



Nanocarbon-based hybrid materials for chemoresistive sensing

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The slide features decorative elements consisting of several circles of varying sizes and colors (orange, green, yellow) scattered in the top-left and bottom-right corners. The main title 'Outline' is positioned in the upper left area.

Outline

- Introduction
- Chemoresistive sensors – background info
- "Nano-carbon" hybrid materials
 - What we mean by "nano-carbon";
 - Material's characterization results;
 - Functional results
 - RH sensing;
 - Ethanol Sensing
- Conclusions and on-going work

ACKNOWLEDGMENTS

Chemoresistive sensors

- The term **chemiresistor** was coined in **1985** by **Wohltjen** and **co-workers** after **investigating copper phthalocyanine** and its **resistive behaviour** when **exposed to ammonia vapour** (Wohltjen et al., A vapor-sensitive chemiresistor fabricated with planar microelectrodes and a Langmuir-Blodgett organic semiconductor film, IEEE Trans. Electron. Devices, 32 (1985), pp. 1170-1174, [10.1109/T-ED.1985.22095](https://doi.org/10.1109/T-ED.1985.22095))
- Chemiresistors act as resistive chemical sensors relying on the chemical interaction between the analyte and the sensing material. This interaction between the sensing material and the analyte can be based on covalent bonding, hydrogen bonding, or molecular recognition;
- Among chemiresistive materials, metal-oxide semiconductors, conductive polymers, metallic nanoparticles and carbon-based nanomaterials like graphene and carbon nanotubes can be cited as the most typical ones

Carbon-based nanomaterials for sensors

– our experience (I)

Carbon nanohorns (oxidized and pristine) and carbon nano-onions

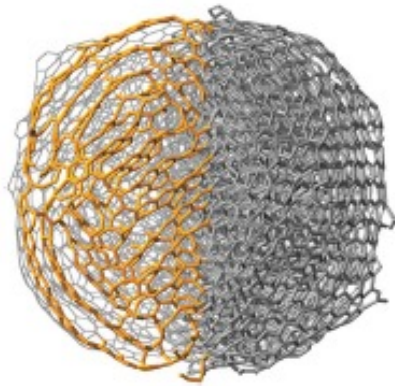
- Single-walled carbon nanohorns (SWCNHs), consisting of horn-shaped sheath aggregate of 38 graphene sheets were first reported by Iijima in 1998;
- These carbon nanostructures exhibit outstanding properties, such as high conductivity, high dispersibility, large specific surface area, versatile synthesis process (no metal catalyst is involved in their synthesis), availability of high-purity samples, etc.
- SWCNHs have been widely investigated for different applications, such as catalyst support or catalyst in the design of fuel cells, gas storage media, drug carrier for controlled release, etc.



“Therapeutic applications of low-toxicity spherical nanocarbon materials”
Jing Wang et al, NPG Asia Materials (2014) 6, e84;
doi:10.1038/am.2013.79

Carbon-based nanomaterials for sensors

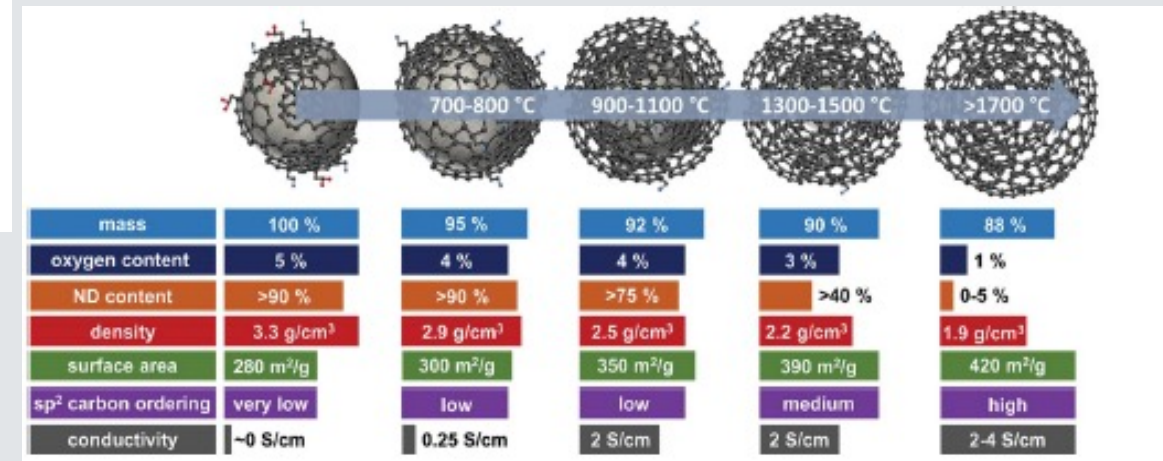
– our experience (II)



Carbon onion features:

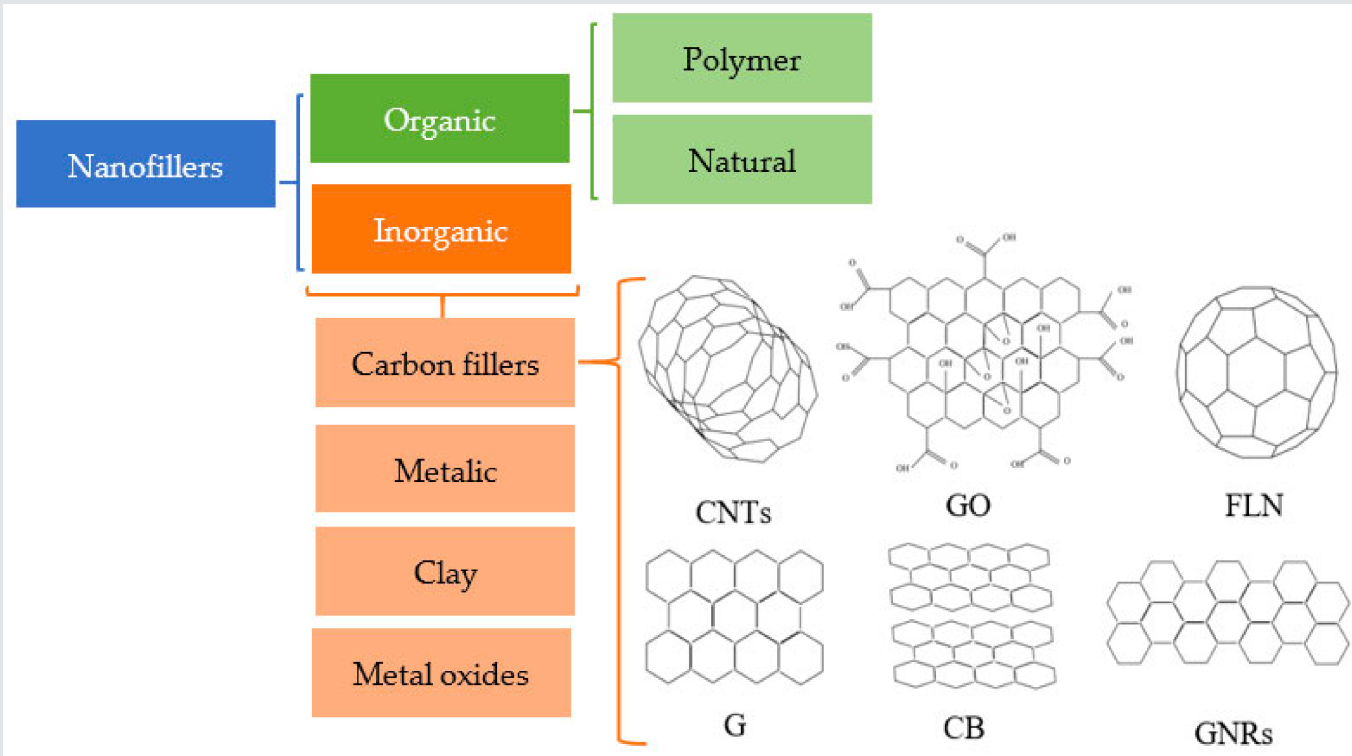
- Multiple shells of sp^2 -hybridized carbon
- Varying degree of carbon ordering within the shell
- Shape varying from spherical to polyhedral
- Typical sizes varying between 5-10 nm (up to 100 nm possible)
- Low amount of heteroatoms
- Possible presence of non- sp^2 -hybridized carbon
- Sometimes hollow core

Marco Zeiger, Nicolas Jackel, Vadym N. Mochalin and Volker Presser, Review: carbon onions for electrochemical energy storage, J. Mater. Chem. A, 2016, 4, 3172, [https://DOI: 10.1039/c5ta08295a](https://doi.org/10.1039/c5ta08295a)



Carbon onions, also called onion-like carbon or carbon nano-onions, are nanoscopic carbon particles, with a nearly spherical shape made of multiple enclosed fullerene-like carbon shells.

Carbon-based nanomaterials for sensors – our experience (III)



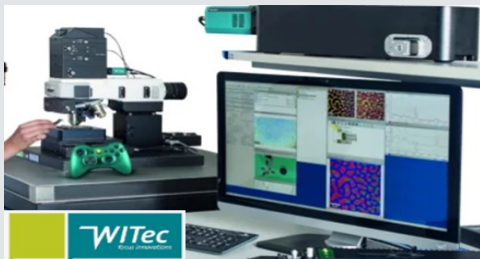
“Carbon is capable of forming several allotropes comprising of sp^2 - and sp^3 -hybridized carbon atoms. Among them **only sp^2 -carbon allotropes, such as Graphene (G) and Graphene-derived nanofillers (e.g., Graphene oxide (GO), reduced Graphene oxide (rGO)) or Graphene nanoribbons (GNRs), carbon nanotubes (CNTs), fullerenes (FLNs), and carbon black (CB), may contribute to the electrical conductivity due to the presence of an extended π -system.**

These nanofillers are normally not affected by a wide variety of solvents, acids, and bases at room temperature, and they are also a cost-effective material for composite manufacturing, which exhibits a diversity of electrical and mechanical characteristics.”

From “*Structure-Function Relationships of Nanocarbon/Polymer Composites for Chemiresistive Sensing: A Review*”, Maryam Ehsani, Parvaneh Rahimi, and Yvonne Joseph (*Sensors* 2021, 21, 3291, <https://doi.org/10.3390/s21093291>)

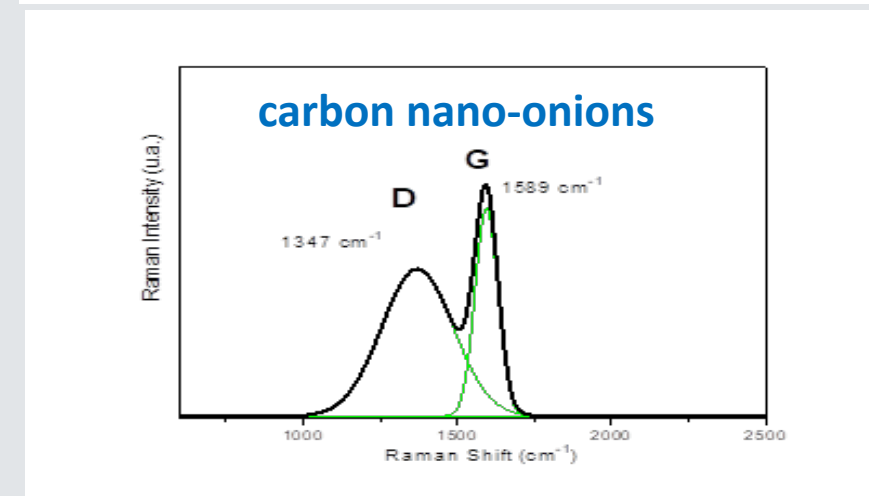
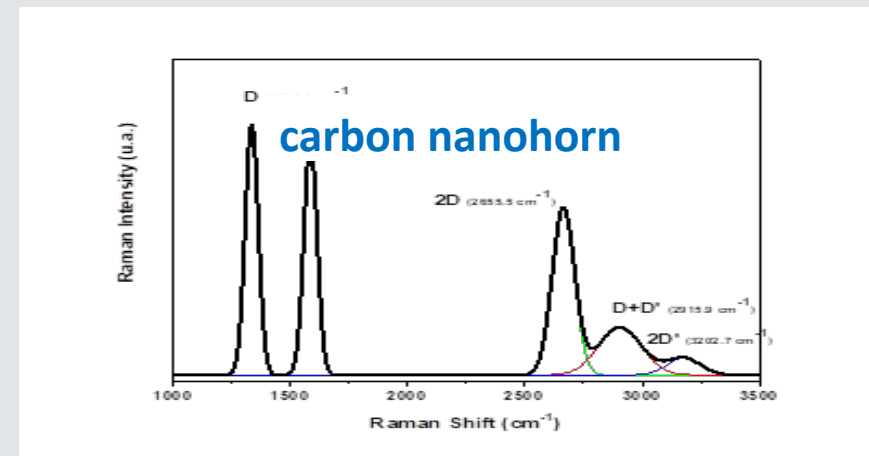
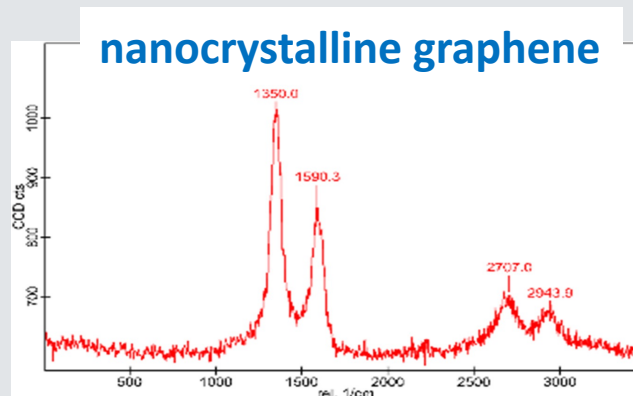
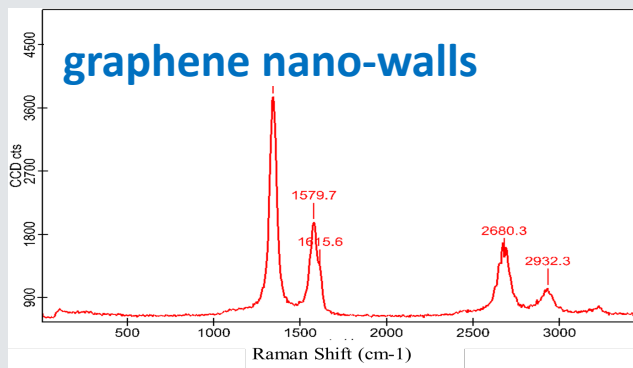
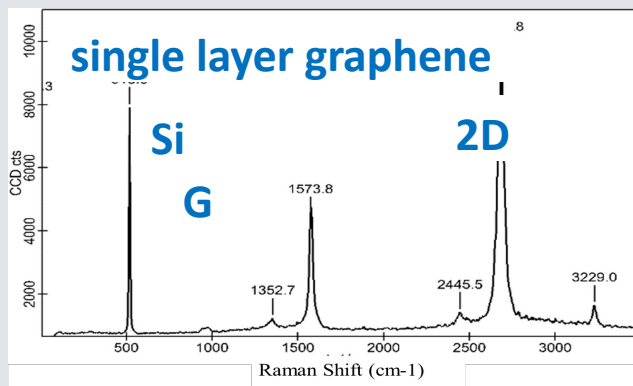
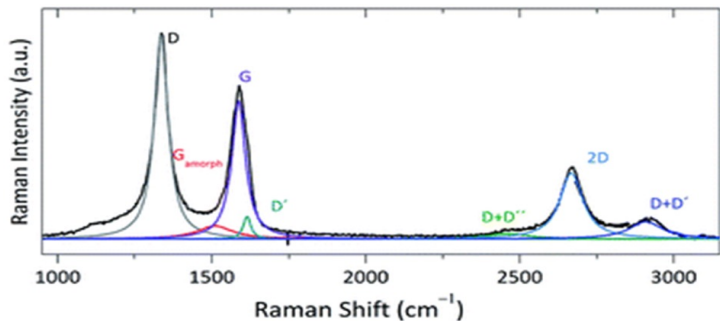
Nanocarbonic materials – characterization (I)

RAMAN SPECTROSCOPY



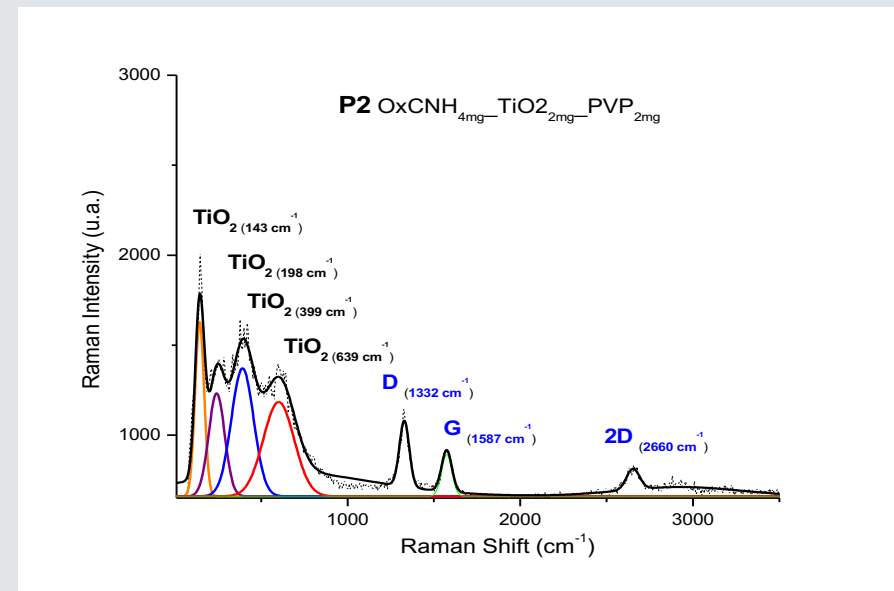
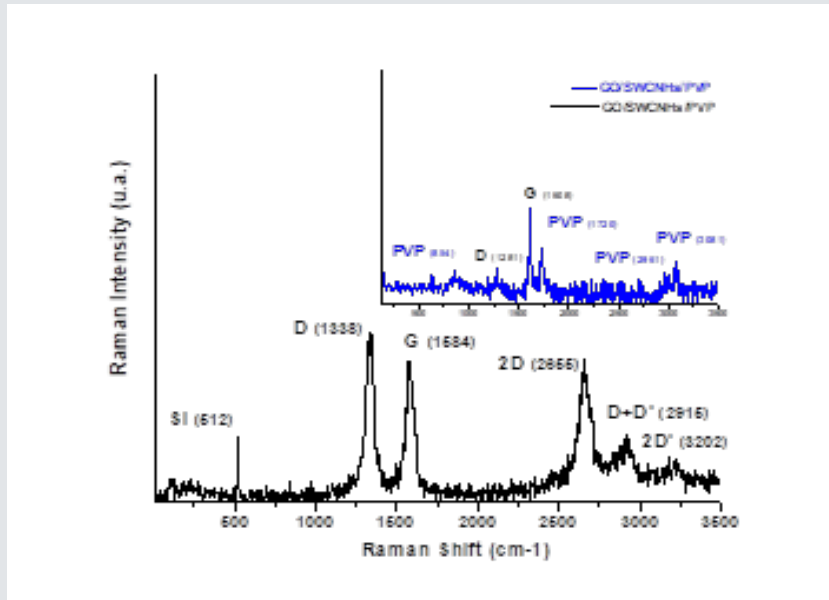
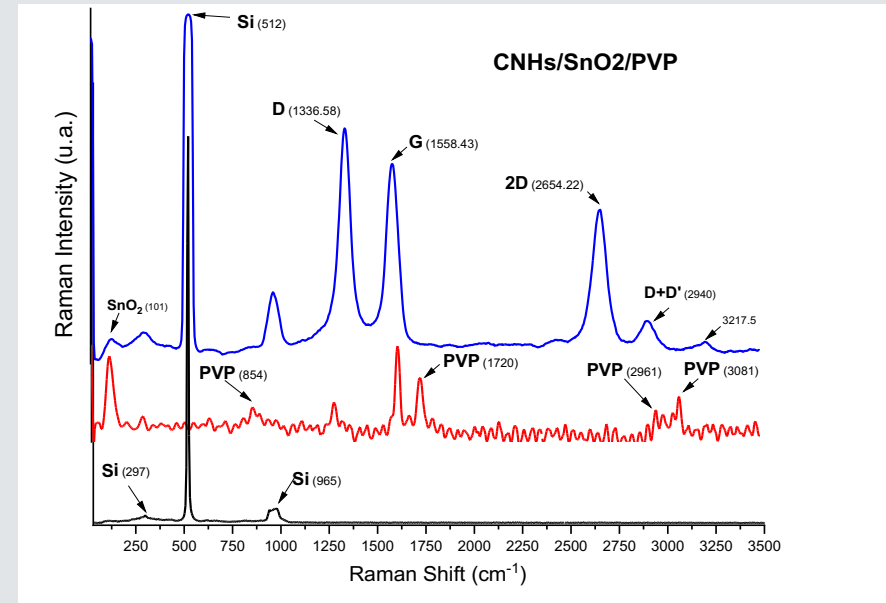
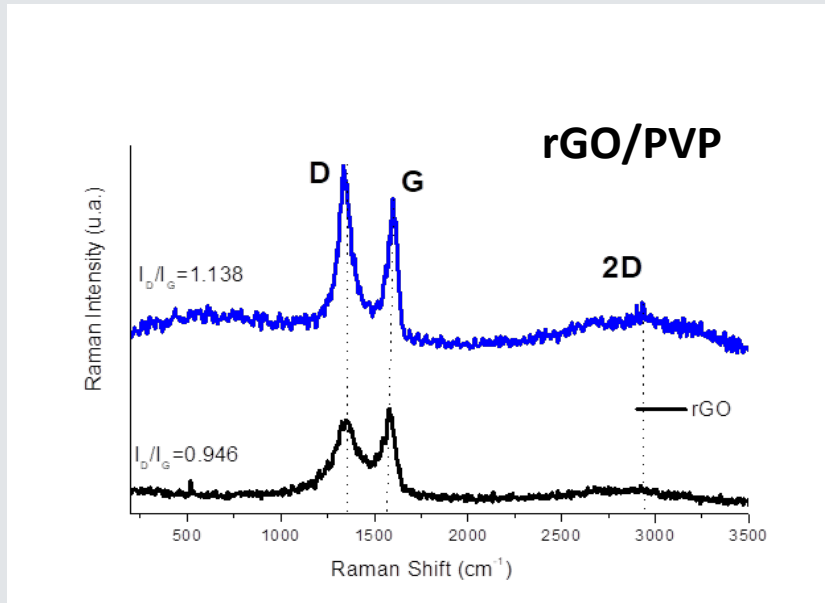
The Raman spectra were recorded with the same system (Witec Alpha 300S/2008 GmbH Germany) using an Nd-YAG laser with 532 nm green excitation.

carbon materials

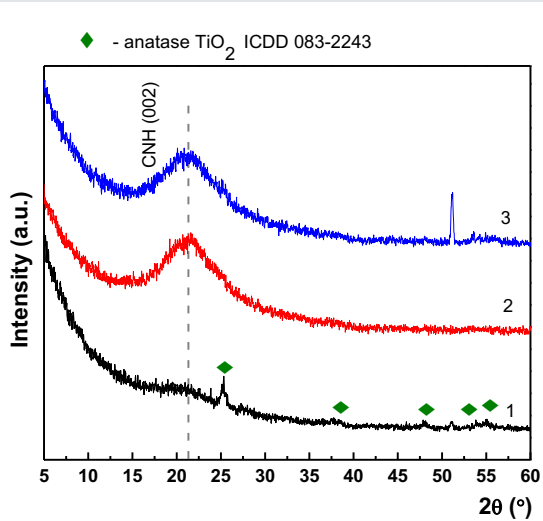


Materials	I _D /I _G	I _{2D} /I _G
SLG	0.04	
MLG	0.84	0.12
GNW	1.97	0.75
NCG	1.18	0.88
CNHs	1.01	0.99
CNOs	0.64	0.17

Nanocarbonic materials – characterization (II)



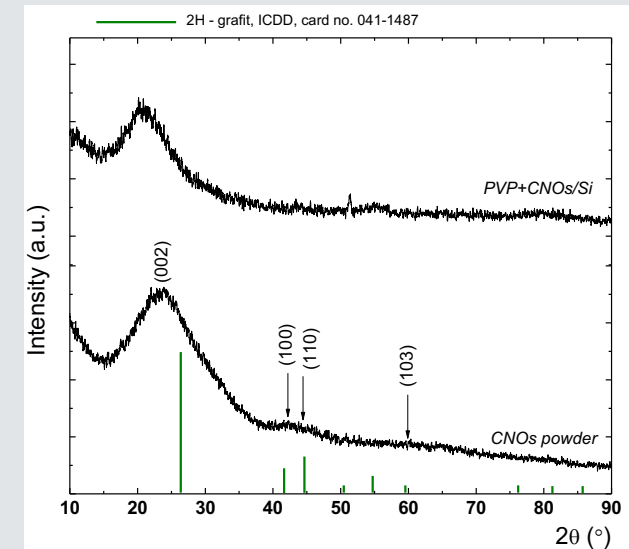
Nanocarbonic materials – characterization (II)



- X-ray diffraction pattern for solid-state films of TiO₂/CNHox/PVP nanocomposite with weight ratios (w/w/w):
- (1) 1/1/1 – black line, (2) 1/2/1 – red line, (3) 1/3/1 – blue line
 - a broad feature at 21.08° becomes more intense at greater C.H.N.s concentration (figure 8). This can be attributed to (002) reflection of CNHox's.
 - the sample with the lowest concentration of CNHox, other features are visible at 25.25°, 37.78°, 48.01°, 54.00° and 55.13°. One can assign unambiguously these diffraction features to (101), (004), (200), (105) and (211) reflections of wurtzite anatase-TiO₂ with unit cell parameters: $a = b = 0.37$ nm; $c = 0.94$ nm. The narrow intense peak from 51.20° is given by the Si substrate.

In the case of the powder, one can observe the presence of a main diffraction maximum at 23.2°, accompanied by other secondary reflections at the angular positions $2\theta = 42.3^\circ$, 44.6° and 60.3° . The large width of the main maximum indicates the semi-crystalline nature of the carbon.

- the low intensity maxima at ~ 42 and 45° indicate the disordered structure ("disorder structure") of the graphene rings inside the "carbon nano onions".
- Furthermore, these experimental positions were compared with the reflections of hexagonal graphite (2H) - the green line - and two things can be observed: (1) the experimental diffraction maximum is positioned to the left of the (002) reflection of graphite and (2) the positions of the secondary reflections are at the same position as those of the graphite.
- Based on the Bragg relation, the investigated carbon has a distance between planes of 0.38 nm, greater compared to graphite (0.34 nm),
- In the case of the PVP/CNOs composite on a Si substrate, only a broad band between $\sim 15^\circ$ and $\sim 25^\circ$ was observed, attributed to the semi-crystalline nature of pure PVP



Relative humidity sensing (I)

Sensing material: ternary nanohybrid comprising CNHox/ZnO/PVP at 5/2/1 w/w/w ; CNHox (diameter of 2–5 nm, length of 40–50 nm); polyvinylpyrrolidone (PVP), mol wt. 40,000; ZnO nanopowder (averaged particle size lower than 100 nm, with purity higher than 99%);

Preparation:

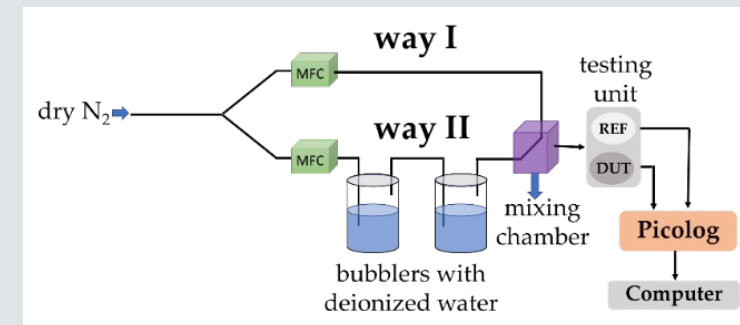
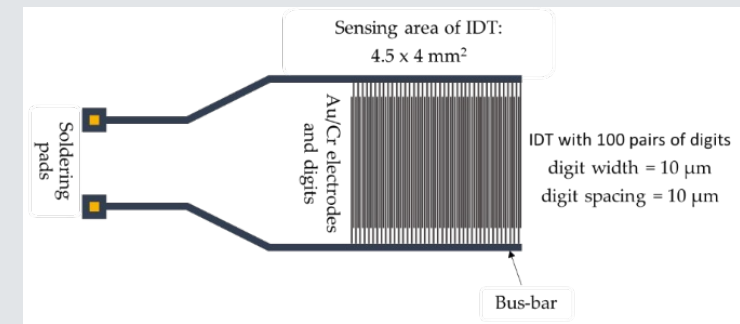
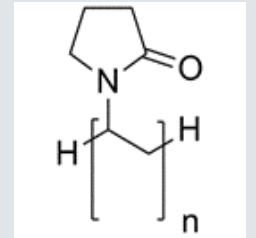
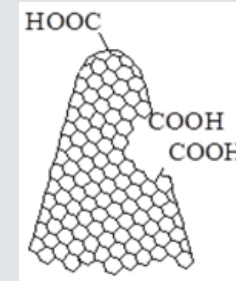
- The PVP solution is prepared by dissolving 0.1 g polymer in 20 mL ethanol under stirring in the ultrasonic bath for 10 min. at room temperature.
- 0.5 g of CNHox powder is added to the previously prepared solution while continued stirring is performed in the ultrasound bath for 6 h, RT.
- 0.2 g of ZnO powder is added to the previously prepared suspension, and continued stirring is performed in the ultrasound bath for 6 h, RT.

Deposition

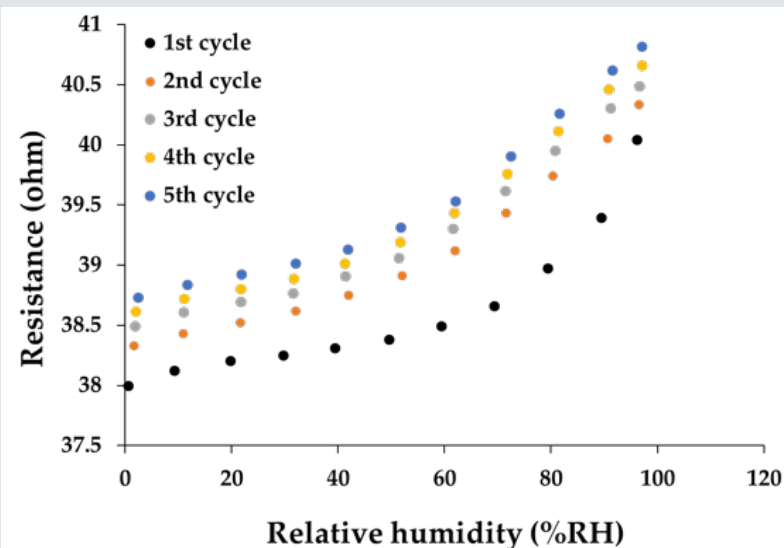
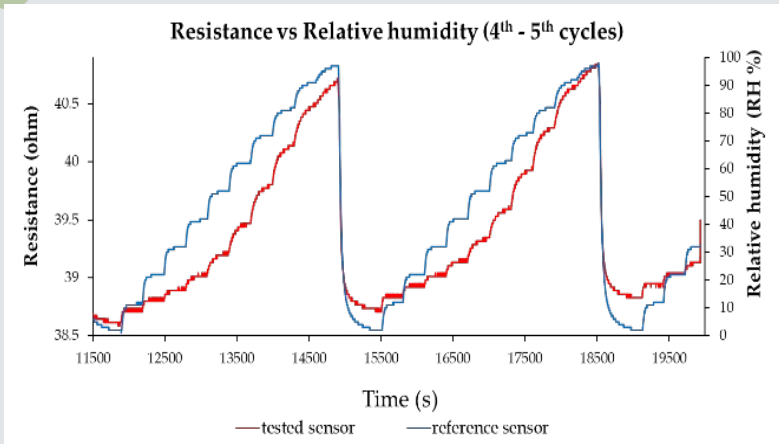
- drop-casting method on the IDT structure while its electrical contact areas were masked.
- a two-step, low-pressure (2 mbar) annealing scheme was performed as follows: 1. heating for 24 h / 80°C ; 2. heating for 12 h /100°C.

Measurement

- dry N₂ was injected through recipients placed in series containing DI water so that a controlled RH variation in the testing chamber, from 0 % to 100%, was achieved.
- The testing chamber includes a tandem of devices: the resistive sensing structure (abbreviated as DUT– device under test) and a capacitive RH commercial sensor (abbreviated as REF). The data was collected and analyzed using a PicoLog logger (PICO Technology, United Kingdom). All the tests were performed at constant RT.



Relative humidity sensing (II)



- CNHox is a hydrophilic p-type semiconductor with a high specific area. CNHox exhibit increased affinity for H₂O molecules compared to pristine CNs and a rapid variation of the electrical resistance in contact with a water molecule in the humidity range from 0% RH to 100% RH. When interacting with CNHox, water molecules increase the electron density in the film matrix by donating their electron pairs.
- PVP: a hydrophilic polymer with excellent binding properties, swells due to the interaction with water molecules. The contact points between the CNHox decrease gradually, with electrically percolating pathways being reduced. This phenomenon leads to the resistance increases, and the sensing layer becomes more resistive. It is anticipated that swelling has a pivotal role at high humidity levels (PVP absorbs up to 25% moisture at 75% RH). This fact can explain the better sensitivity of thin matrix film at RH > 60%.
- ZnO: the defects present in the semiconducting structure may promote water dissociation into H⁺ and OH⁻. The protons may tunnel from one water molecule to another, increasing the conduction of the sensing film. Obviously, this type of sensing has a minor contribution, taking into consideration the overall increasing resistance of the sensing layer. Most probable, the percolating paths of CNHox shunt these heterojunctions. However, ZnO may increase sensitivity towards RH in two different manners:
 1. through CNHox, leading to alterations in the pore distribution, which increase the specific surface area;
 2. through interaction with PVP, leading to an increase of free volume of hydrophilic polymers.

Ethanol sensing (I)

Sensing material: a quaternary nanohybrid comprising CNHox, GO, SnO₂ and PVP at 1/1/1/1 w/w/w/w mass ratio;

Preparation:

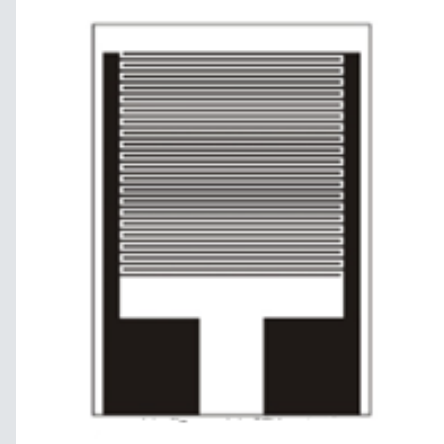
- preparing a PVP solution by dissolving 2 mg PVP in 5 mL ethanol for 10 mins in an ultrasonic bath working at 42 kHz (70 MW output power);
- a 2mL of GO dispersion in water (1 mg/mL) was added to the PVP solution and stirred in the ultrasonic bath for 1 h at room temperature (RT);
- 2 mg CNHOx powder was added to the resulting dispersion, and the mixture was stirred in an ultrasonic bath for 4 h at RT;
- 2 mg of nanometric SnO₂ powder was added in the final dispersion and stirred in an ultrasonic bath for 3 h at RT.

Deposition

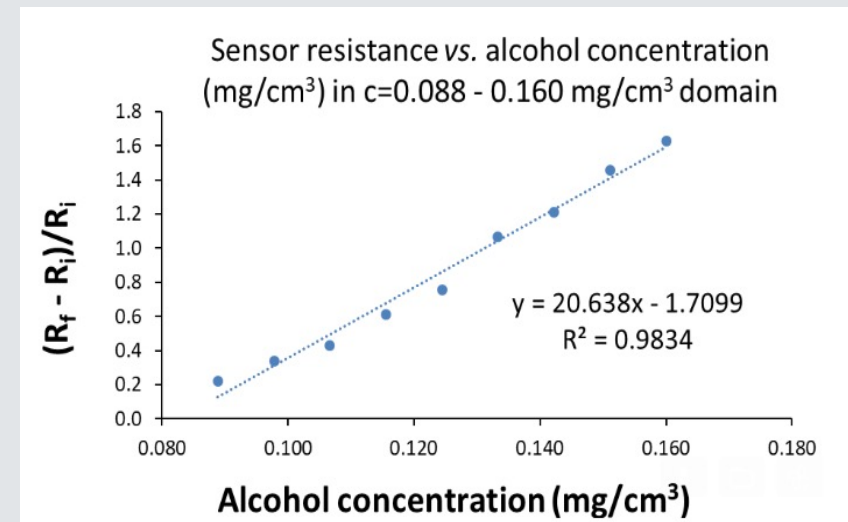
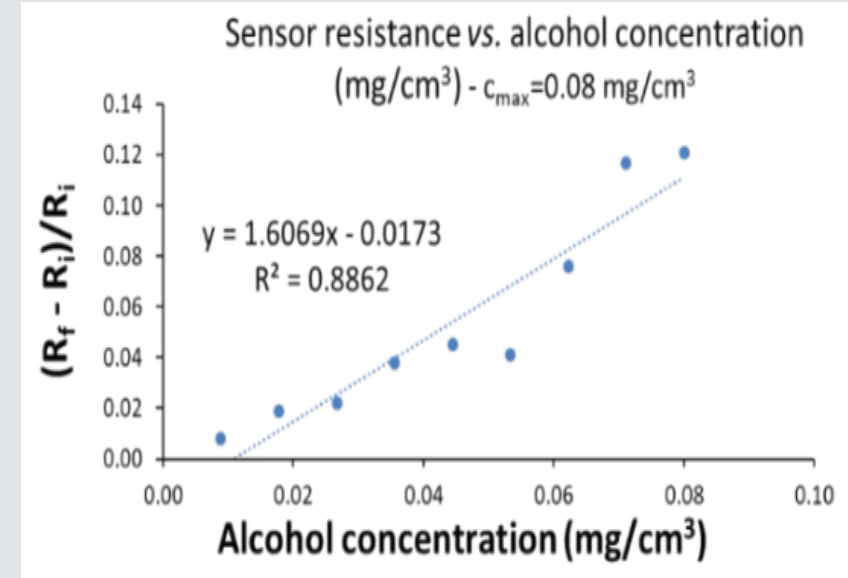
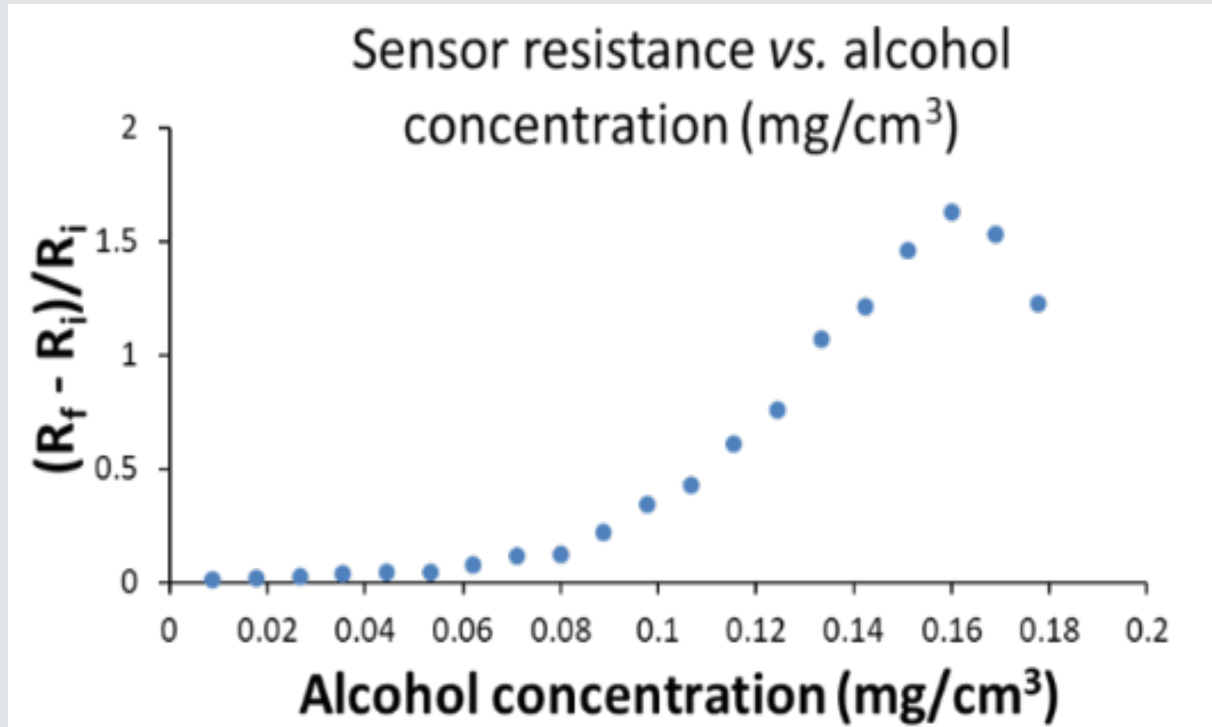
- via the drop-casting method, on the IDT polyimide flexible structure (Fig. 1) while its electrical contact areas were masked. All samples were dried at 363 K, for 4 h, before the tests.

Measurement

- To measure the variation of the resistance of the sensing structure a dried chamber with a volume of 0.27 L was used (wet air was removed from the room by nitrogen purging, resulting in relative humidity (RH) < 2%).
- Ethanol was injected in the chamber in a controlled manner in two ways: a) for small ethanol concentrations, with a micropipette of 0.1 - 2 microliters (by 5 volumes: 0.5 μL, 1 μL, 1.5 μL, 2 μL, 2.5 μL); b) for high ethanol concentrations, with a microsyringe (by drops weighing 2.4 mg).
- After sealing the chamber with a cover (in which the ethanol sensor was mounted), the complete evaporation of the alcohol was achieved with a magnetic stirrer (1,000 rpm, 4 minutes).



Ethanol sensing (II)



Hysteresis in RH sensing (I)

Sensing materials: conductive polymer Poly3,4-EthyleneDiOxyThiophene: Polystyrene Sulfonate (PEDOT: PSS) mixed with different binders: Polyvinylpyrrolidone (PVP), Polyethylene Glycol (PEG) and Ethyl Cellulose (EC)

Preparation

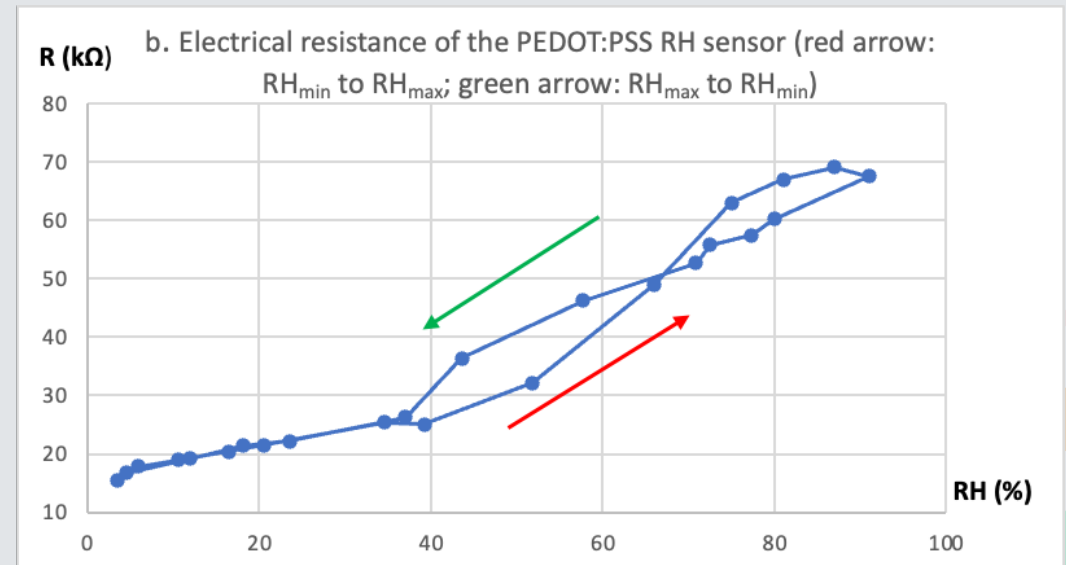
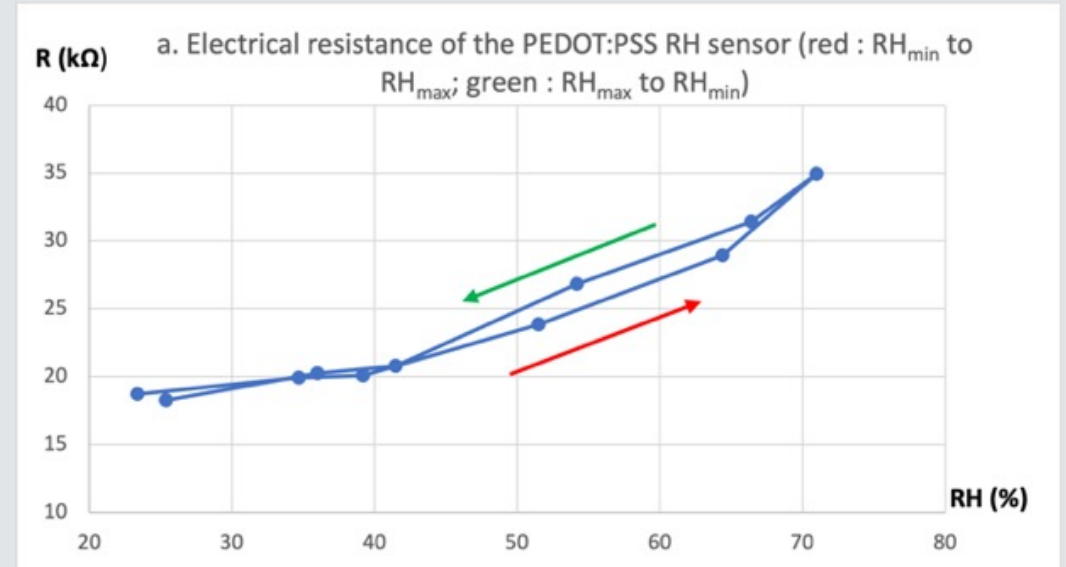
- PEDOT: PSS was 2% diluted in H₂O DI, dispersed in an ultrasonic bath for 15 minutes, diluted 1:1 in IPA again, and dispersed for 10 minutes in an ultrasonic bath, resulting the 1% dilution.

- In the case of a mixture with binders, PEDOT: PSS was diluted only 1.6 % in H₂O DI, binder (PVP or PEG from Sigma Aldrich) was diluted 0.4 % in IPA, then the two solutions were dispersed separately for 15 minutes in an ultrasonic bath. Both solutions are mixed in an ultrasonic bath for 10 minutes, resulting the 1% dilution.

- When using EC as a binder (0.2 % in IPA), the PEDOT: PSS was diluted at only 1.8 % in H₂O DI. The two solutions were separately dispersed in an ultrasonic bath for 15 mins. Finally, both solutions are mixed in an ultrasonic bath for 10 minutes, resulting the 1% dilution. The sensitive material was treated on a hot plate at 100 °C for one hour.

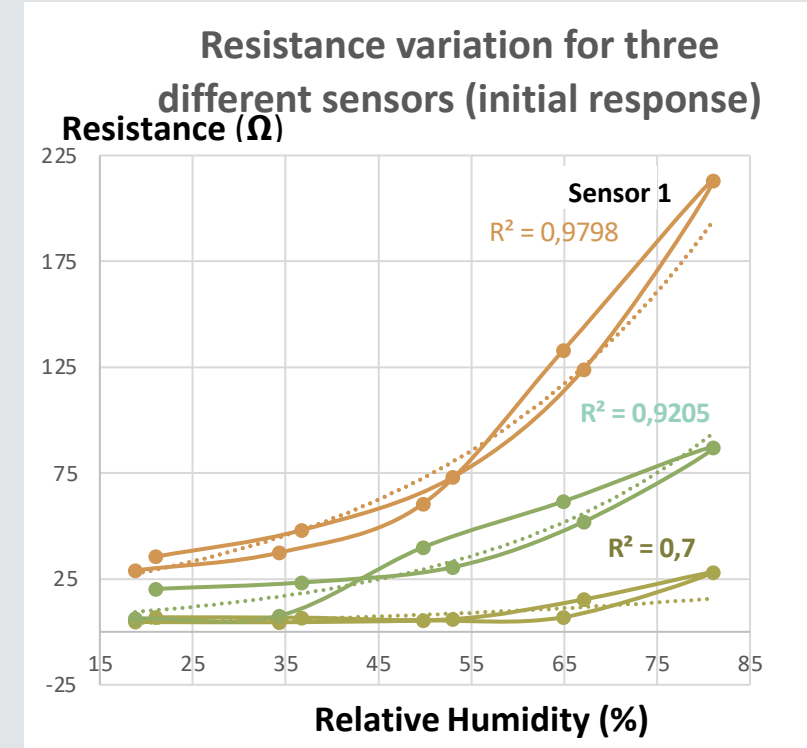
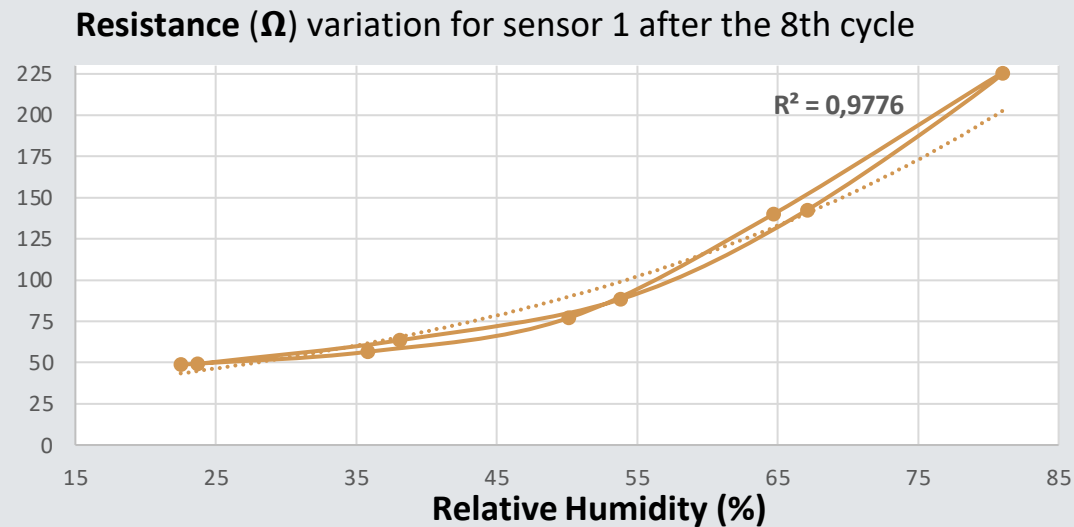
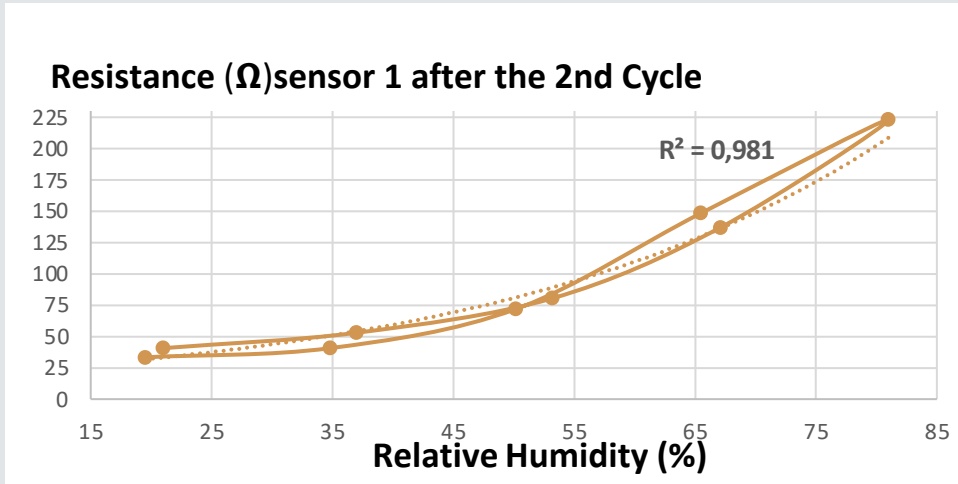
Deposition

- drop casting - 2 μ l of the solution prepared before on an IDT transducer on PI, having finger/space equal to 25 μ m.



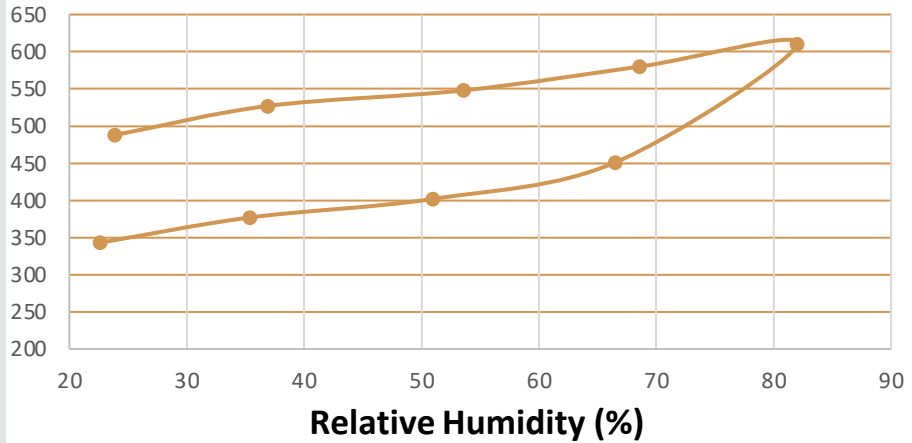
Hysteresis in RH sensing (II)

- Sensing materials: carbon nano – onions (CNO):PVP: IPA
- Drop casting on PI IDTs – 25 microns

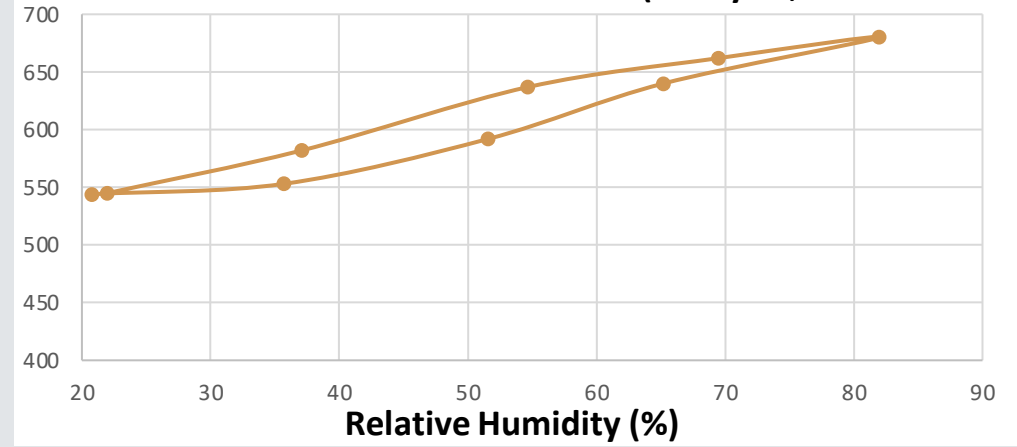


Hysteresis in RH sensing (III)

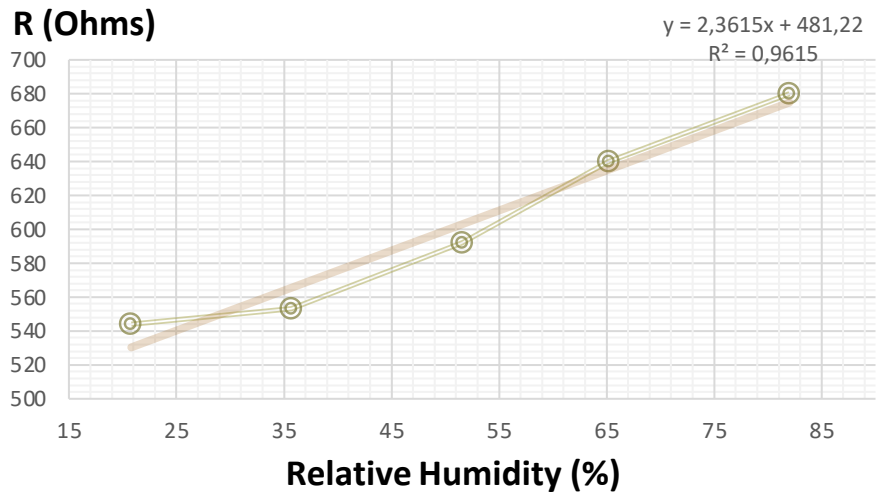
Resistance variation Sensor 6 (first cycle)



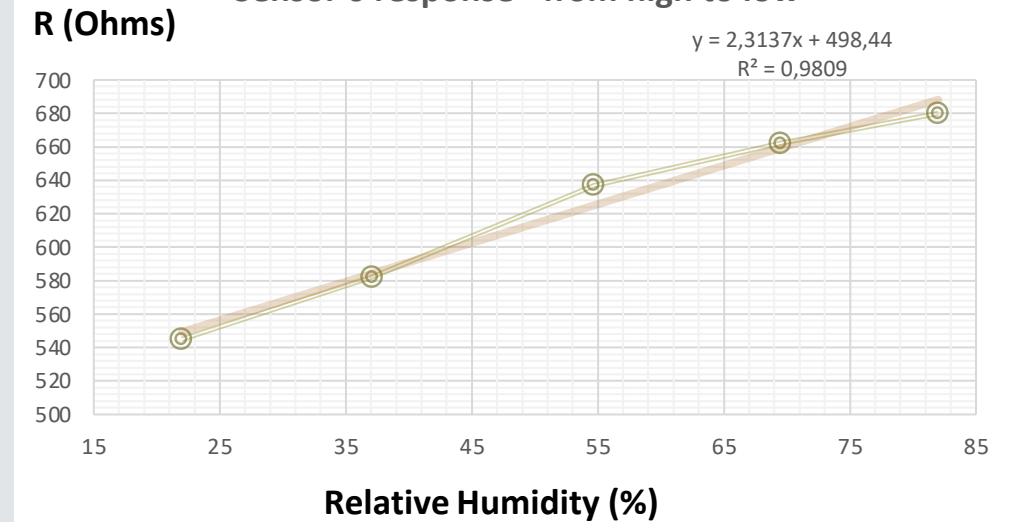
Resistance variation Sensor 6 (7th cycle)



Sensor 6 response - from low to high



Sensor 6 response - from high to low



- Excellent sensitivity (ΔR vs RH variation);
- Linearization after a small no of cycles;

Conclusions and on-going work

- Chemoresistive structures are relatively easy structures to manufacture, but as always, **“the devil is in the details”**;
- A range of substrates can be used for achieving the IDTs; we used lithographic techniques for achieving ours, but printing techniques are also feasible (under testing) for flexible substrates (including paper-like);
- The sensing structures – once produced – need to be further tested and “cycled”, as highlighted by the CNOs/PVP and PEDOT: PSS samples;
- Many other tests must be further carried out to identify the best compositions in terms of hysteresis, sensitivity, and lifetime.
- The group has XX papers and YY patent applications* and 2 EU-granted patents connected to the work on nanocarbon-based hybrid materials for sensing (2018-2023)
- Need to upgrade the experimental base by including a Raman microscope and XPS.

Acknowledgments

- Many thanks to our former colleague and friend – Dr Cornel Cobianu. Also, the support of Mr. Viorel Avramescu for performing some of the functional characterisation experiments is greatly acknowledged.
- The authors would like to acknowledge the financial support from the following programmes and projects:
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 - the UEFISCDI contract no 364PED/2020.
 - The UEFISCDI contract no 673PED/2022.