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Conductimetric microsensors integrating phthalocyanine nanolayers : high-performance sensing devices for the measurement of NO₂ at ppb level in atmosphere

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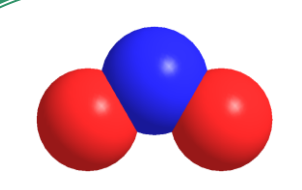
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Scientific context and objectives

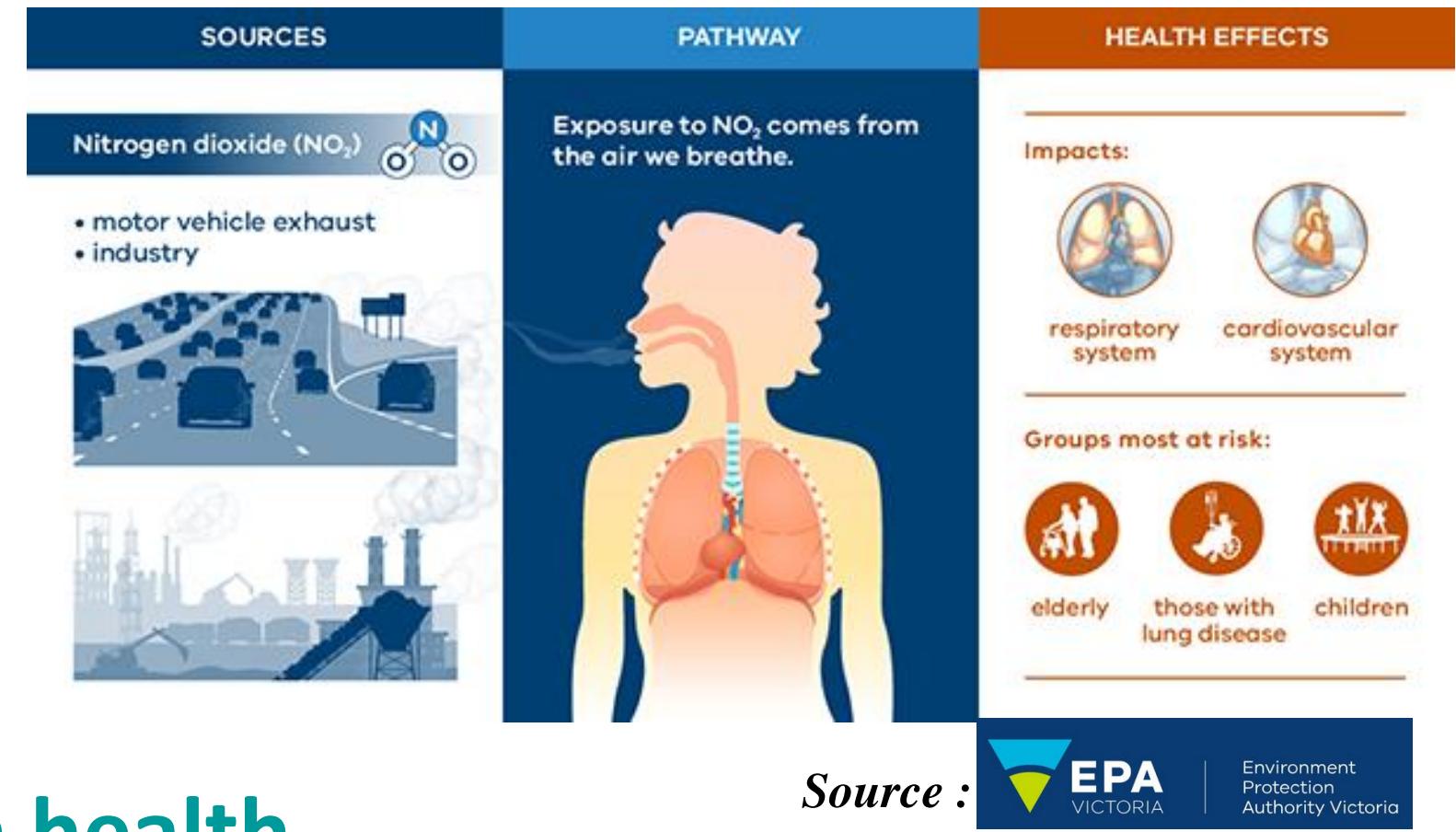
Metallophthalocyanines constitute an extended class of molecular organic semiconductors that the extrinsic electronic conductivity can be strongly modulated by the adsorption of oxidizing species. Taking into consideration the great number of π -electron delocalized on each macrocycle, adsorbed oxidizing pollutants like NO₂ and O₃ induce high p-type conductivity variations whereas adsorbed reducing pollutants like CO, NH₃ or H₂S not lead to significant conductimetric response in the same range of concentrations.

Results reported here highlight the high sensitivity of phthalocyanine-based conductimetric microsensors to NO₂ associated to a limit of detection and resolution closed to few ppb, at low working temperature. The effect of sensing layer thickness on metrological performances as well as influence of humidity on response is investigated in this range of concentrations. A special attention is focused on selectivity, especially towards ozone O₃ which remains the major interfering pollutant leading to substantial cross-sensitivity and long-term degradation of sensing layer according to an ozonolysis process. Sensing performances of conductimetric microsensors integrating nanolayer of phthalocyanines as sensing membrane are illustrated and discussed.



Why a special attention on NO₂ ?

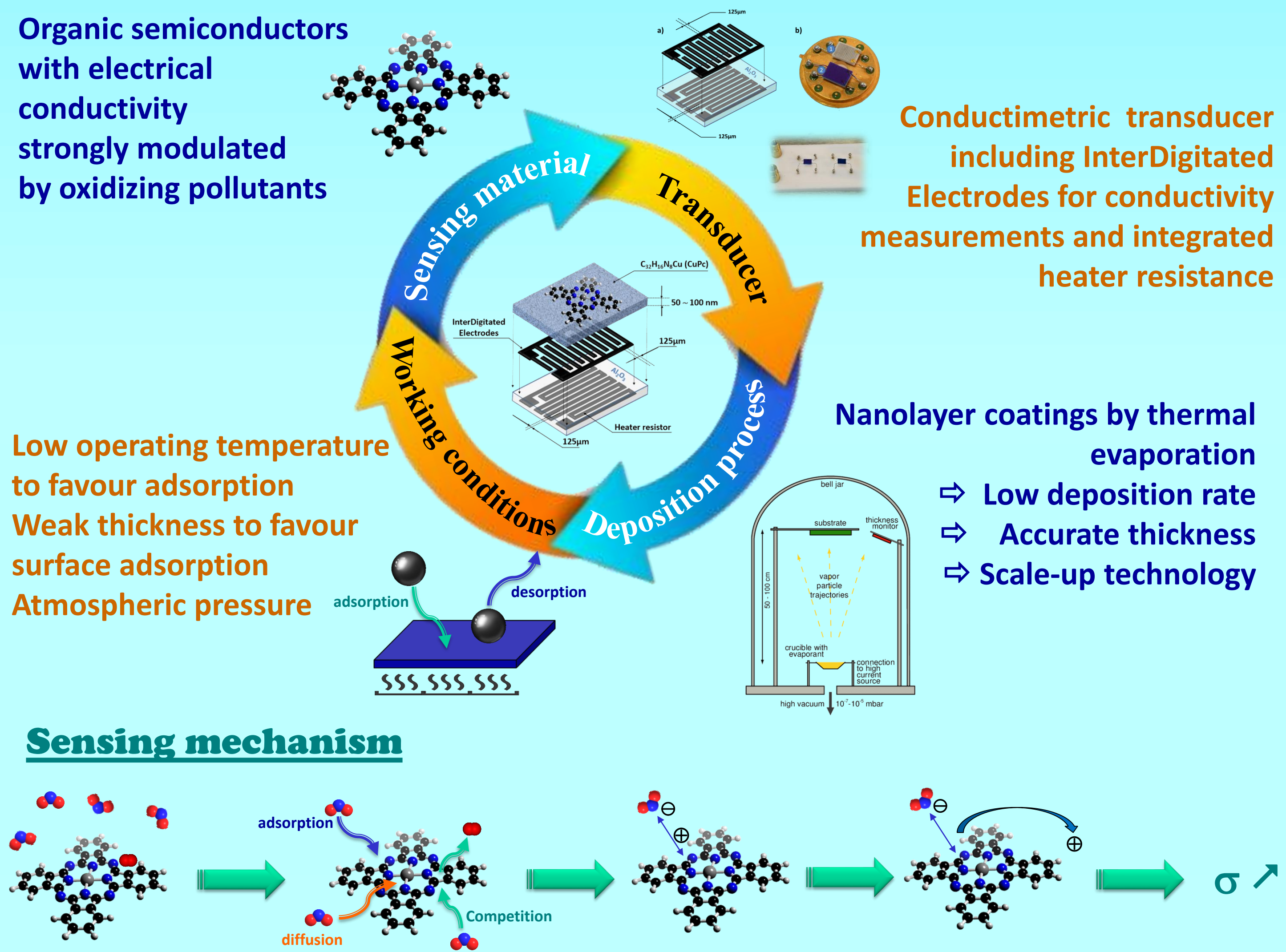
- ✓ **Ubiquitous pollutant**
 - ✓ Present in urban, suburban and rural area
 - ✓ Indoor & outdoor pollutant
 - ✓ Dispersion in a large spatial scale
- ✓ **Source of environmental troubles**
 - ✓ Precursor of ozone
 - ✓ Formation of acid rains
 - ✓ No significant and efficient remediation in EU
- ✓ **High toxicity prejudicial to human health**
 - ✓ cough, nasal and eyes irritations
 - ✓ [NO₂] > 80 ppb: ↗ respiratory infections
 - ✓ 100 ppb: hourly mean concentration recommended for public protection



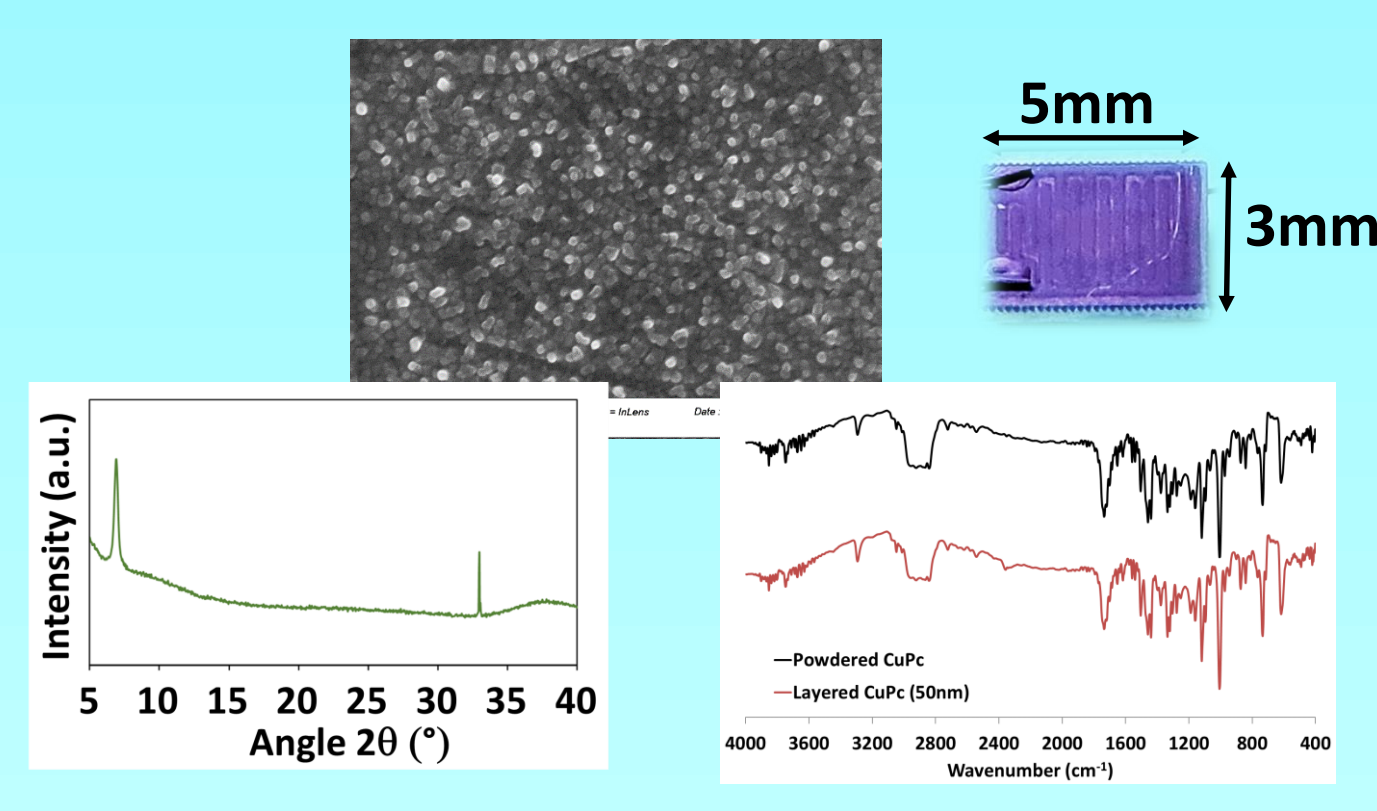
Source : EPA

From sensing material to microsensors : strategy, development, characterization

Scientific approach

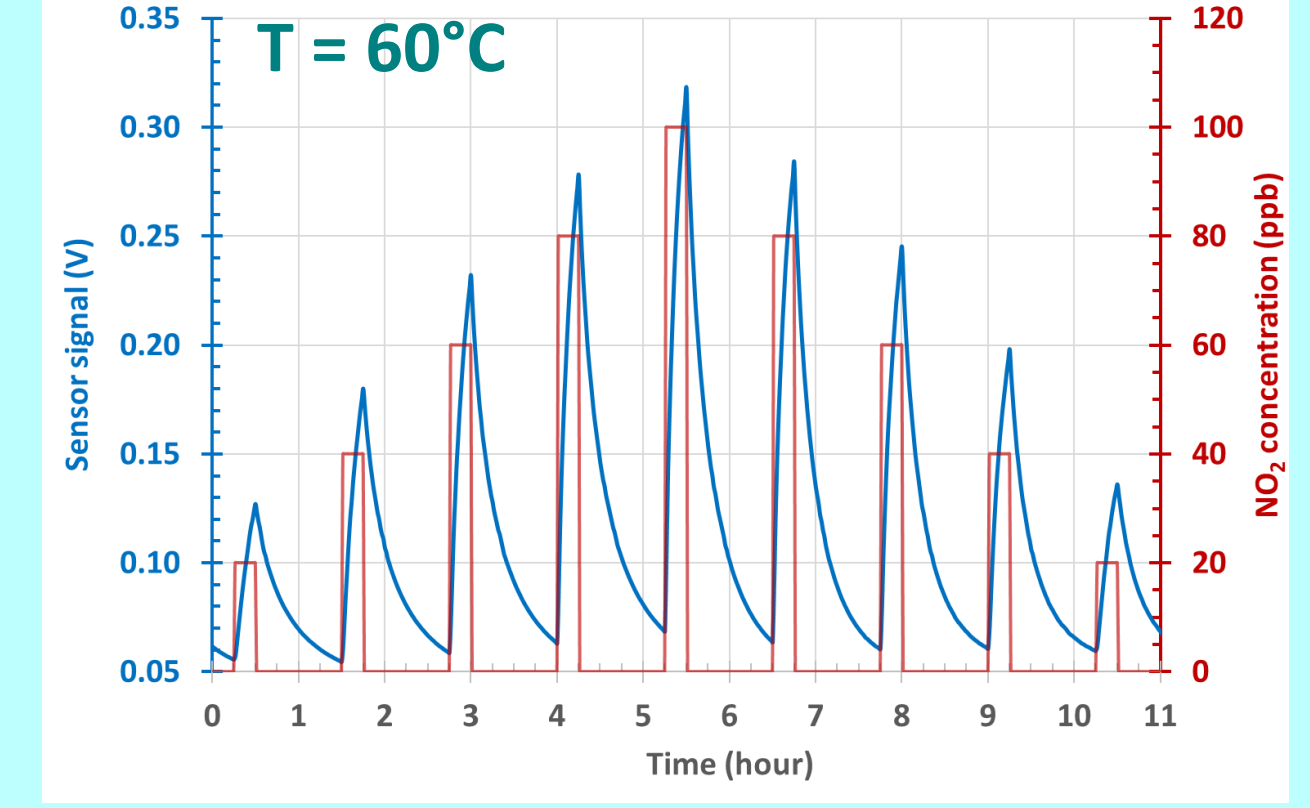


CuPc Nanolayer morphology



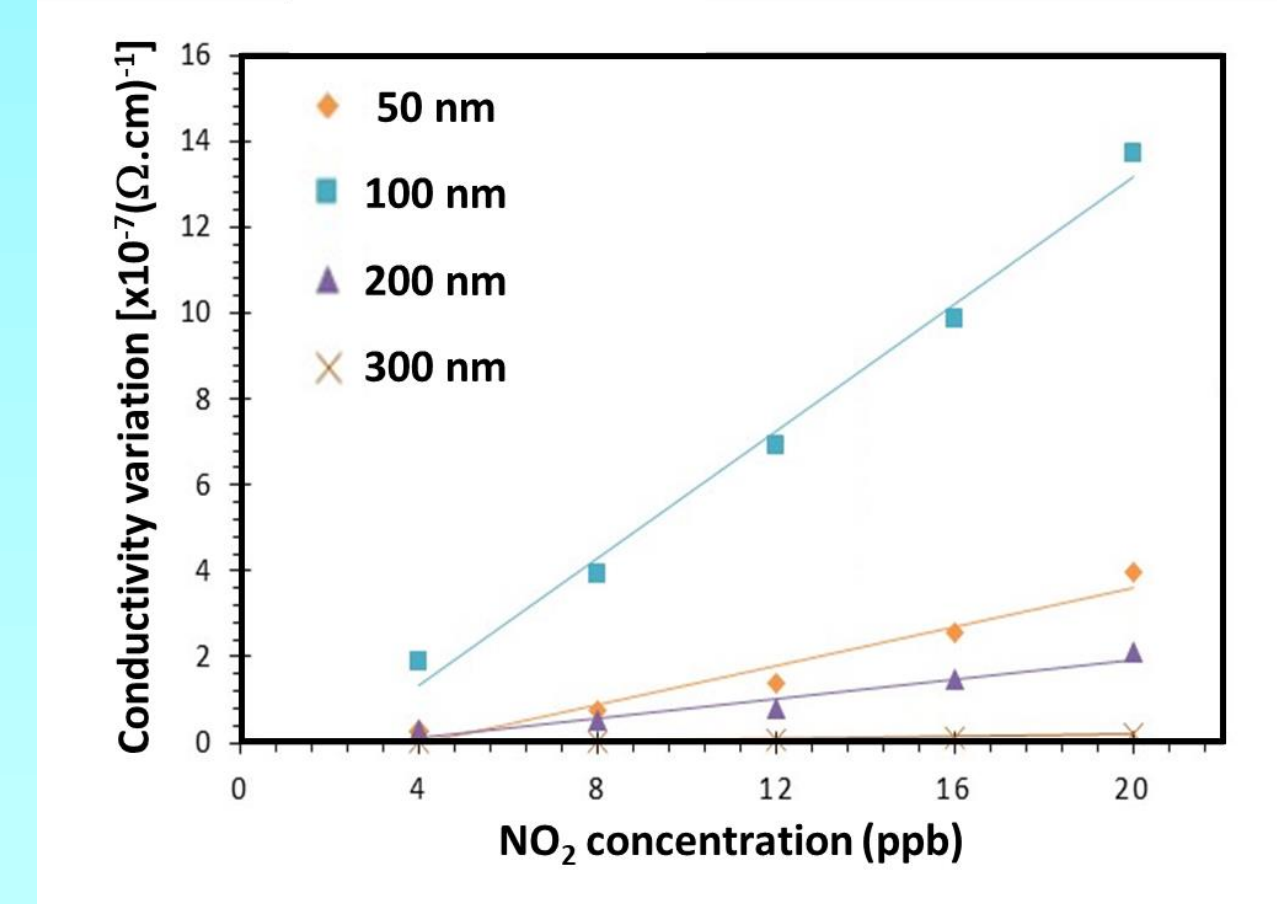
Homogenous, amorphous and unaltered nanolayers

Typical response towards NO₂



High sensitivity Slow desorption

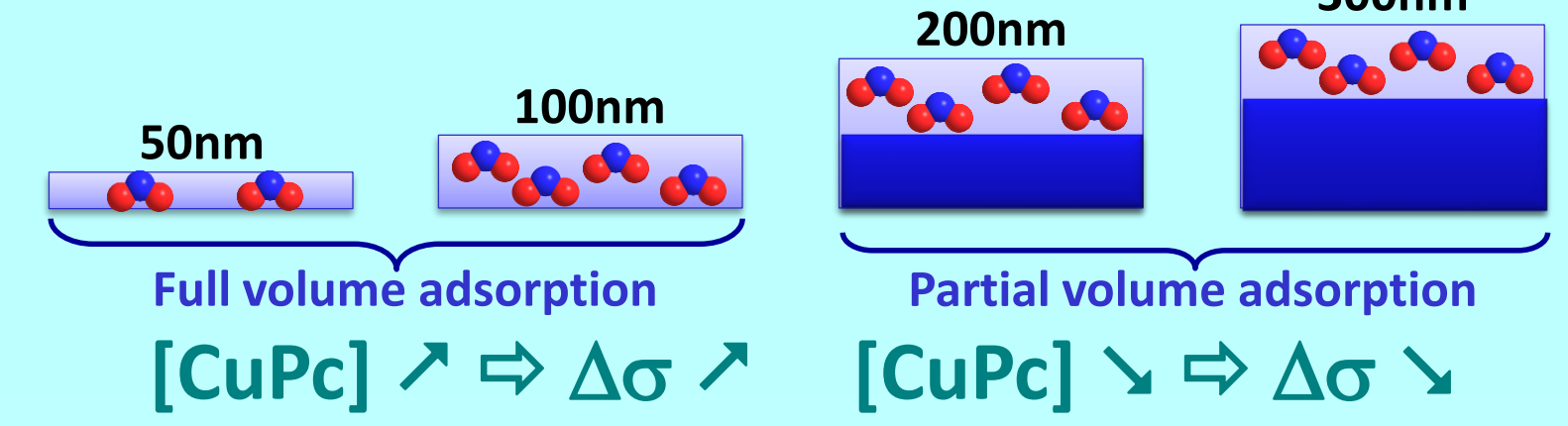
Effect of layer thickness on response



Extrinsic conductivity σ of CuPc exposed to NO₂

$$\sigma = \mu \cdot e \cdot \sqrt{[\text{NO}_2] \cdot [\text{CuPc}]} \cdot \exp\left(\frac{1}{2kT} (E_{12}^{\text{red}} - E_{12}^{\text{ox}})\right)$$

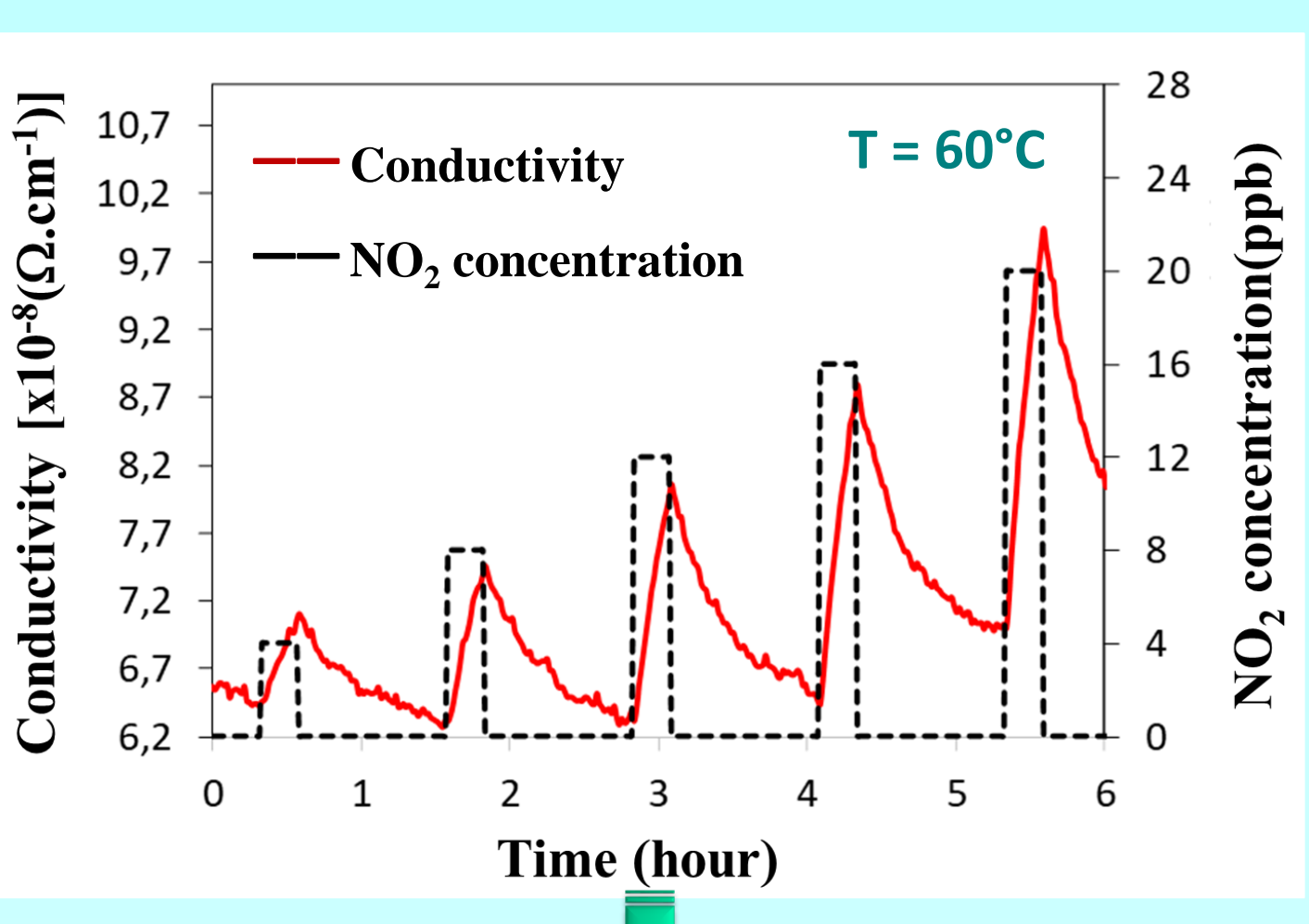
For [NO₂] = constant ⇒ $\sigma = k \cdot [\text{CuPc}]^{1/2}$



$\Delta\sigma$ maximum for layer thickness $e = 100\text{nm}$

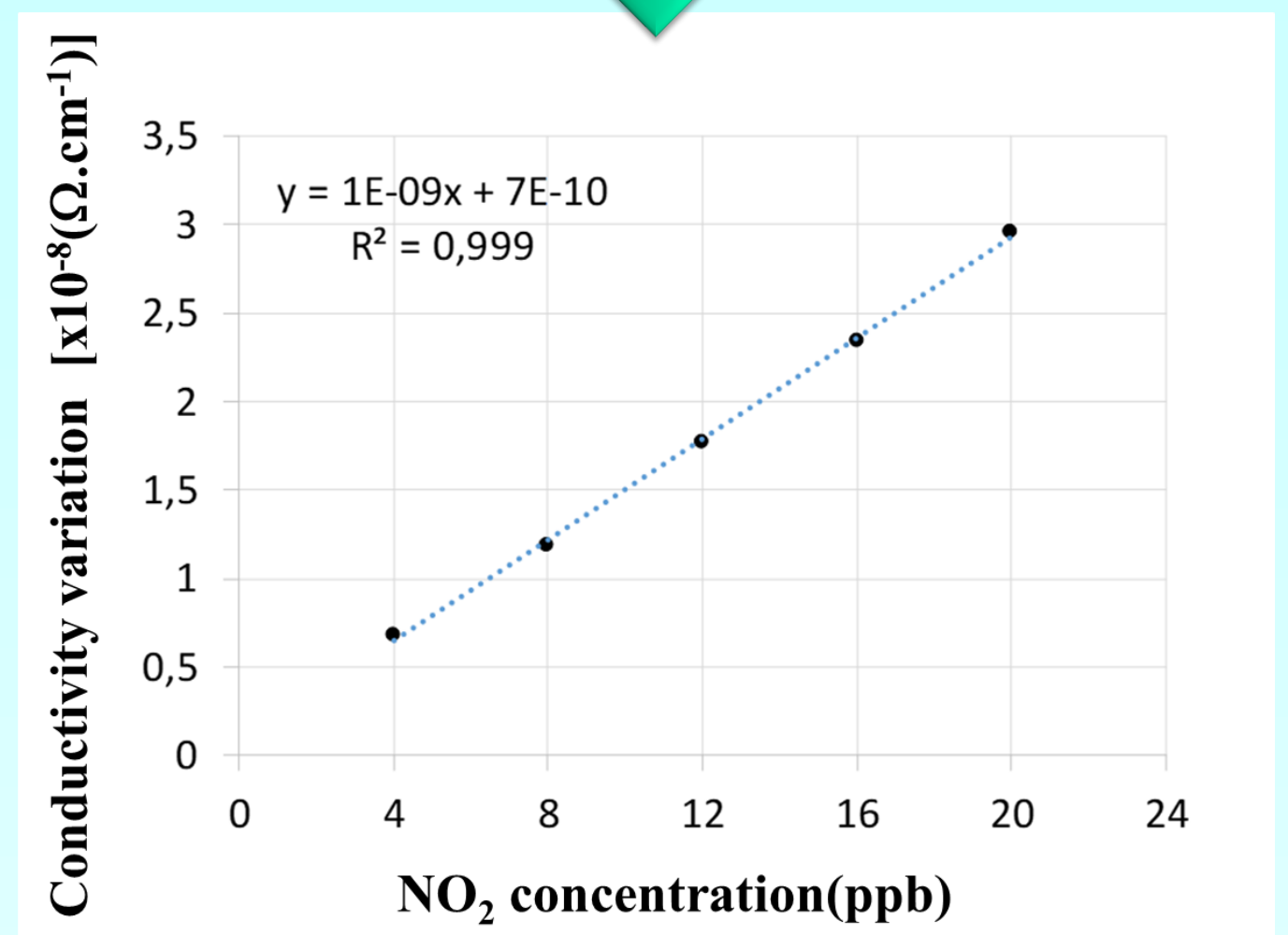
Sensing behavior and metrological performances towards NO₂

Sensitivity, resolution and threshold

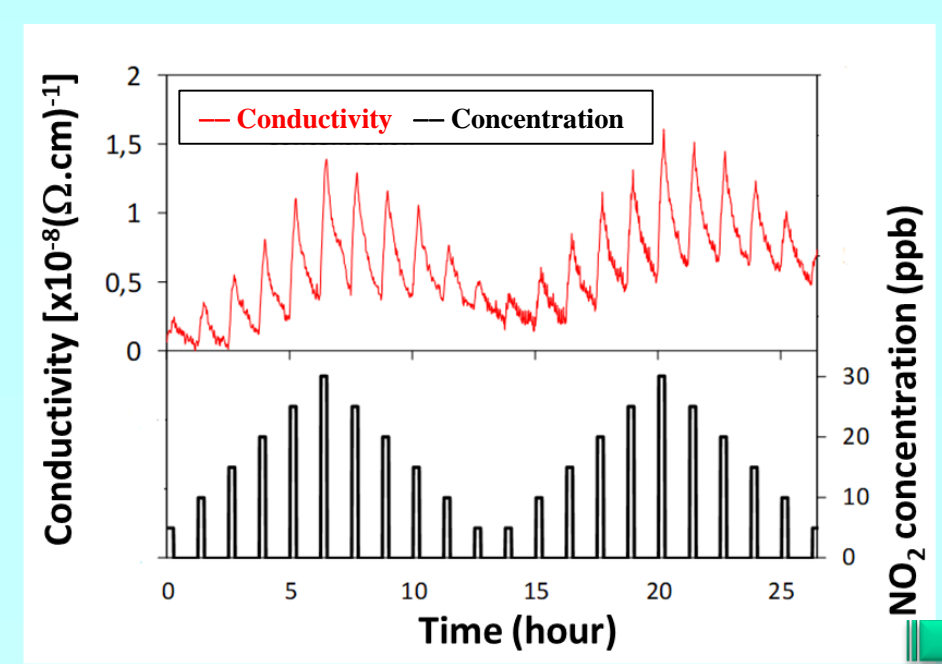


Performances

- Linear response**
- Efficient even at low operating temperature**
- Sensitivity = $1,4 \cdot 10^{-9} (\Omega \cdot \text{cm})^{-1} \cdot \text{ppb}^{-1}$**
- Noise level = $1,7 \cdot 10^{-10} (\Omega \cdot \text{cm})^{-1}$**
- ⇒ **LOD = 0,5 ppb**

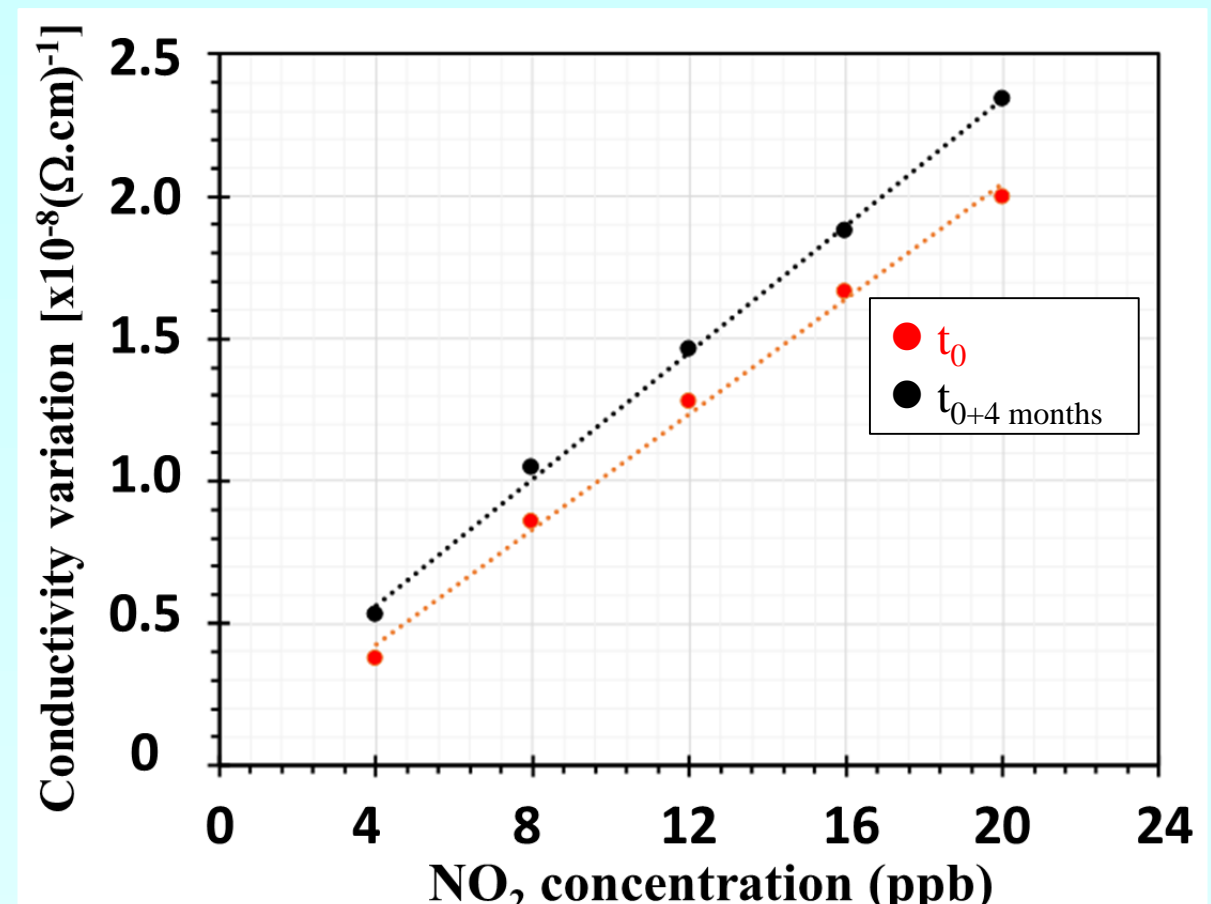
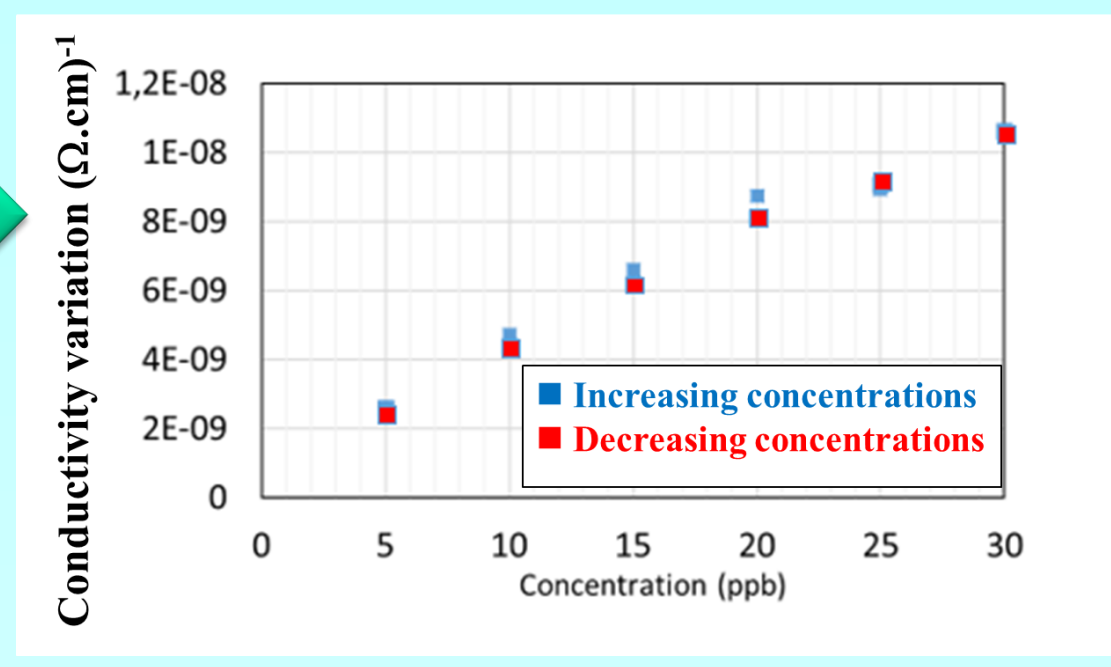


Repeatability, stability



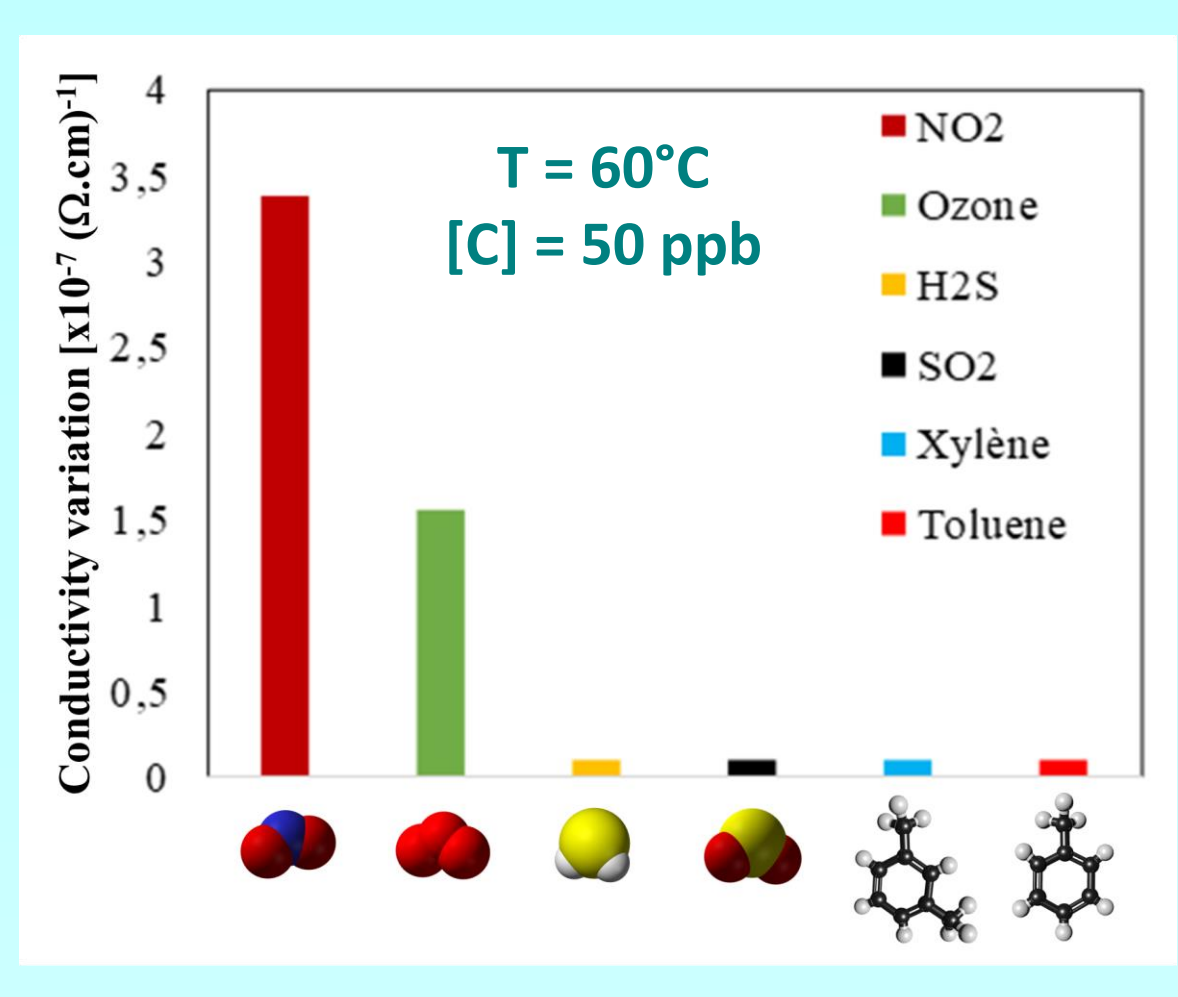
Good repeatability
Resolution ≈ 4 ppb

Operating conditions
 T = 60°C; RH ≈ 0.3%;
 Exposure time = 15min
 Recovery time = 1hour



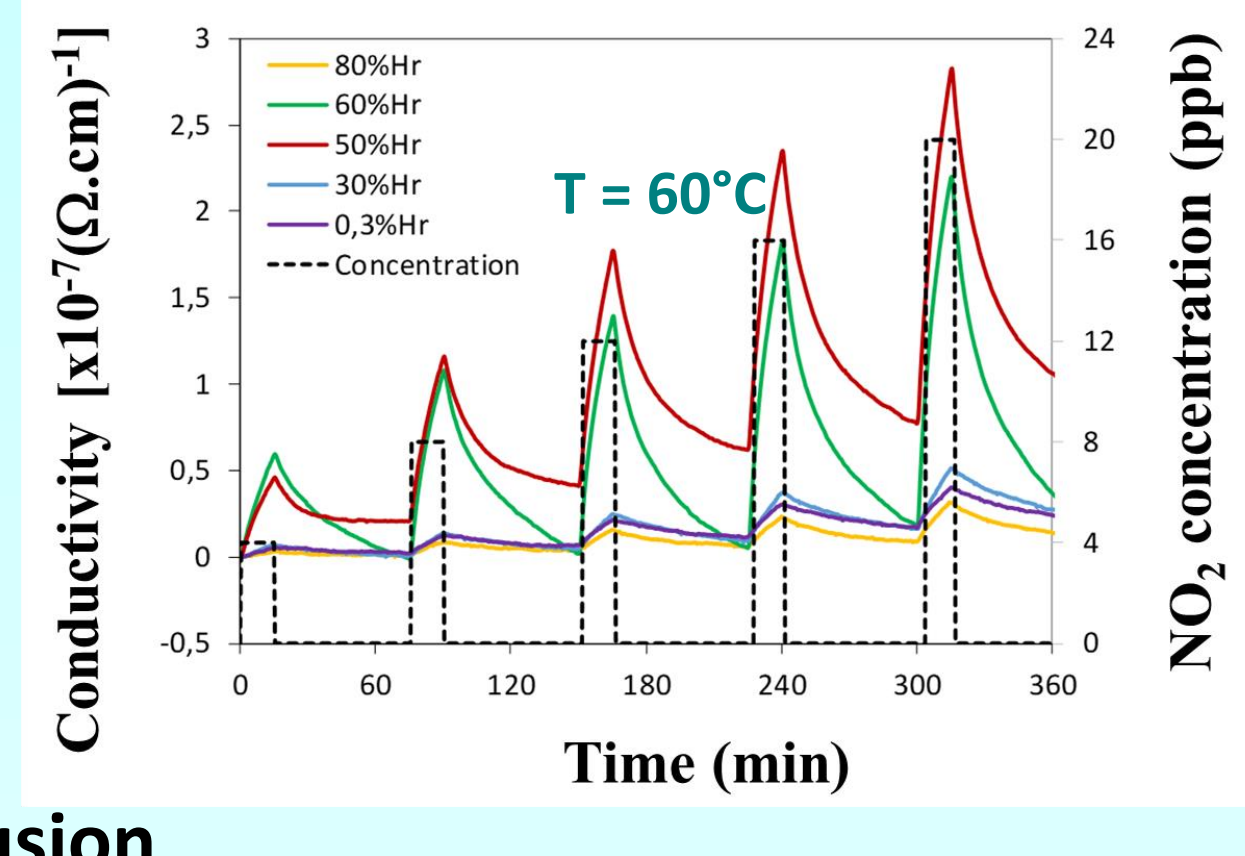
↗ of responses after 4 months of storage @ room temperature & ambient hygrometry
 ↓ **Non-intentional doping by O₂ and H₂O molecules**
 Better stability for sensor stored into N₂

Selectivity, influence of humidity



Weak responses to reducing & aromatic gases
Higher response to NO₂
 ↓
Partial selectivity to oxidizing pollutants
O₃ = main interfering gas

- **Low RH** ⇒ low electrical conductivity in dry air
- **Medium RH** ⇒ ↗ of NO₂/CuPc charge transport by H₂O species
- **High RH** ⇒ ↘ in inter-macrocycle conductivity due to excessive H₂O diffusion



Higher responses to NO₂ for moderate relative humidity

Main results and conclusions

Sensing strategy

Phthalocyanines as sensing materials

- Cheap, thermally and chemically robust class of material
- Well-controlled layering by thermal evaporation even @ nanoscale
- Extrinsic electrical conductivity highly modulated by oxidizing gases

Microsensor devices

- Best sensitivity for sensing layer thickness close to 100 nm
- Suitable for ppb measurement even at low operating temperature
- Low-power consumption

Performance level

Metrological performances

- Linear response in the [4 - 30 ppb] NO₂ concentration range
- Good repeatability leading to resolution better than 4 ppb
- Limit of detection close to 500 ppt
- Storage in neutral atmosphere required for stability

Influence of interfering species

- Negligible cross-sensitivity towards non-oxidizing gases
- Cross-sensitivity ≈ 40% towards O₃
- Higher NO₂ responses in moderate relative humidity (40-65%)

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