Electrospray printing of graphene layers for chemiresistive gas sensors

Sergio Masa

Email: sergio.masa@csic.es

Spanish National Research Council

Institute for Physical and Information Technologies

Interreg Sudoe Nan Sen-AQM

CSIC Consejo Superior de Investigaciones Científicas

itefi Instituto de Tecnologías Físicas y de la Información

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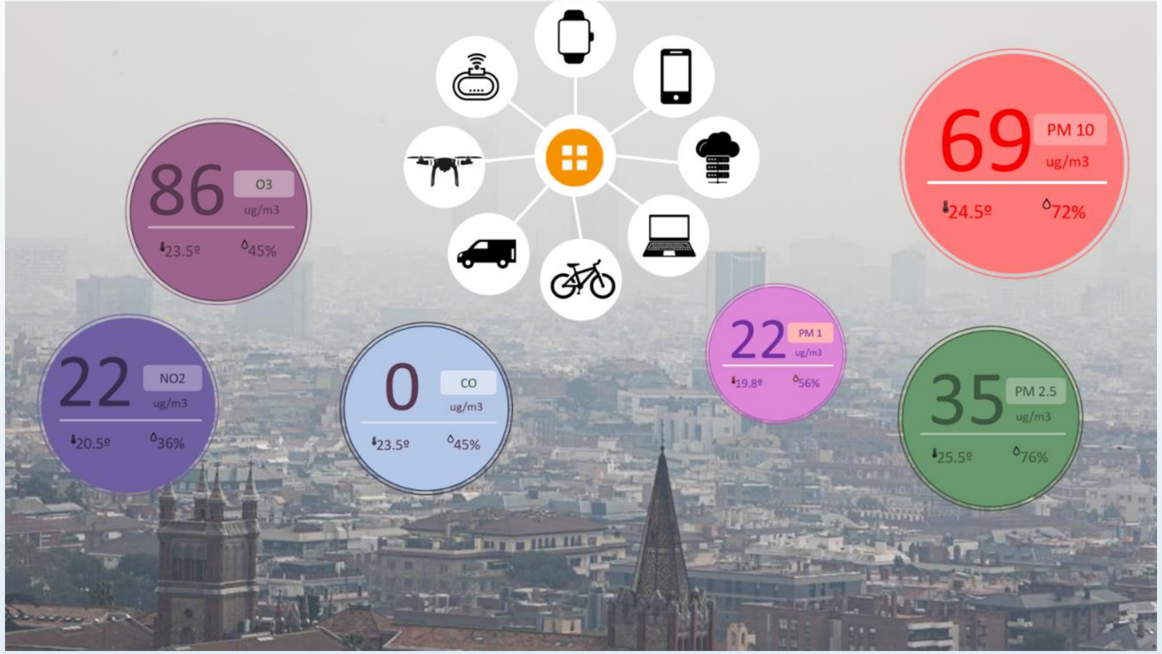
MDPI sensors chemosensors

CONTENT

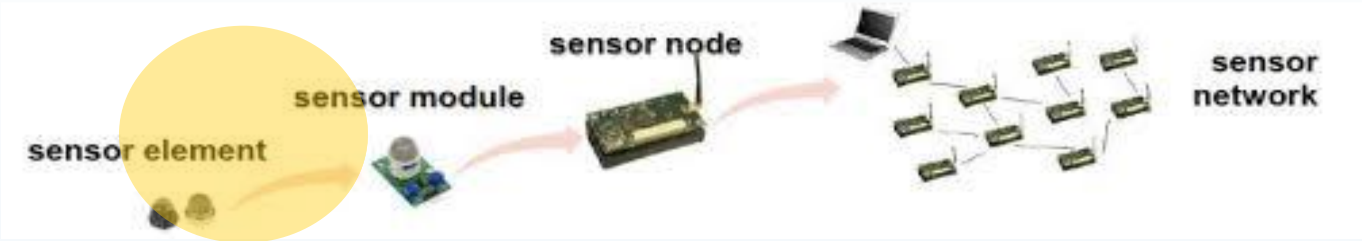
Wireless Sensor Networks (**WSN**)

Air Quality Monitoring (**AQM**)



Low cost **Low power** **High resolution (x, t)**

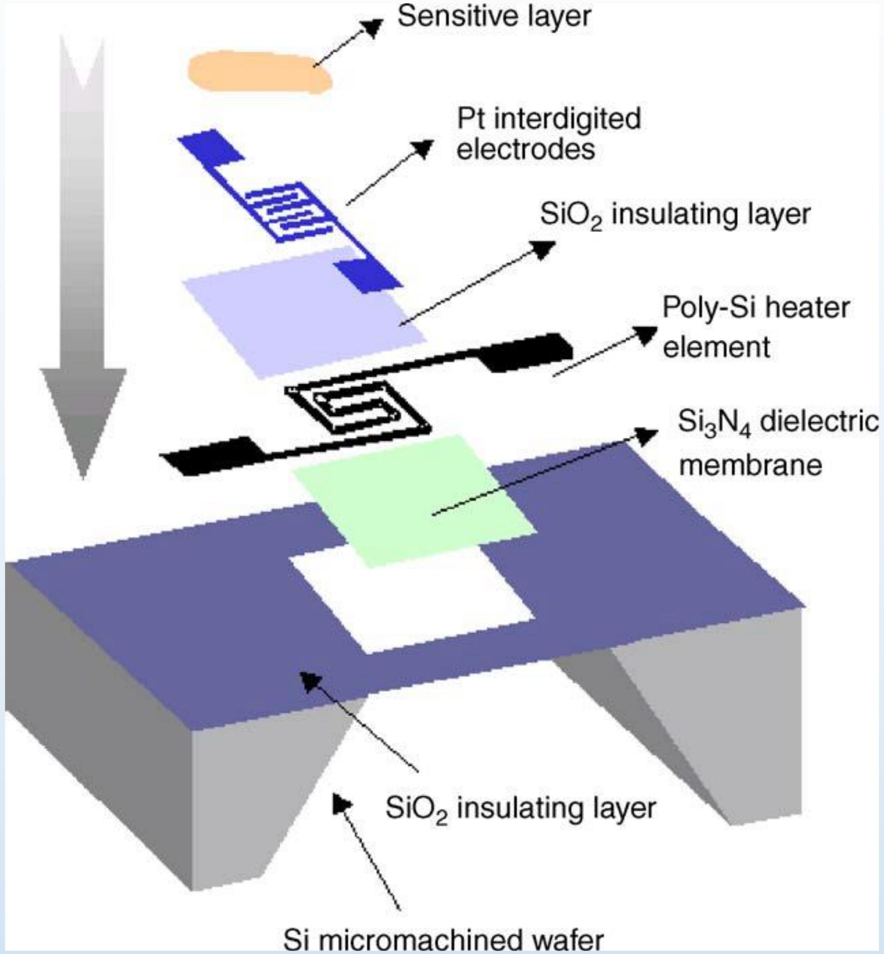
Distributed **Massive** **Ubiquitous…**

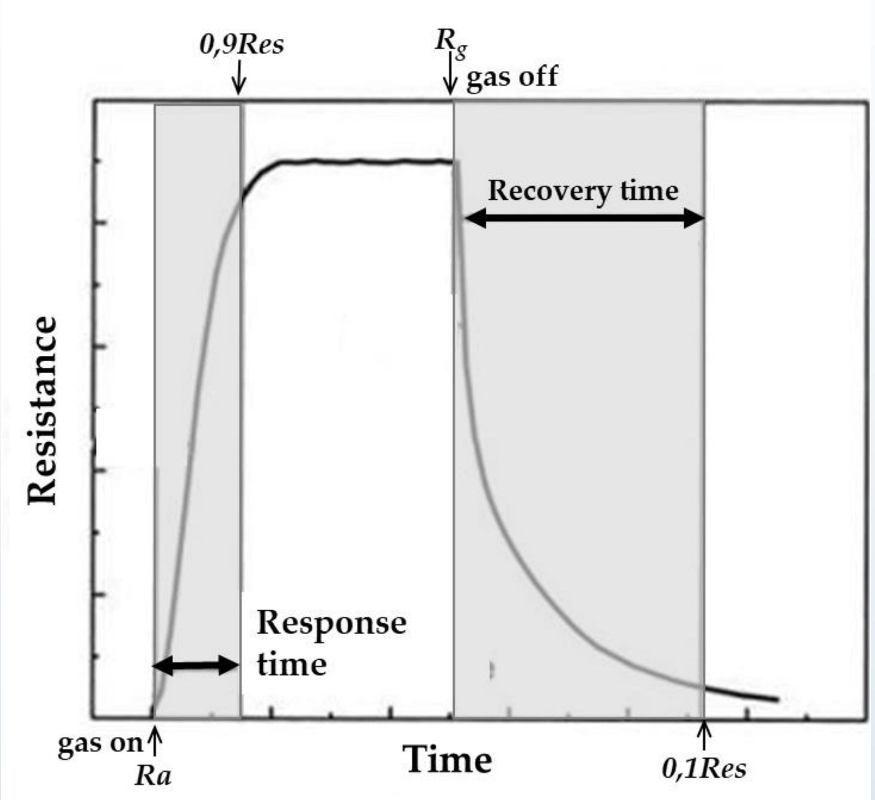


- **Target** *NO_2, O_3, CO, VOCs, …*
- **Cost** *Materials, fabrication process, scale-up*
- **Power** *Operation temperature*
- **Size** *Miniaturization, micro- & nanofabrication*
- **Performance** *Low pollutant concentrations, sensitivity, selectivity, response/recovery time*
- **Life-time**
- **Accuracy**
- **Stability**
- **Repeatability**

Metal Oxide Semiconductor (MOS) sensors

MOS sensors are produced by means of **costly technologies** (e.g. silicon processing, MEMS) and require **high power consumption** due to the high working temperature (>300 ºC).



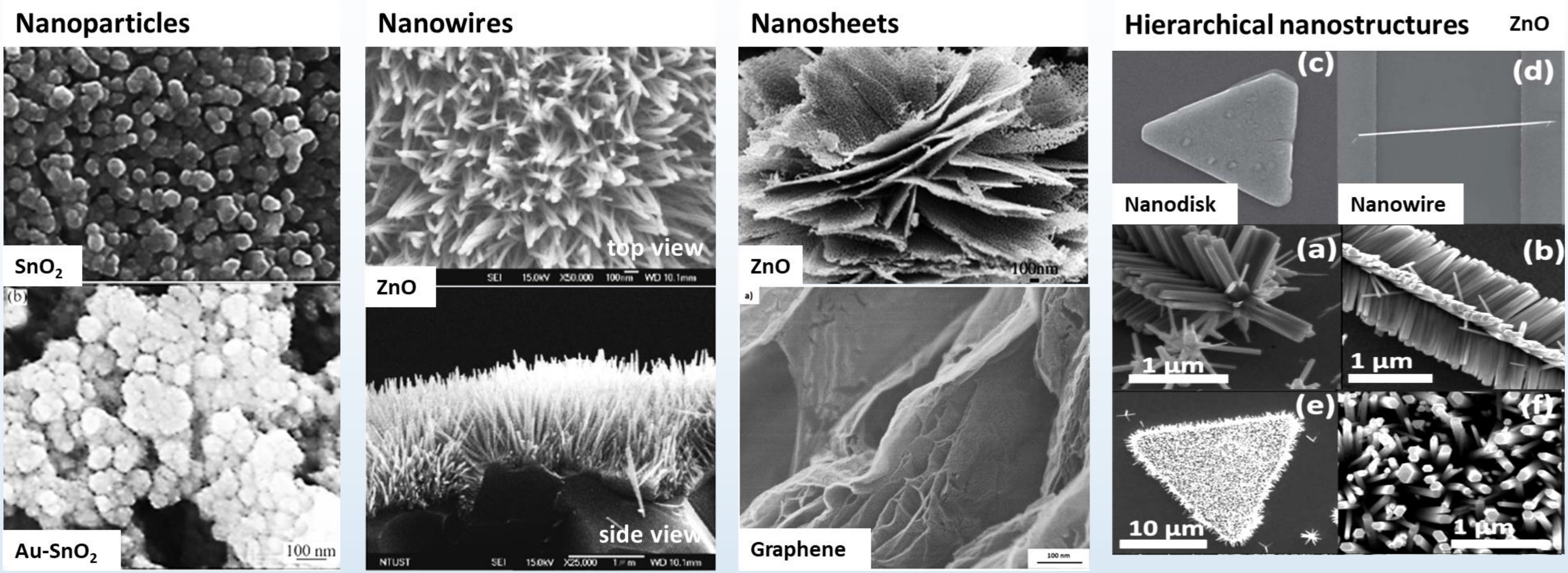


Response

$$Res = \frac{R_g - R_a}{R_a}$$

2.1. NANOSTRUCTURES

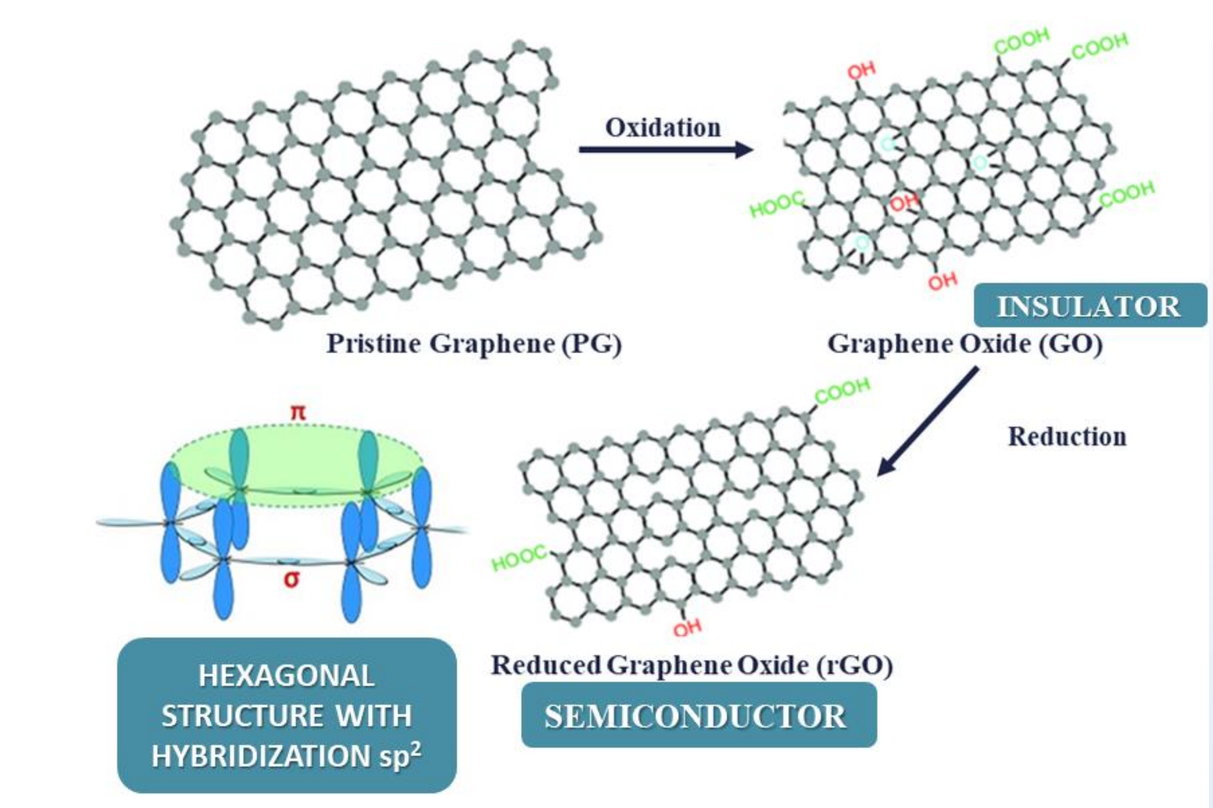
Sensor based on nanostructured active layers **(nanosensors)**



0D **1D** **2D** **3D**

2.2. GRAPHENE

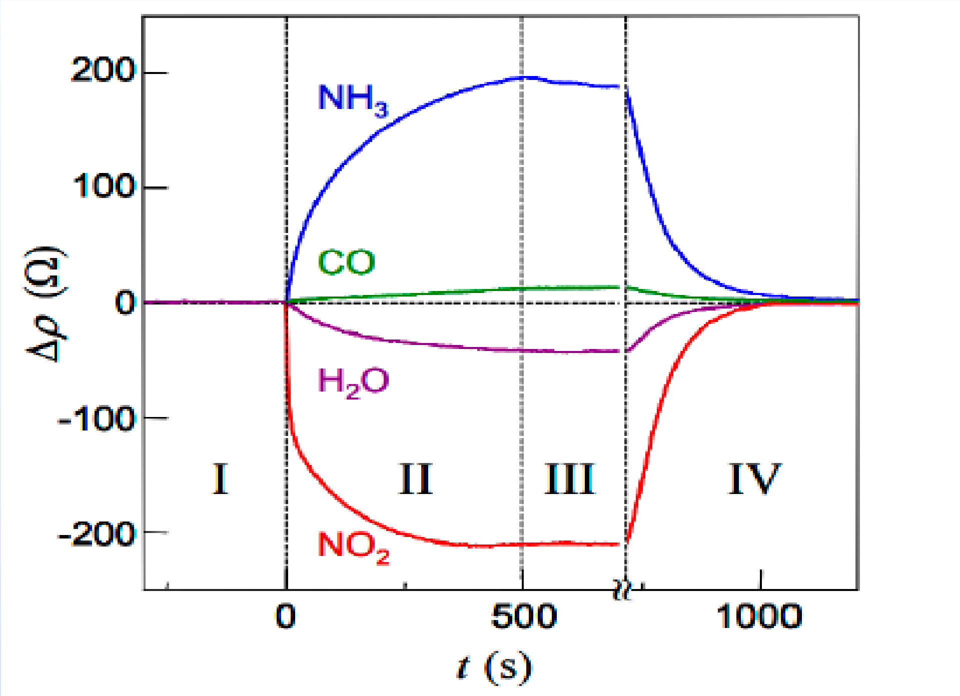
Graphene materials (2D)



- **PG** has <u>high conductivity</u> but is <u>inert</u> (lack of defects, oxygen groups) and needs to be functionalized (polymers, metals, metal oxides), <u>costly non-scalable production</u>
- **GO** has <u>low conductivity</u> but is <u>very reactive</u> (multiple oxygen groups)
- **rGO has intermediate properties between PG and GO**, **sustainable mass production**

Resistive gas sensors

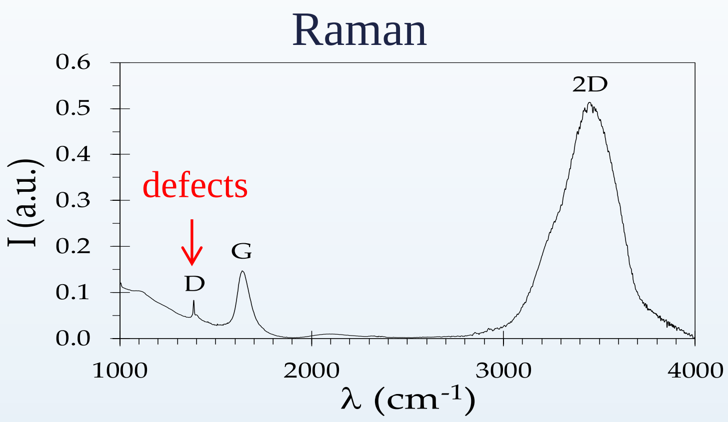
Classification	Oxidizing gases	Reducing gases
n-type	Resistance ↑	Resistance ↓
p-type	Resistance ↓	Resistance ↑

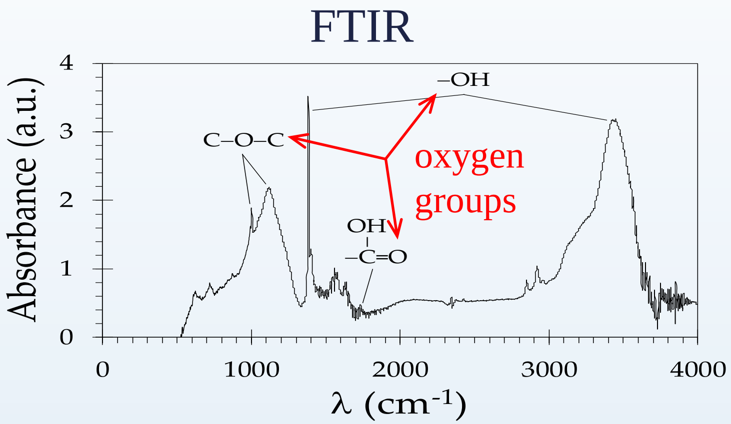


Precursor suspension

rGO in isopropyl alcohol (0.1mg/ml)

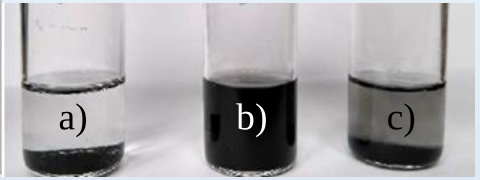
rGO powder (E800, Abalonyx AS, Norway)





after 1h sonication

after 24h at rest

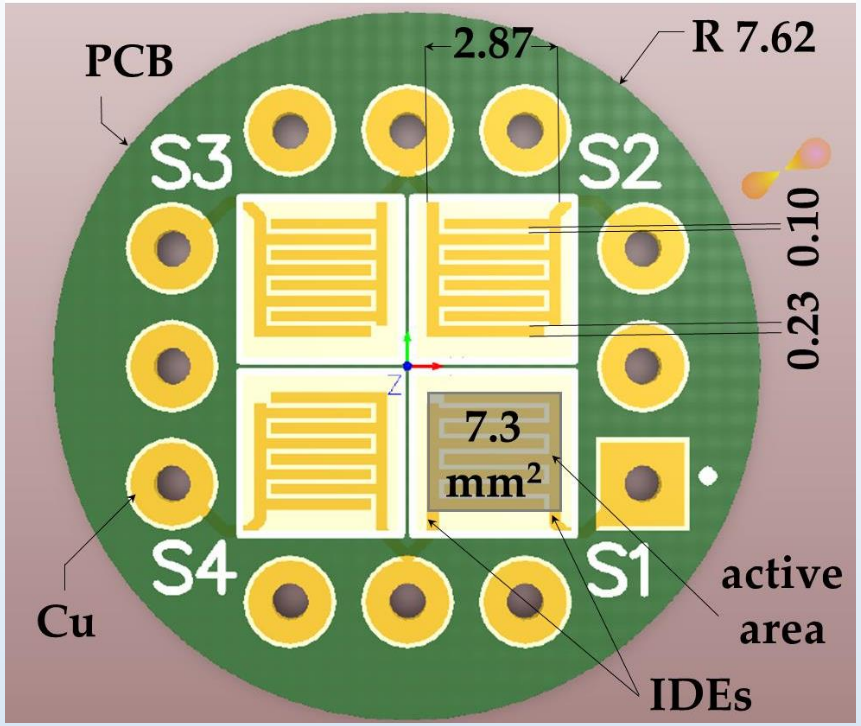


a) acetone
b) isopropyl alcohol
c) ethanol

- Specific surface area 436 m^2/gr
- Electrical conductivity 20 S/m
- Carbon-to-oxygen-ratio 35
- Number of layers 7

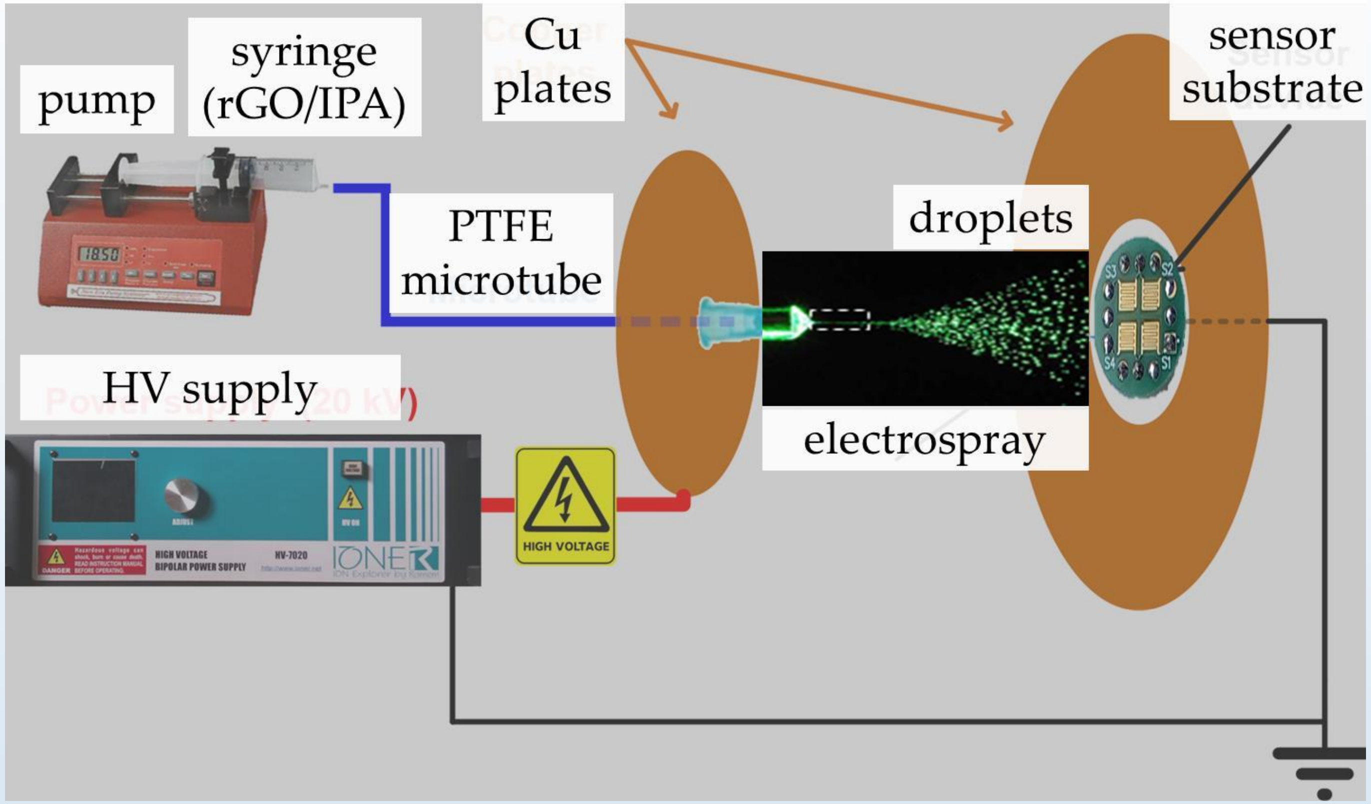
Sensor substrate

Polymer (PCB) with printed interdigitated electrodes (Cu)



3.2. ELECTROSPRAY (I)

Sensors are prepared by **electrospray** of a rGO/IPA dispersion (0.1 mg/ml)



Parameters

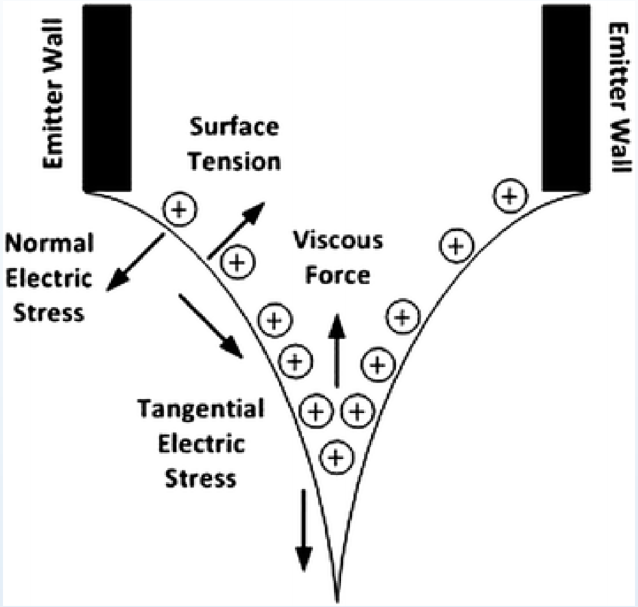
- **Needle inner/outer diameter** 0.3 / 0.5 mm
- **Distance needle-substrate** 5 - 30 mm
- **Voltage** 2 - 6 kV
- **Feed flowrate** 3 - 10 µL/min
- **Deposition time** 5 - 20 min

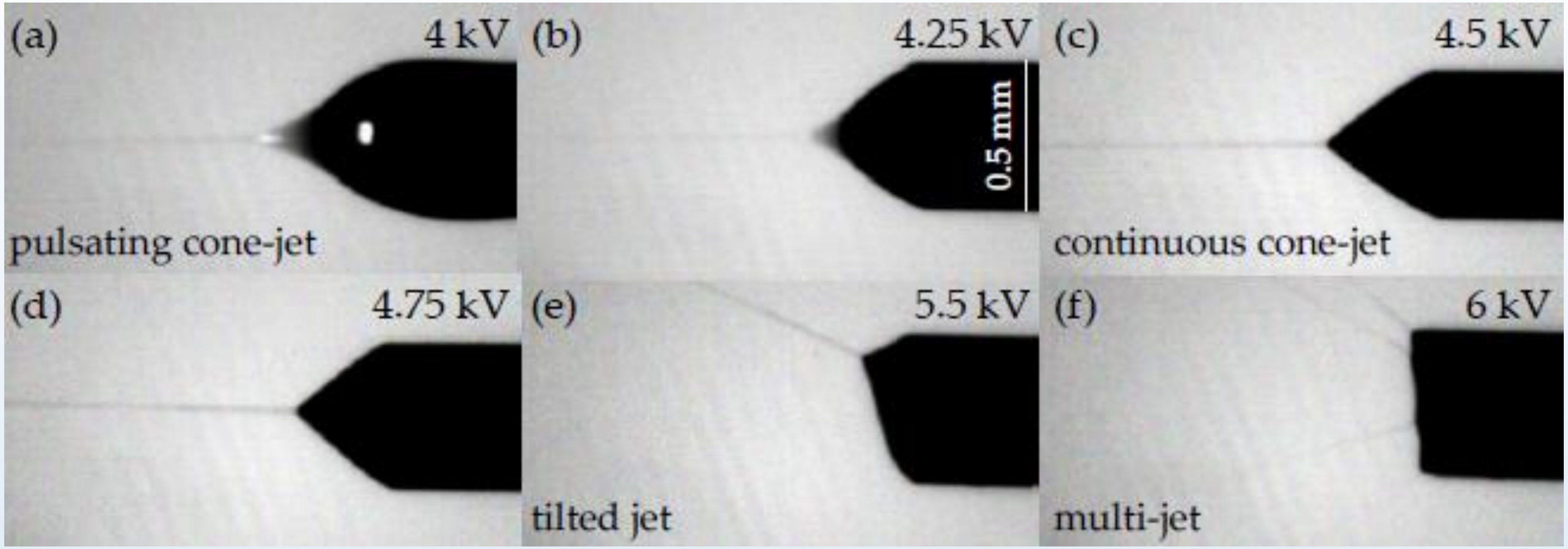
Requirements

- **Stable dispersion** *Short deposition time*
- **Stable electrospray** *Optimal flowrate and voltage*
- **Solvent evaporation** *Highly volatile solvent, large distance*

3.2. ELECTROSPRAY (II)

Electrospray regimes through increasing voltage:
dripping, pulsed cone-jet, **continuous cone-jet**, tilted-jet and multi-jet .



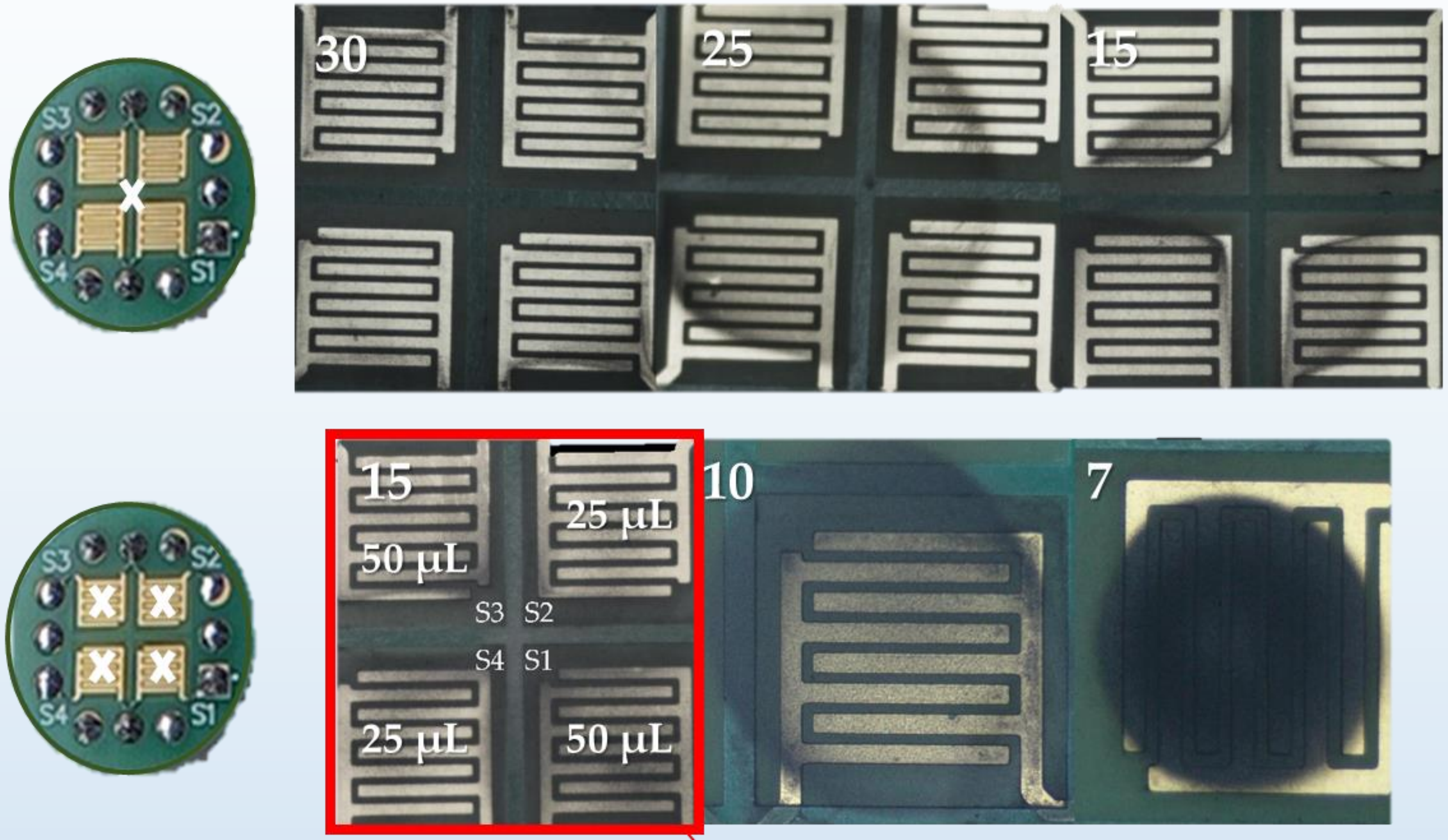


The liquid meniscus narrows and elongates under the action of the **surface tension** and the **electric field** force and at a critical voltage the **Taylor cone** is formed. With further increasing of the electric field, the cone becomes unstable and a very **thin jet** (small and thin compared with the capillary diameter) is emitted from the cone apex.

Circular spots of rather uniform deposits of rGO are obtained in stable cone-jet mode.
The diameter of the spot increases with the increasing needle-substrate distance

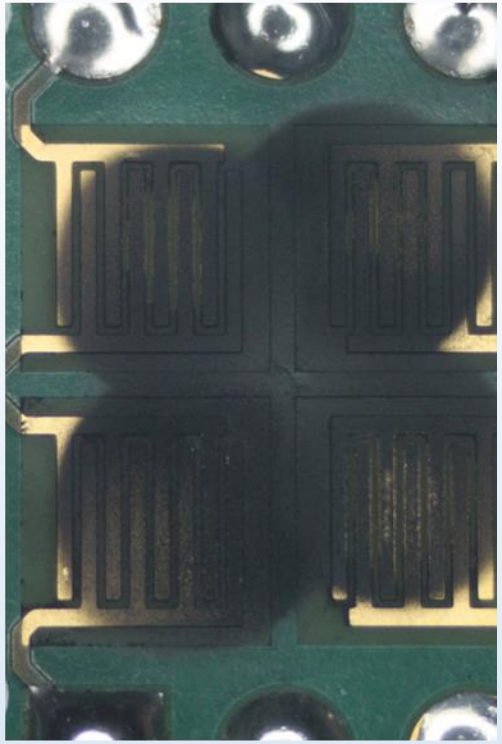
Needle-substrate distance (mm)

Needle centering point

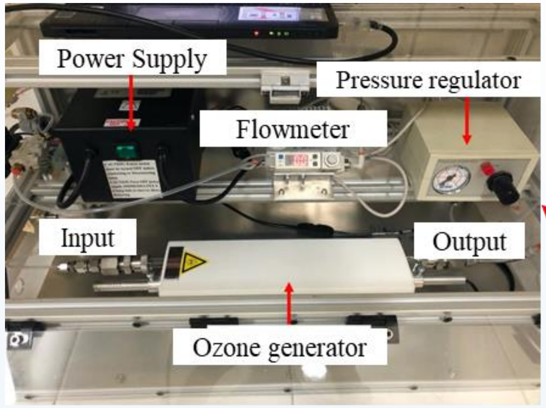


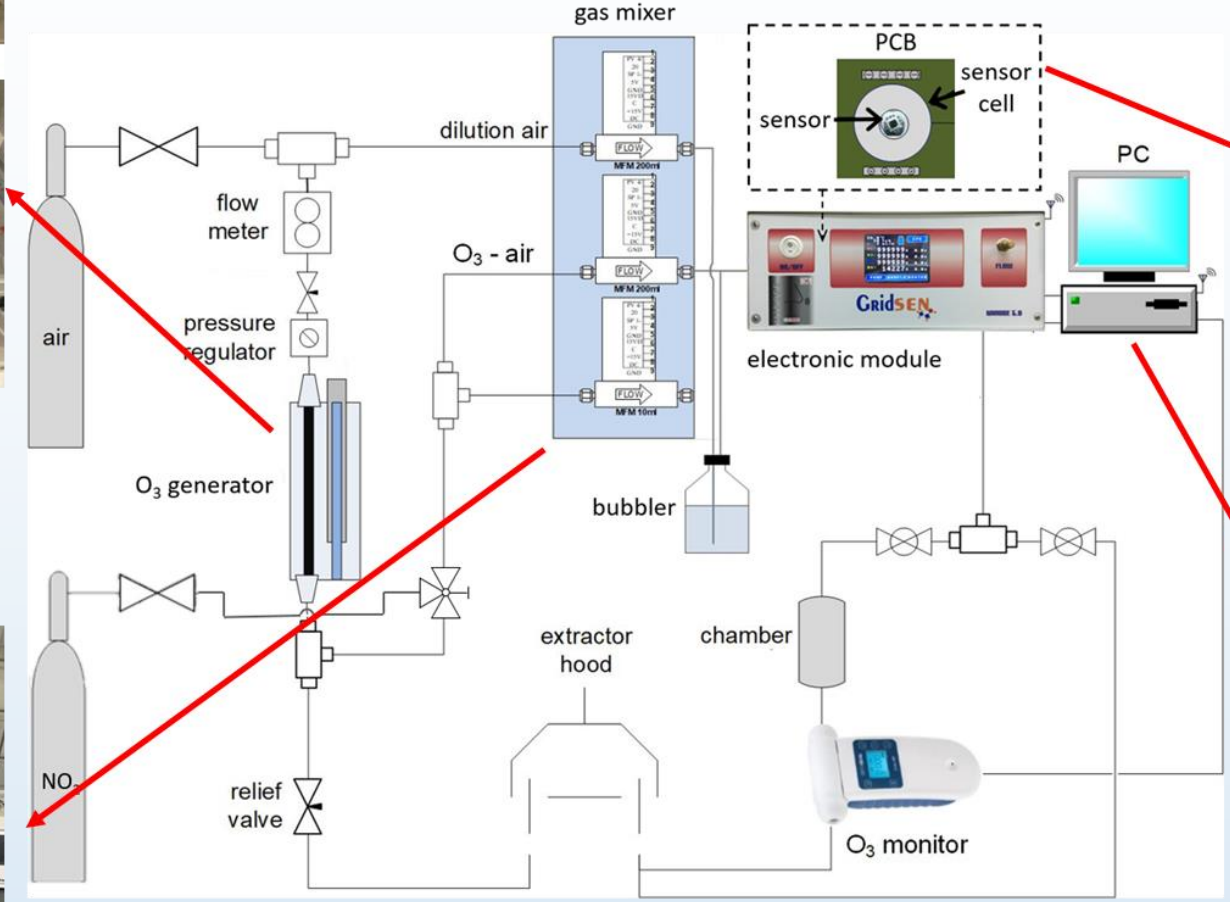
characterization for gas detection

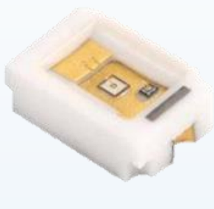
Repeatability

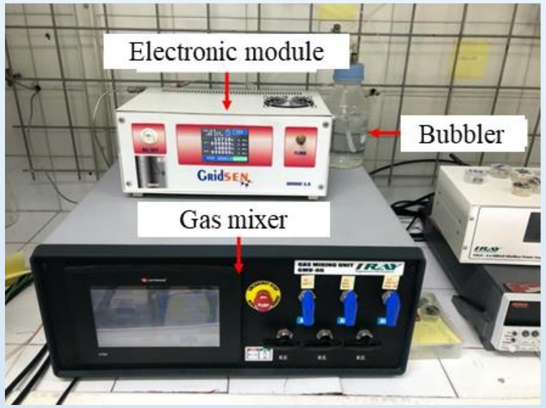


4. SENSOR CHARACTERIZATION



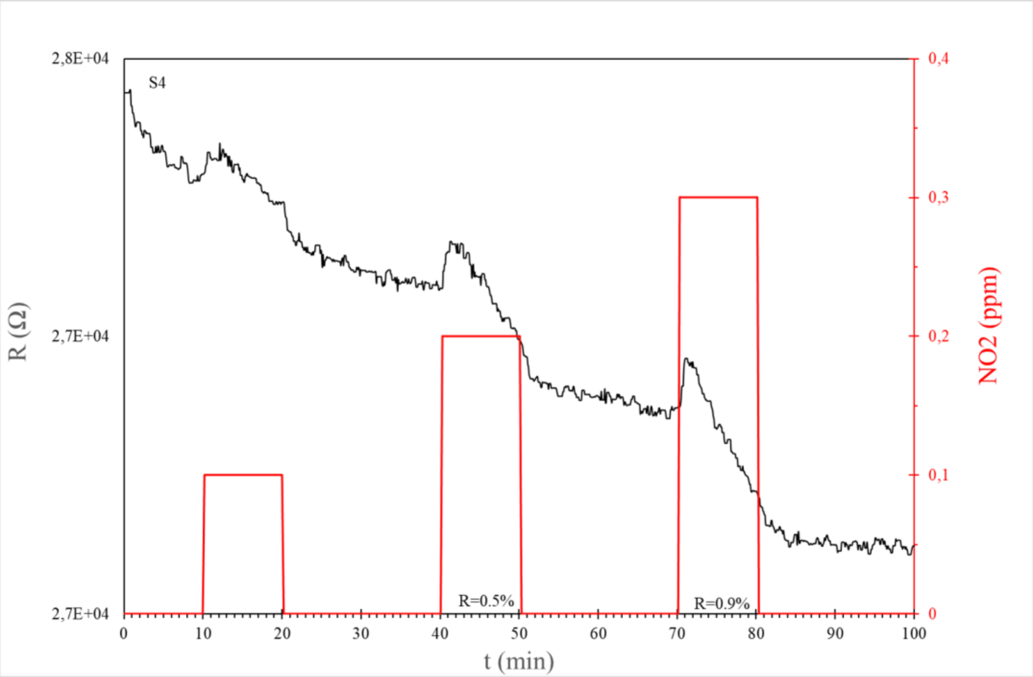






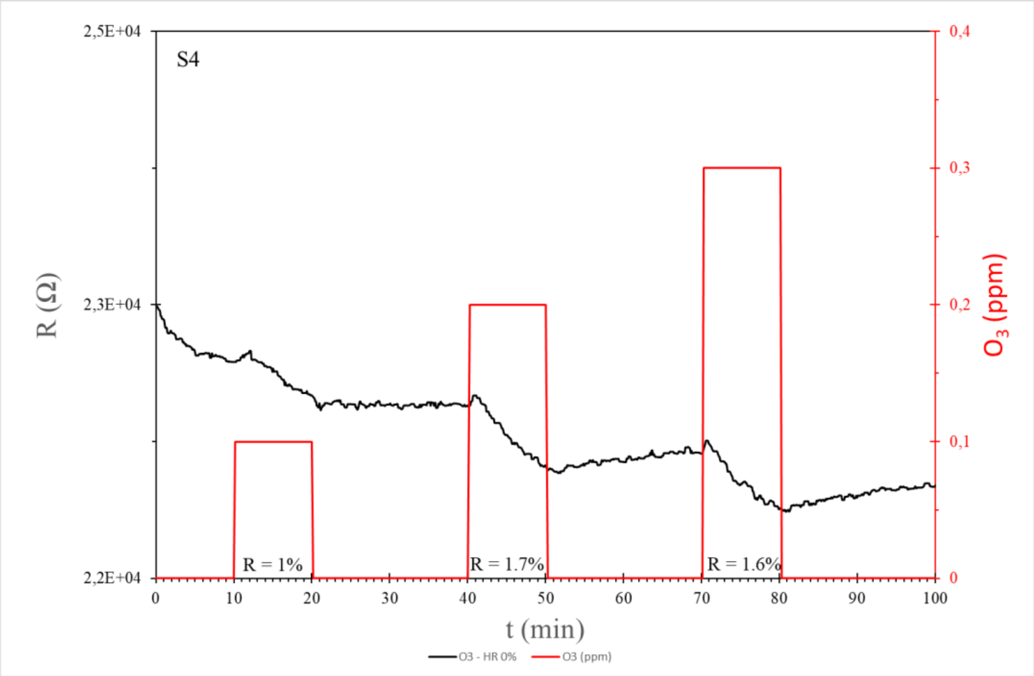
4.1. GAS DETECTION (NO_2, O_3, CO)

NO_2



HR < 5%

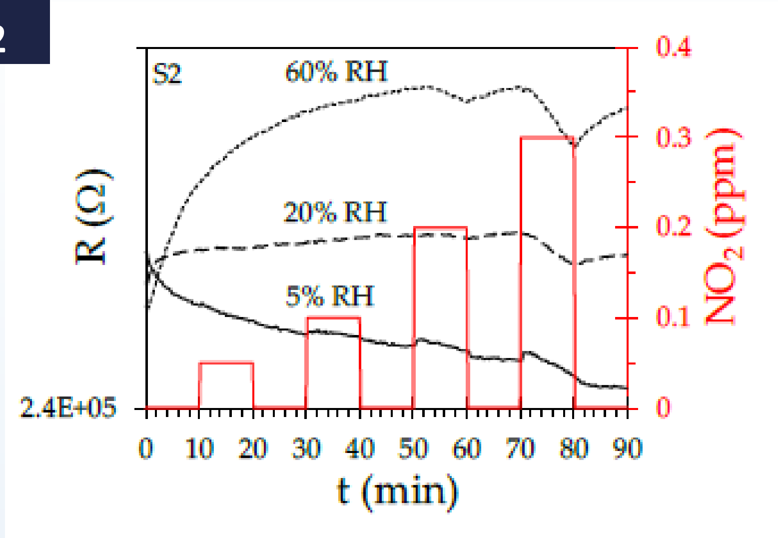
O_3

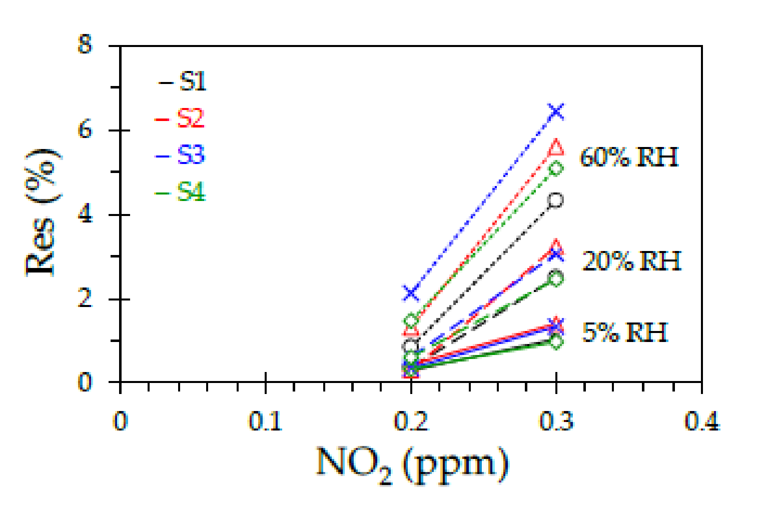


- **P-type semiconductor**
- **Long recovery times**
- **Sensitivity O_3 > NO_2**
- **No detection of CO (<5ppm)**

4.2. HUMIDITY

NO_2



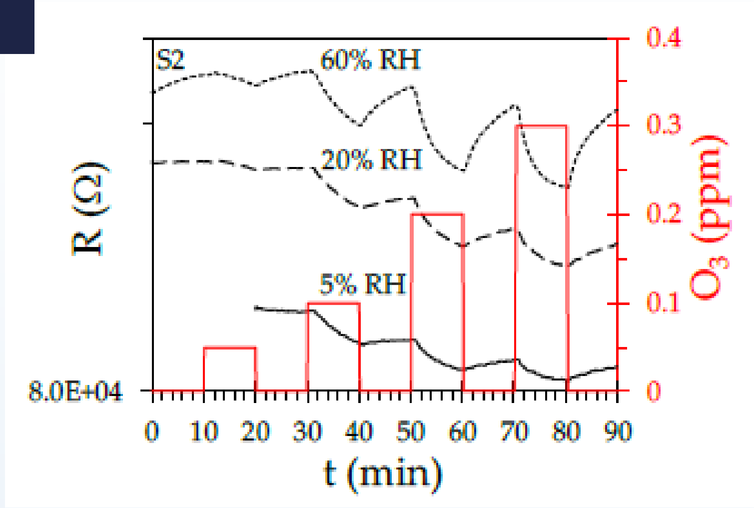


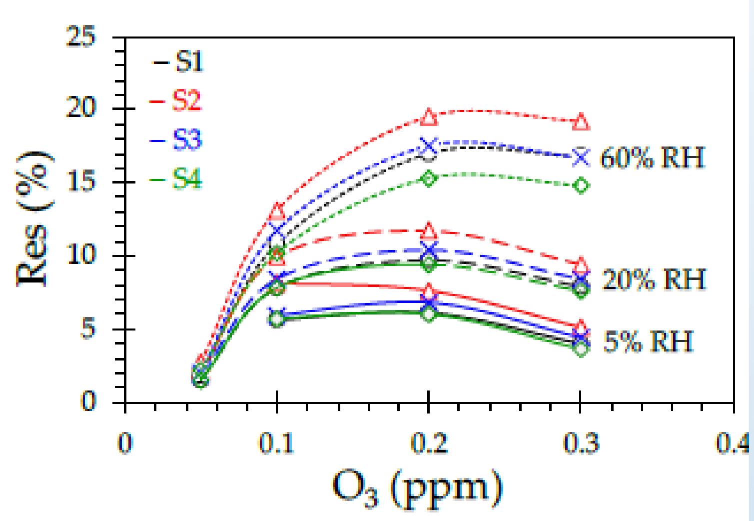
↑ Resistance

↑ Response

↓ Recovery time

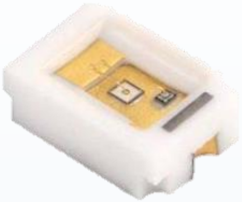
O_3



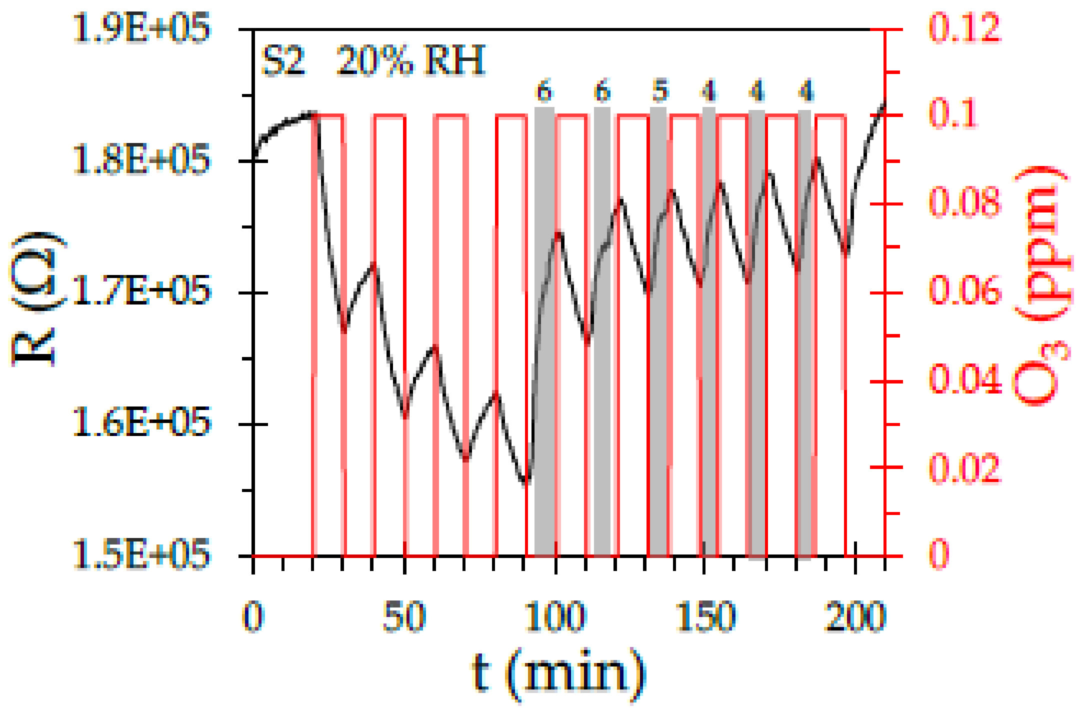


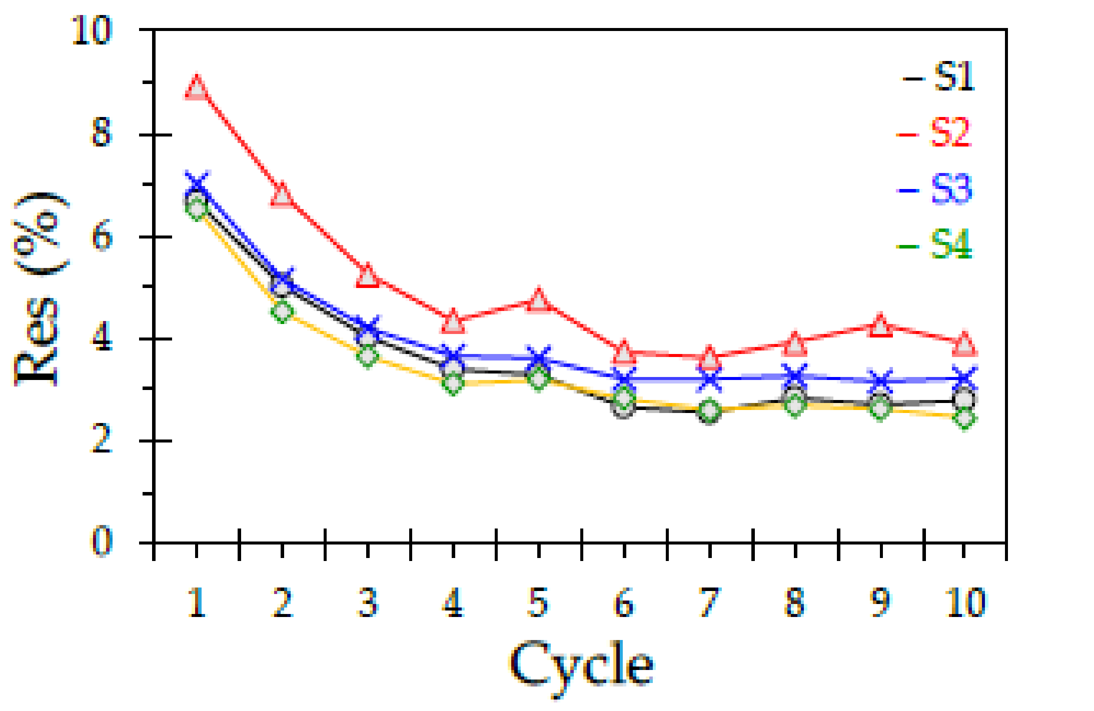
UV-LED

- $\lambda_{peak} = 356$ nm



UV irradiation → Active gas desorption





5. CONCLUSIONS (I)

Sensors based on electrospray printing of **rGO** layers have been characterised for low level detection of **NO_2, O_3 (< 300 ppb) and CO (< 5 ppm)**:

- Detection limits (**LOD**) for **O_3** and **NO_2** are **not suficient** for air quality monitoring
- **Not CO sensitive** up to 5 ppm levels
- Sensors based on rGO **have very long recovery time** but it **decreases** with **increasing** air humidity
- **UV** irradiation **speeds-up gas desorption** at **room temperature, reducing recovery time**

5. CONCLUSIONS (II)

Effects of electrospray parameters

- **Surface area** of rGO deposit **increases** with increasing **needle-substrate distance**
- **Homogeneous deposits** are obtained in a **stable cone-jet regime** and they are **reproducible**
- **Voltage** and **flowrate** determine the **spatial distribution** of rGO over the substrate
- **Deposition pattern** is very **sensitive to the applied voltage**. Small desviations from the voltage at stable cone-jet mode lead to drastic changes in the rGO spatial distribution

5. FUTURE WORK

- **Surfactants** or **dispersants** to optimize the long-term **dispersion of rGO**
- Effect of **rGO type** (C/O) on the sensor's detection sensitivity to air pollutants (NO_2, O_3, CO)
- **Doping rGO** for CO detection
- **Effect of UV light source parameters** (wavelength and intesity) on:
  - P/N-type performance of rGO
  - Sensitivity of rGO
  - Recovery time

Thank you

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