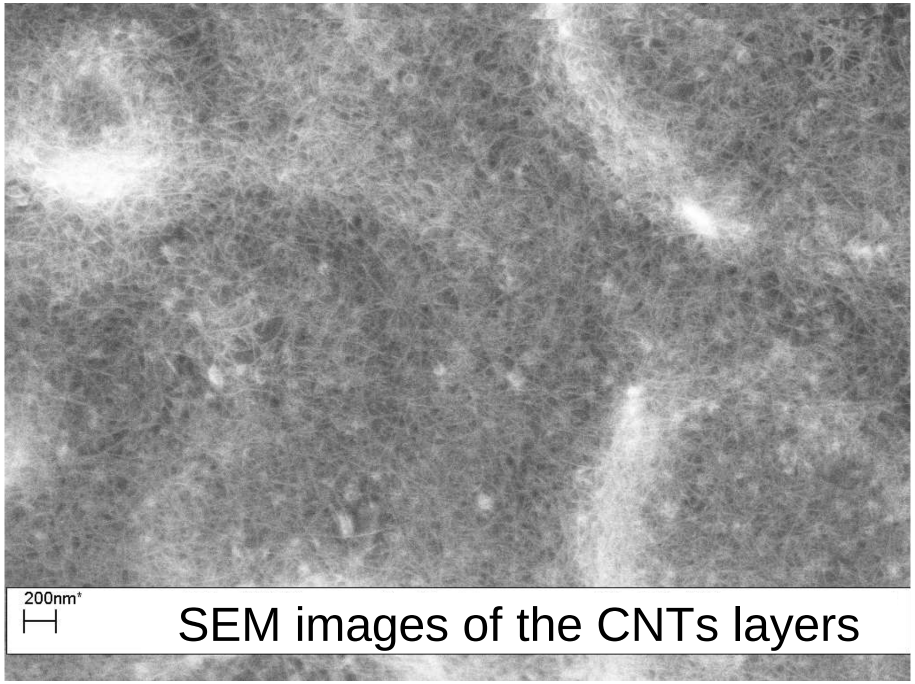


- ❖ **Resistance decrease under NO_2**
  → electron withdrawing power of NO_2.
  (p-type semiconducting behaviour of the CNTs)
- ❖ **Annealing improves the responses**

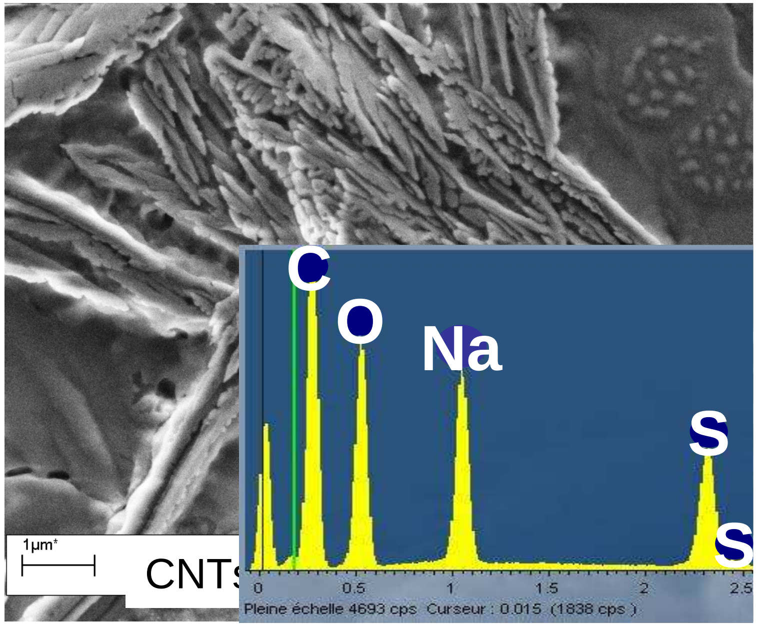
◈ **NB: After annealing at 300 ℃:**

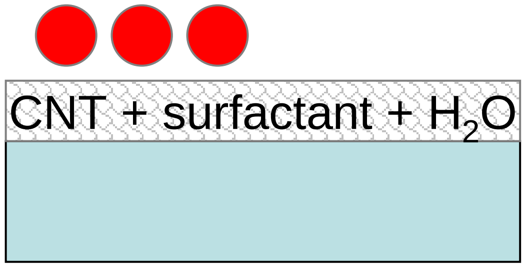
- **No valuable responses of the CNTs-based sensors layers?**

SEM characterisation of the sensing layers:

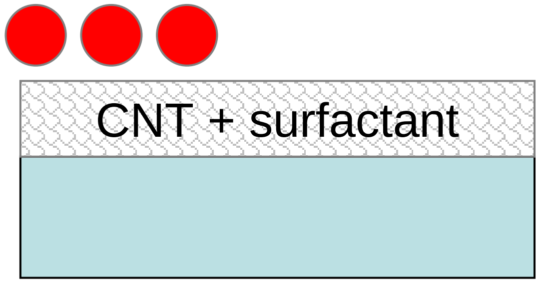


SEM images of the CNTs layers

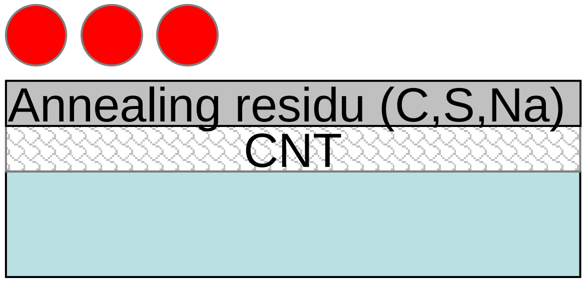




Without annealing



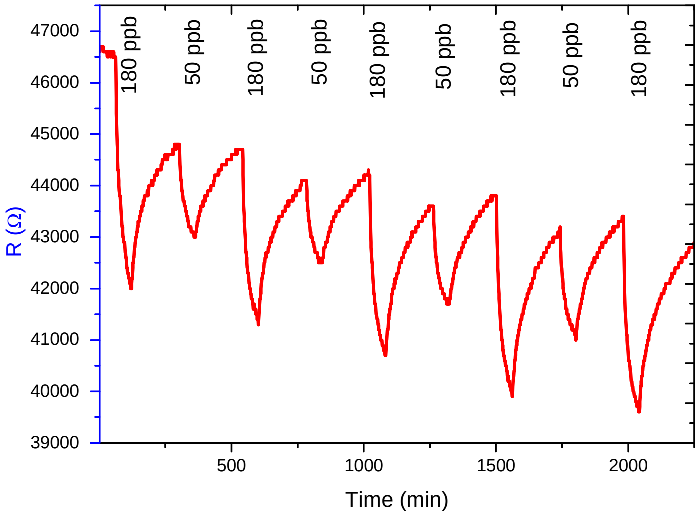
Annealing at 150 °C

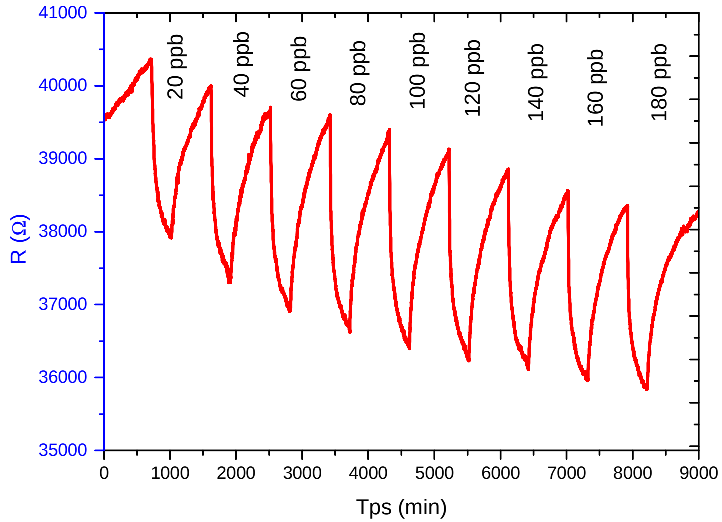


Annealing at 300 °C

CNTs for gas sensors: Dispersion route using a surfactant

Sensor development and experimental results towards O_3 :





- ❖ **Resistance decrease under O_3**
  → oxidising nature of O_3. (p-type semiconducting behaviour of the CNTs)
- ❖ **Significant baseline up drift (no complete recovery)**
- ❖ **Decreasing sensing performance after some exposure cycles**

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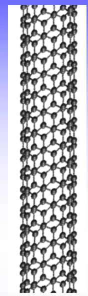
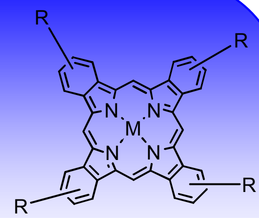
Functionalisation of Carbon Nanotubes (CNTs) by Macrocycles (MCs)

CNTs:



- mechanical properties (high tensile strenght)
- optical properties
- versatile electrical properties (semiconducting, metallic etc.) (SWNTs)
- high surface area

MCs:



R= ^{t}Bu; M=Cu

- redox properties
- stability at high temperature
- highly delocalised π-system
- functionalisation

- changes (conductivity) (due to adsorbed species)

- high number of adsorption sites (high sensitivity)

+

- interaction sites for BTX (π-system)

- functional groups (tailored interaction)

Functionalisation of CNTs: covalent *vs.* noncovalent route

→ covalent functionalisation :
based on the creation of covalent bonding

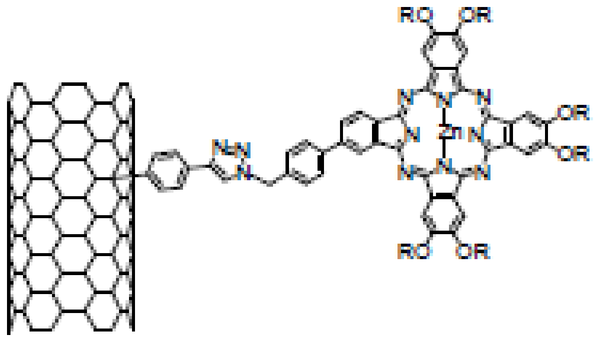
- **more stable assemblies**
- **irreversible**
- **solubilisation**

- **alteration of the properties (electrical, optical etc.)**

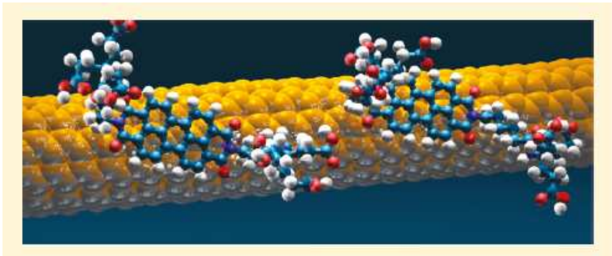
→ noncovalent functionalisation :
based on self-assembling (π–π interaction)

- **instable assemblies**
- **reversible**

- **preserved electrical properties**



Campidelli, Torres *et al.* *J.A.C.S*. 2008, 130, 11503.



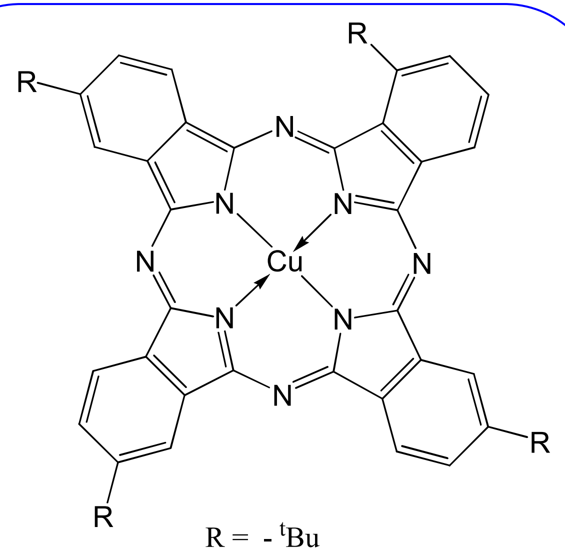
perylenediimide/SWNT electron donor−acceptor hybrids
Hirsch, Guldi *et al.* *J.A.C.S*. 2011, 133, 4580.

Tassi, Prato *et al.* Chem. Rev. 2006, 106, 1105.

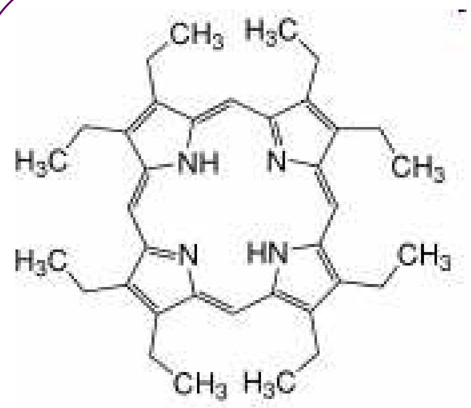
Takeuchi *et al.* J. Phys. Chem. C. 2011, 115, 4533.
Yang *et al.* J. Phys. Chem. C. 2011, 115, 4584.
Guldi, Prato *et al.* J. Mater. Chem. 2006, 16, 62.

Functionalisation of CNTs: choice of the MCs

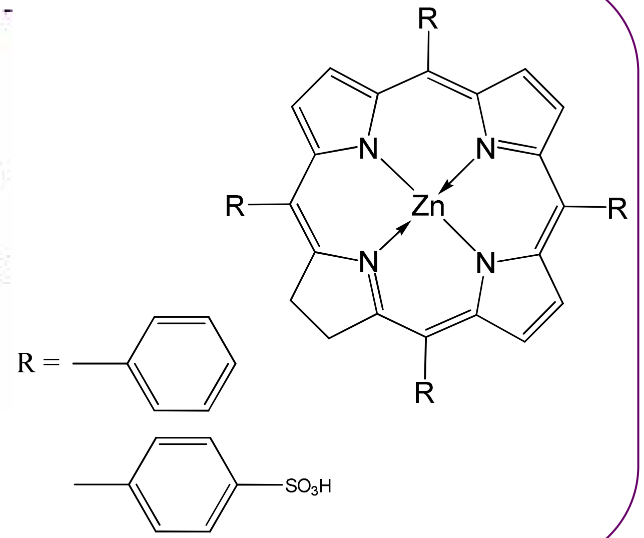
Phthalocyanines derivatives



Porphyrines derivatives



OEP

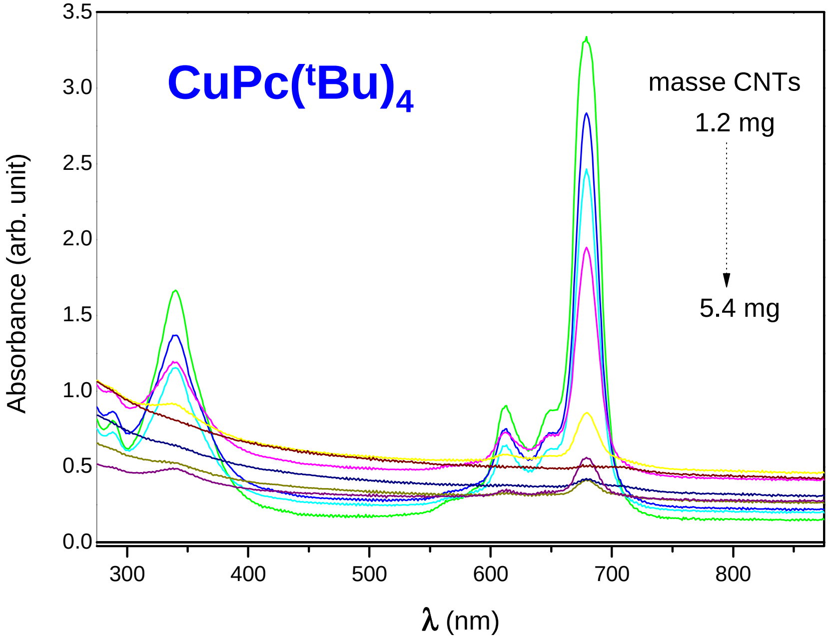


→ **Strong absorption:**
 - functionalisation monitoring

→ **R functional groups:**
 - solubility
 - modulation of the adsorption

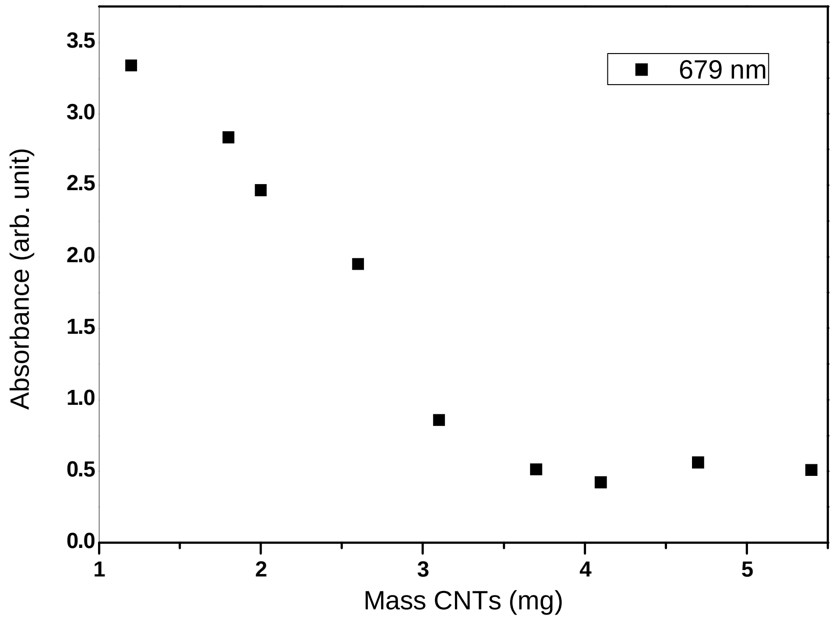
→ **π-system:**
 - π–π interactions (BTX, CNTs)

Functionalisation of CNTs with a Phthalocyanine derivative: UV-Vis



UV-Vis absorption spectra of CNTs/CuPc(^{t}Bu)$_4$ dispersions

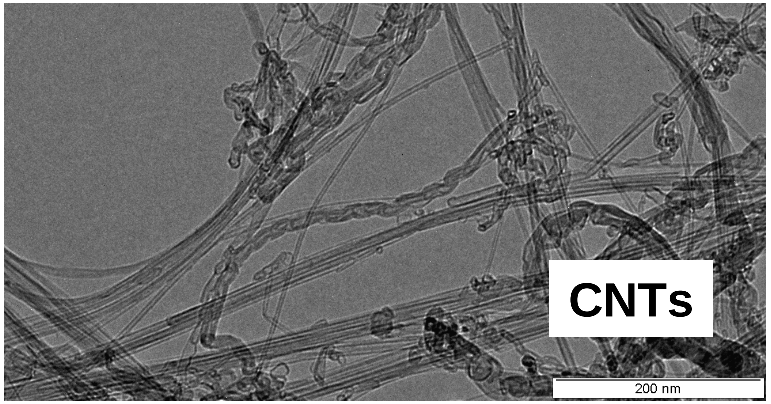
Evolution of the 679 nm absorption band (Q band) after addition of CNTs

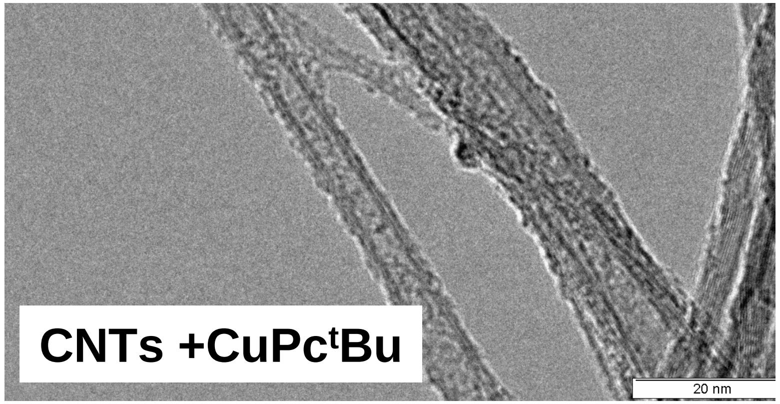


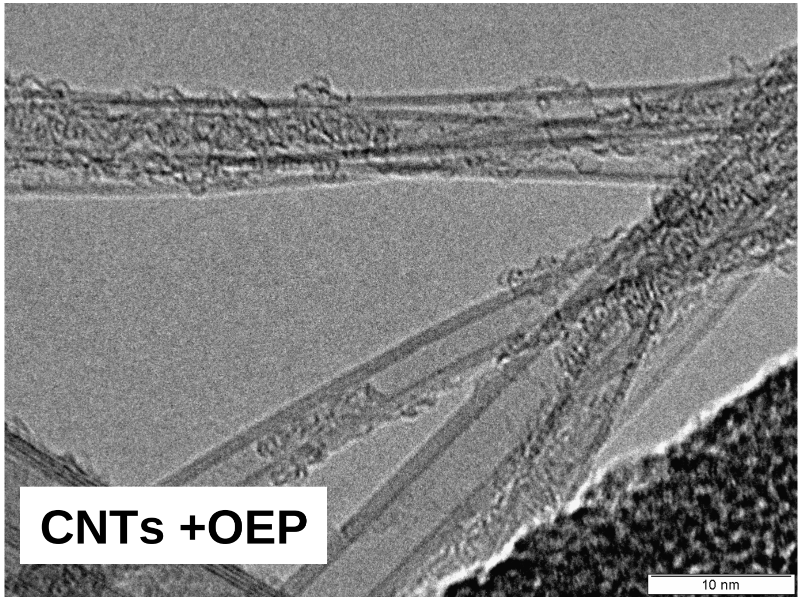
[CuPc^{t}Bu]= 1.785 x 10^{-5} M
10ml $CHCl_3$

→ Decrease in absorbance highlights the functionalisation

Functionalisation of CNTs with Macrocycles: TEM



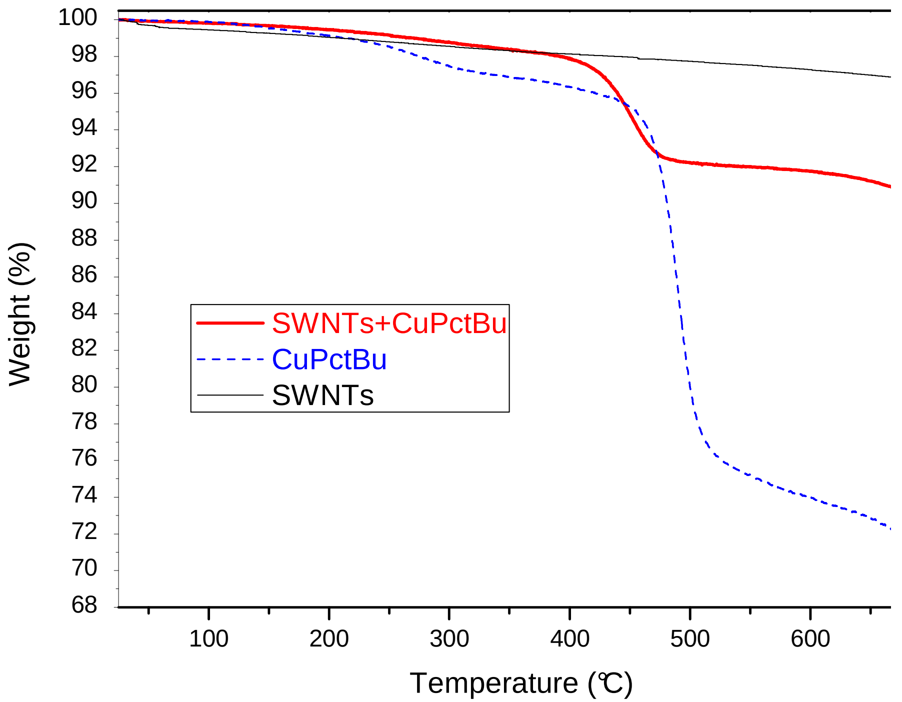


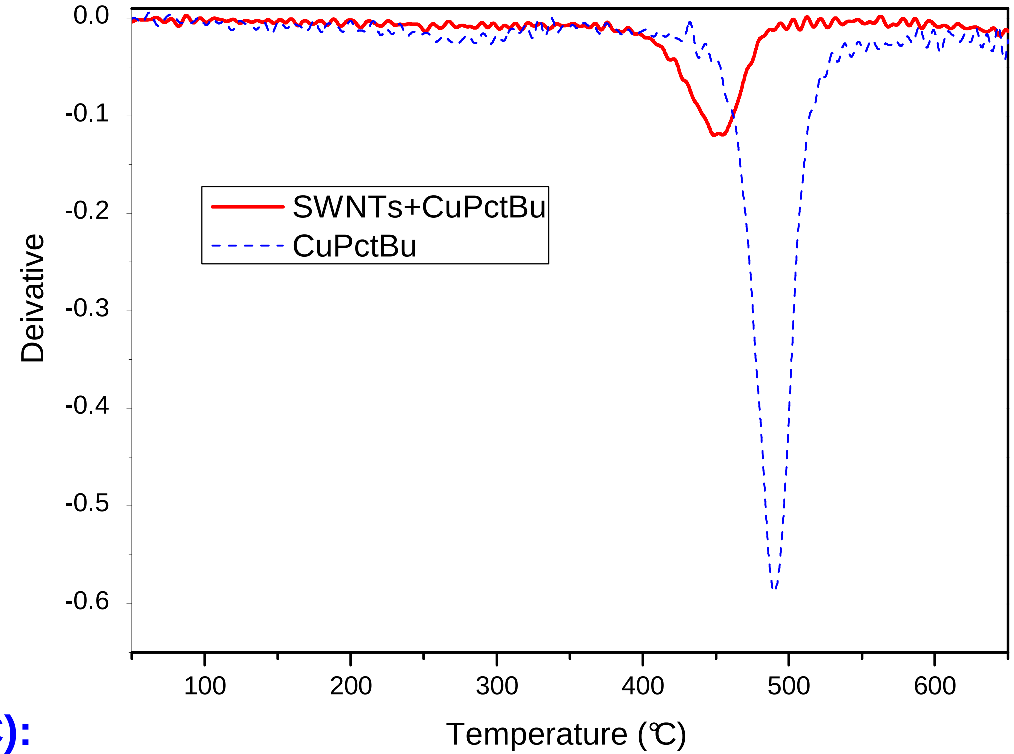


→ **Adsorbed structures on the CNTs Walls**

→ **Noncovalent functionalisation of CNTs (random way)**

Functionalisation of CNTs with a Macrocycle: TGA analysis





❑ **Considering the weight losses (at 600℃):**
2.8 % : CNTs weight loss (mainly impurities)
26 % : MCs weight loss (decomposition)

→ a real weight loss of 20.7 % in the CNTs/CuPctBu mainly due to the presence of MC.

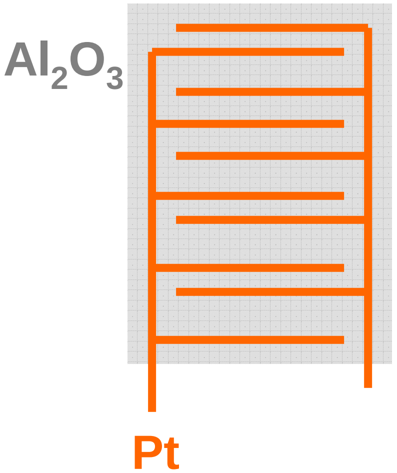
❑ **MCs on the CNTs walls decompose more easily than free MCs:**
→ thermal stability is weaken

Development of the sensing devices: transduction modes

CNTs-MCs based Materials:

2 transduction modes

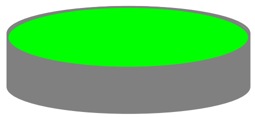
IDE's



Interdigitated electrodes (IDE's)
→ Resistance variation (ΔR)

QCM

Quartz Crystal Microbalance (QCM)
→ Mass variation (i.e frequency)

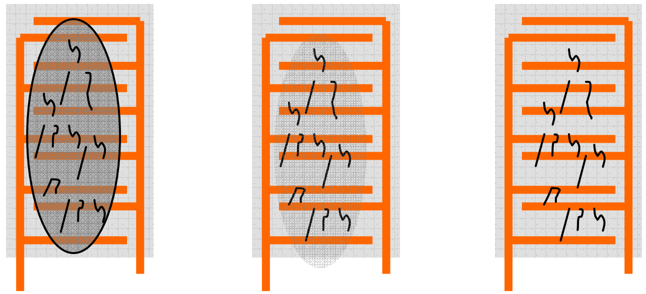


Quartz crystal with
Au electrodes

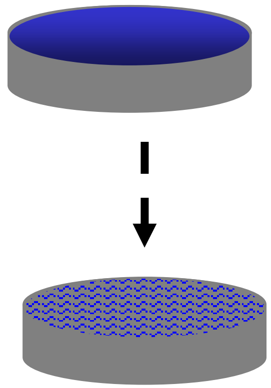
Elaboration of the sensing devices: sensor preparation

IDE's

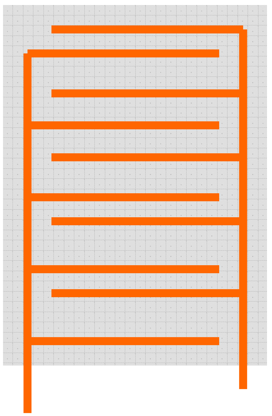
QCM



I   II   III



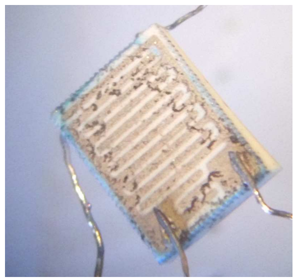
Al_2O_3



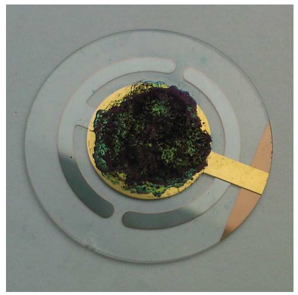
Pt

I: drop-cast deposition
II: solvant evaporation
III: annealling

→ Deposition T°

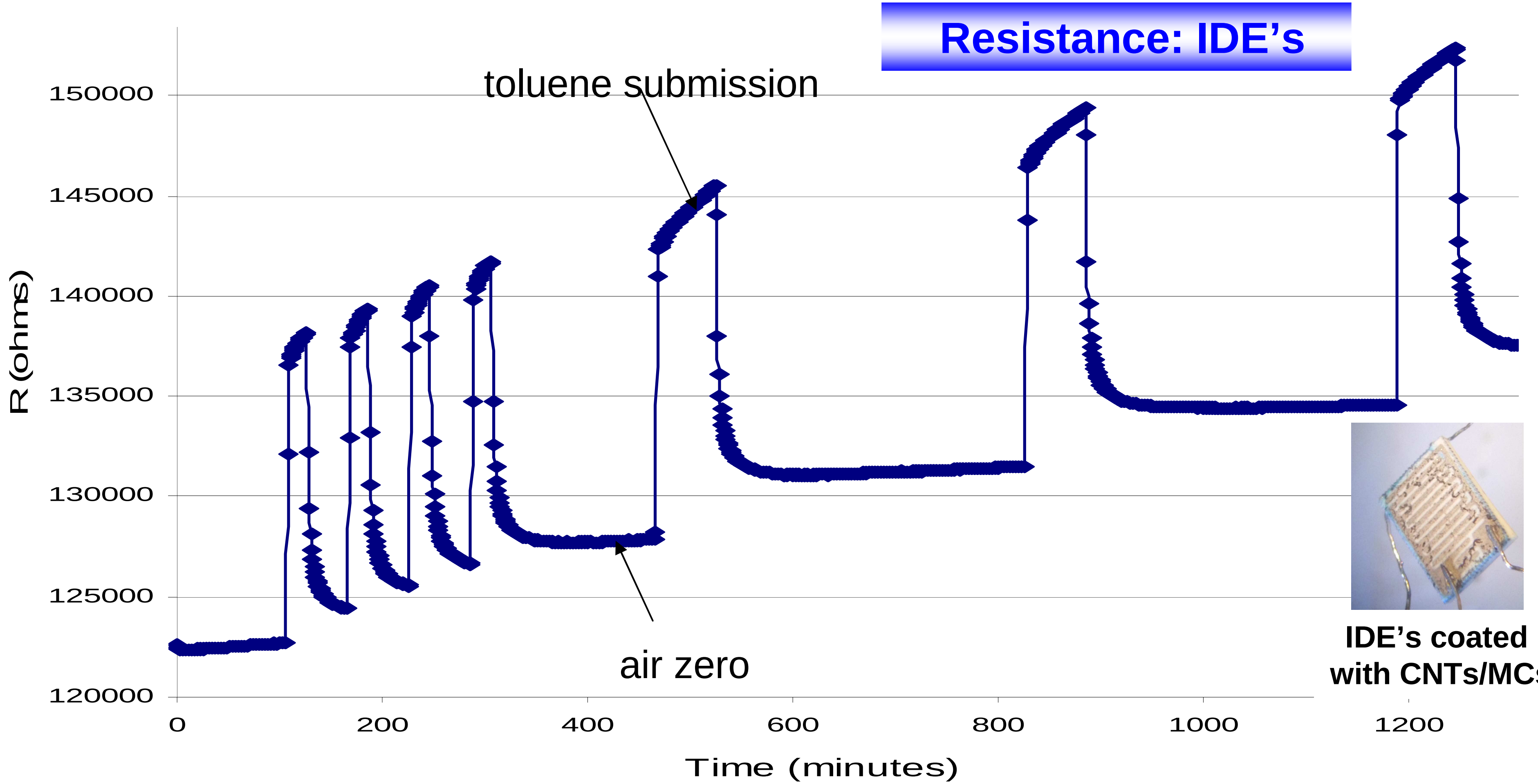


IDE's coated with CNTs/MCs



QCM coated with CNTs/MCs

Elaboration of the sensing devices: sensor response towards toluene (RT°)



IDE's coated with CNTs/MCs

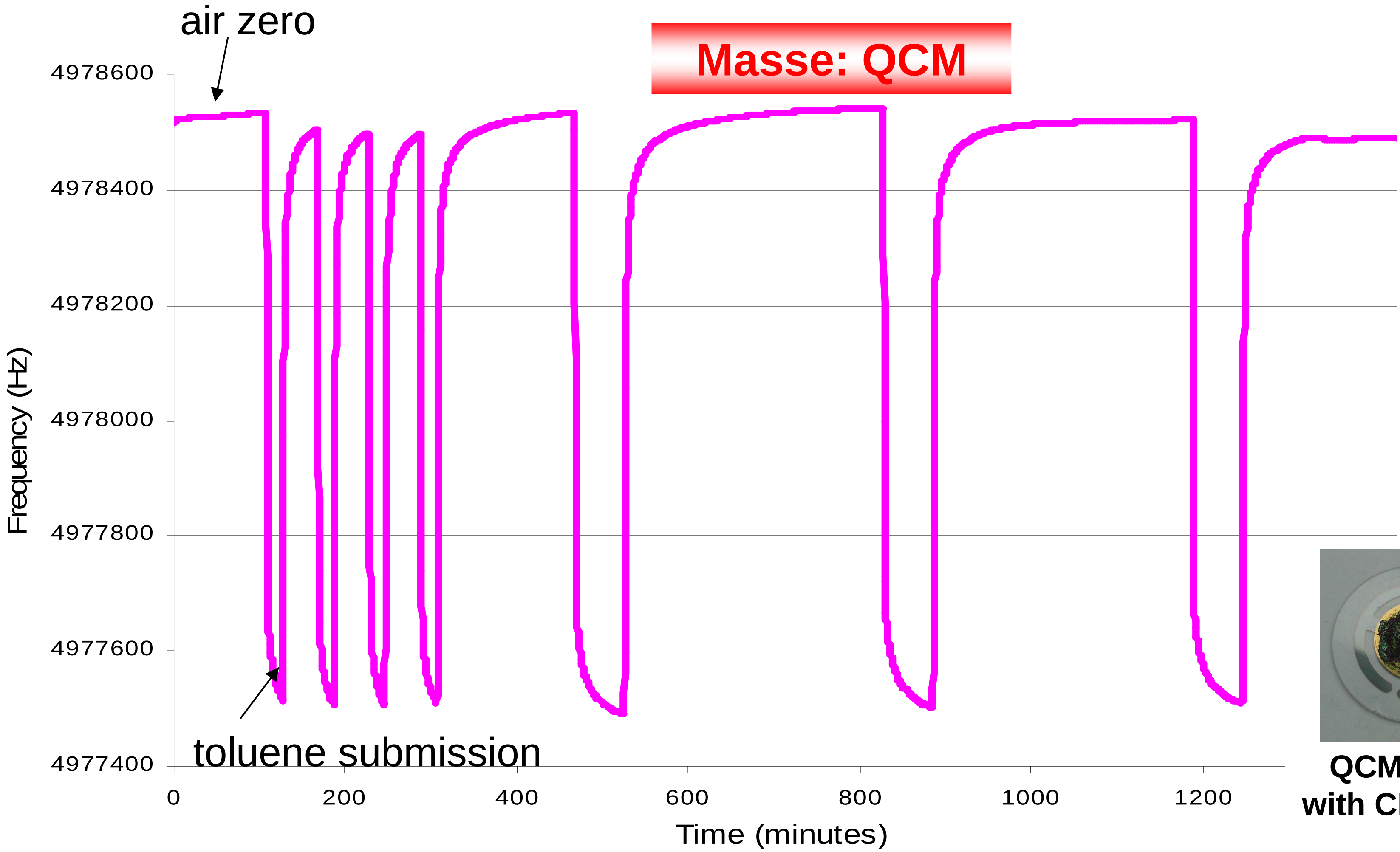
→ Resistance increases during toluene exposure (reducing gas)

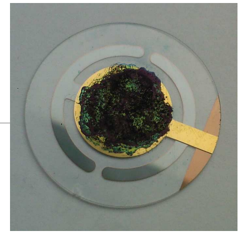
→ Reversible process **→ Good repeatability**

3- CNTs-based sensors: Sensors elaboration for BTX Detection

Elaboration of the sensing devices: sensor response under toluene (RT°)

Masse: QCM





QCM coated with CNTs / MCs

→ Frequency decreases (i.e. Mass increases) under toluene exposure

→ Reversible process **→ Good repeatability**

3- CNTs-based sensors: Sensors elaboration for BTX Detection

$\Delta f = -C_f \times \Delta m$ **(Sauerbrey Equation)**

Δf: frequency variation (Hz)
Cf: sensitivity factor (Hz/ng/cm^2) [Cf= 0.056 Hz/ng/cm^2 for 5 MHz crystal)
Δm: mass variation per unit area (g/cm^2)

Materials	Response (Hz/ng deposited material)	Remarks
SWNTs + CuPctBu	**0.009**	Stable, repeatable
CuPctBu	**0.002**	Moreless stable
SWNTs + OEP	**0.008**	Stable, repeatable
OEP	**0.0005**	Not stable

f_{A0}: frequency value at equilibrium under Air 0
f_{Tol}: frequency value at equilibrium under Toluene

Δf: f_{A0} - f_{Tol} → Sensor response

Better response of CuPctBu compared to OEP: → benzyl moiety
→ amorphous/crystalline

Improvement of the response in the hybrids system (CNTs/MCs) compared to MCs:
- CNTs (High SSA)
- CNTs-OEP >>> CNTs- CuPctBu (metal)

Plan

1 - Pollutants: introductory view

2 - CNTs-based sensors: Sensors elaboration for NO_2 and O_3 Detection

→ Dispersion route using a surfactant
→ Characterisation of the CNTs-based sensors
→ Sensor development and experimental results towards NO_2 and O_3

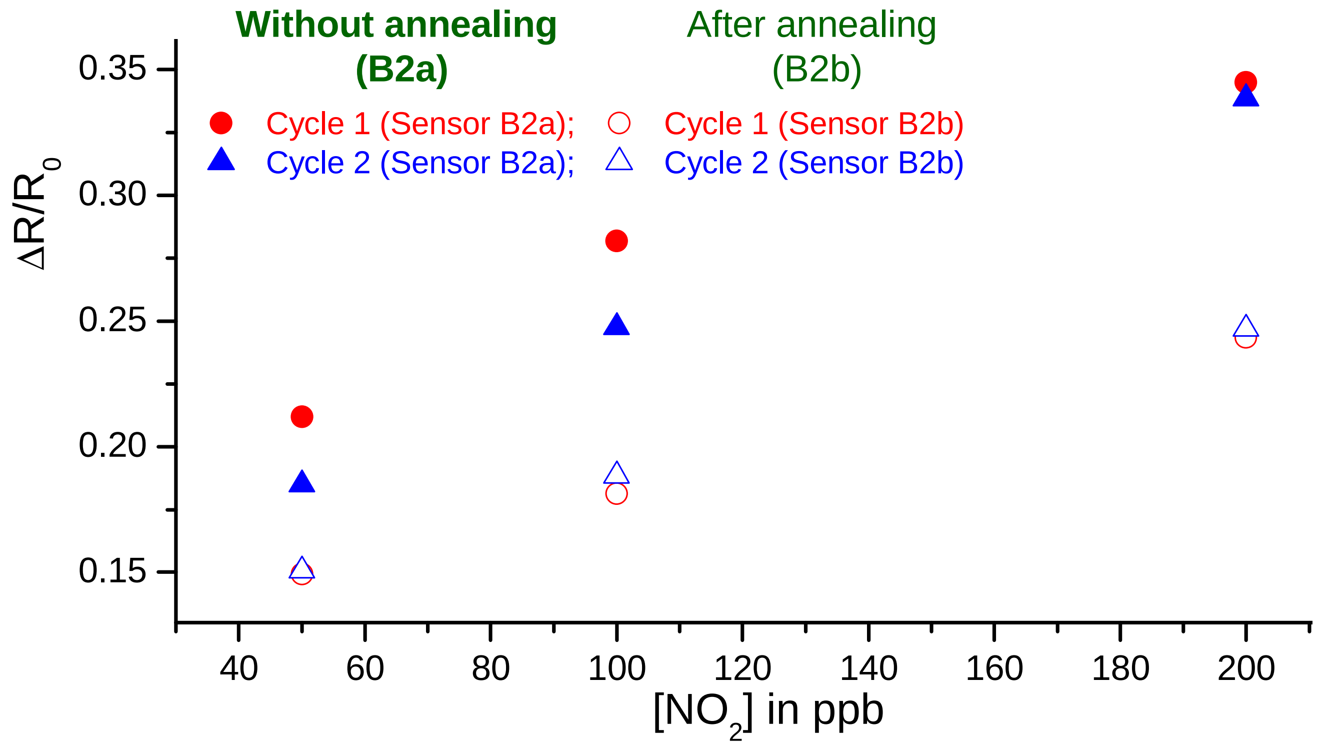
3 - CNTs-based sensors: Sensors elaboration for BTX Detection:

→ Noncovalent functionalisation method
→ Characterisation of the CNTs-MCs hybrid materials
→ Sensor development and experimental results towards toluene

4 - Conclusion and perspectives

4- Conclusion and perspectives

CNTs-based sensors: Sensors elaboration for NO_2 and O_3 Detection



Sensor response

$\Delta R/R_0 = (R_0 - R) / R_0$

- R = R under NO_2
- R_0 = R under Air zero at equilibrium.

Conclusion

- **Better response and repeatability given by the annealed layers**
- **No surfactant effect on the sensors responses**
- **Low annealing conditions seems to be necessary**

- **For O_3, no sensors sensitivity after long time exposure**

4- Conclusion and perspectives

CNTs-based sensors: Sensors elaboration for BTX Detection

Functionalisation:

- efficient functionalisation way (noncovalent) leading to a better processing of the CNTs and preserving the properties
- choice of the MCs for tailoring the adsorption of BTX:
  - → benzyl moiety
  - → metal free
- combination of CNTs and MCs:
  - → higher response (sensitivity increase due to SSA)

Sensors responses:

- low operating temperature (Room Temperature)
- reversible process, good repeatability

❑ **Gas sensing experiments for the detection of Benzene and Xylenes are under investigations.**

❑ **New phthalocyanine derivatives (Metal free)**

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Thank you for your attention