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and

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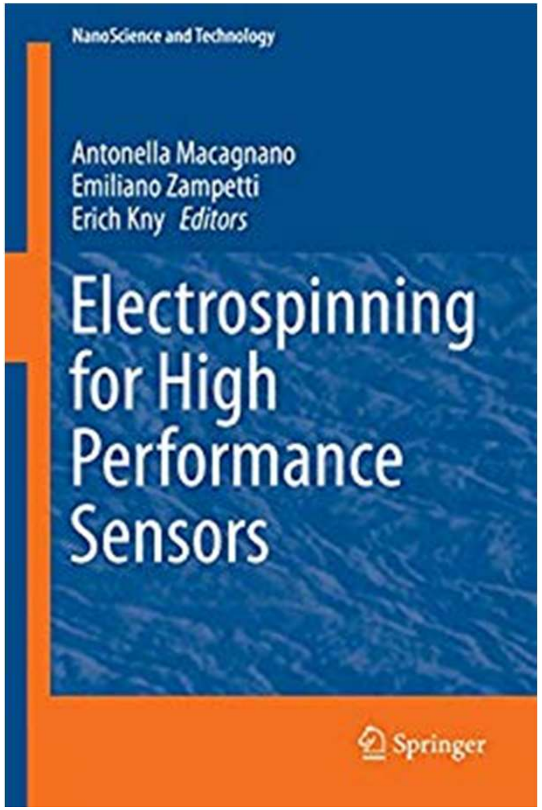
Heterogeneous nanofibrous polymer layers to get ultra-sensitive and tunable conductive sensors for indoor monitoring

Sviluppo di materiali nanocompositi per sensori di gas e composti volatili

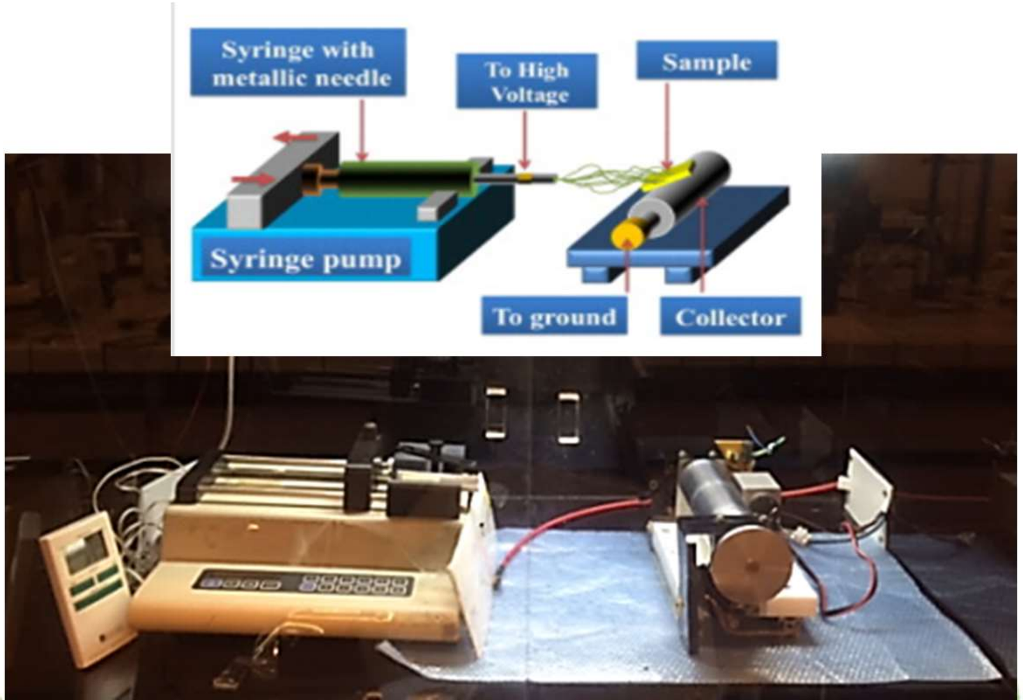
DESIGNING SENSORS FOR INDOOR AND OUTDOOR POLLUTANTS

of potential interest in various work ambients

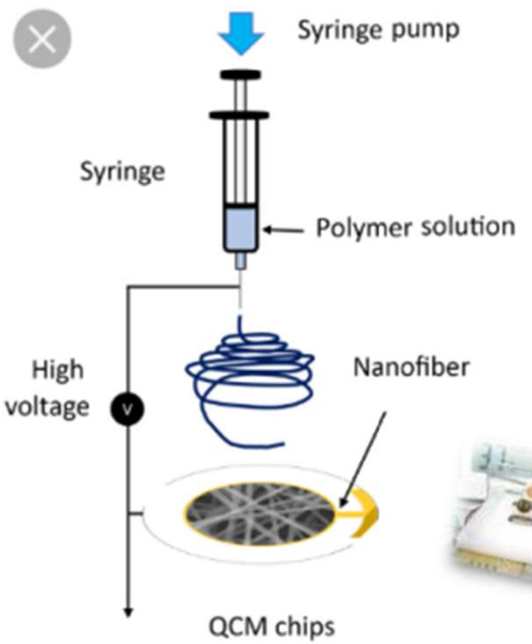
BIOINSPIRED SENSORS

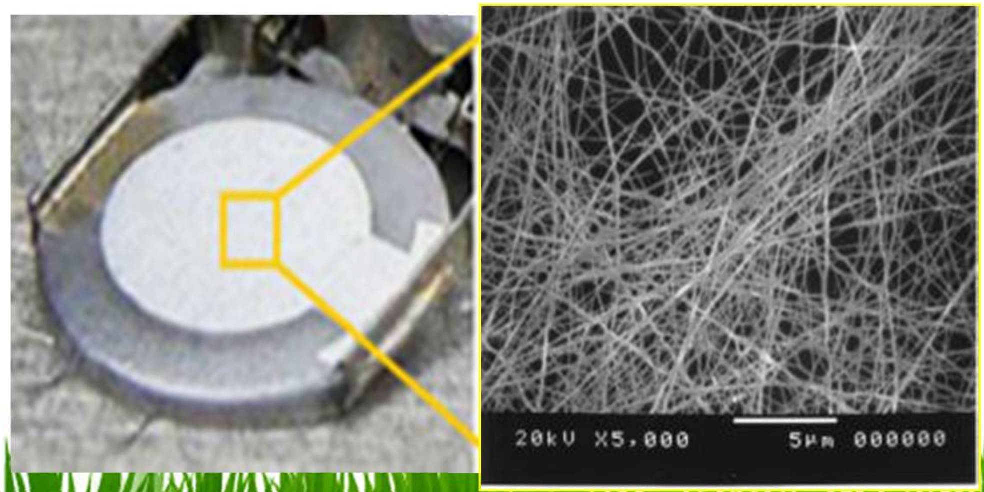


ELECTROSPINNING TECHNOLOGY
can generate bioinspired nanomaterials (structures like olfactory cilia) to be used in biomimicking electronic devices as nanofibrous sensors

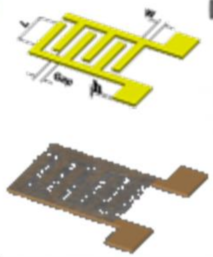


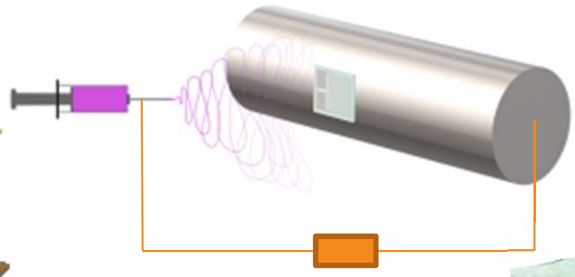
QCM: GRAVIMETRIC SENSORS

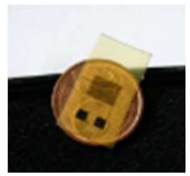


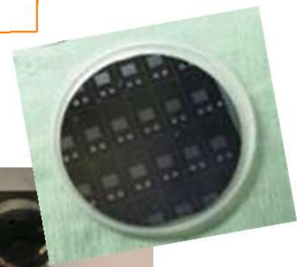


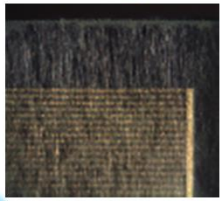
IDE: CONDUCTIVE SENSORS

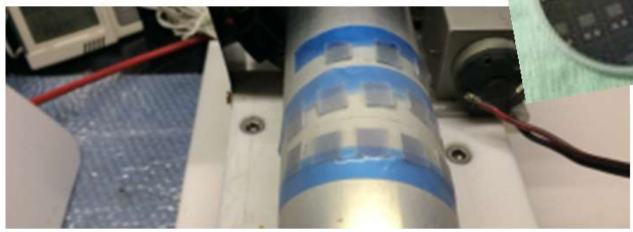


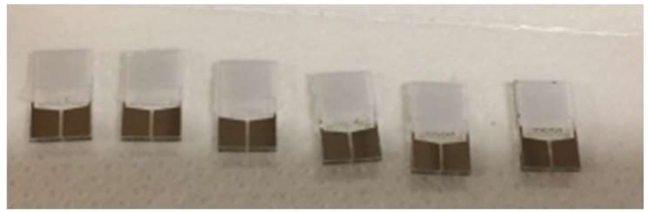






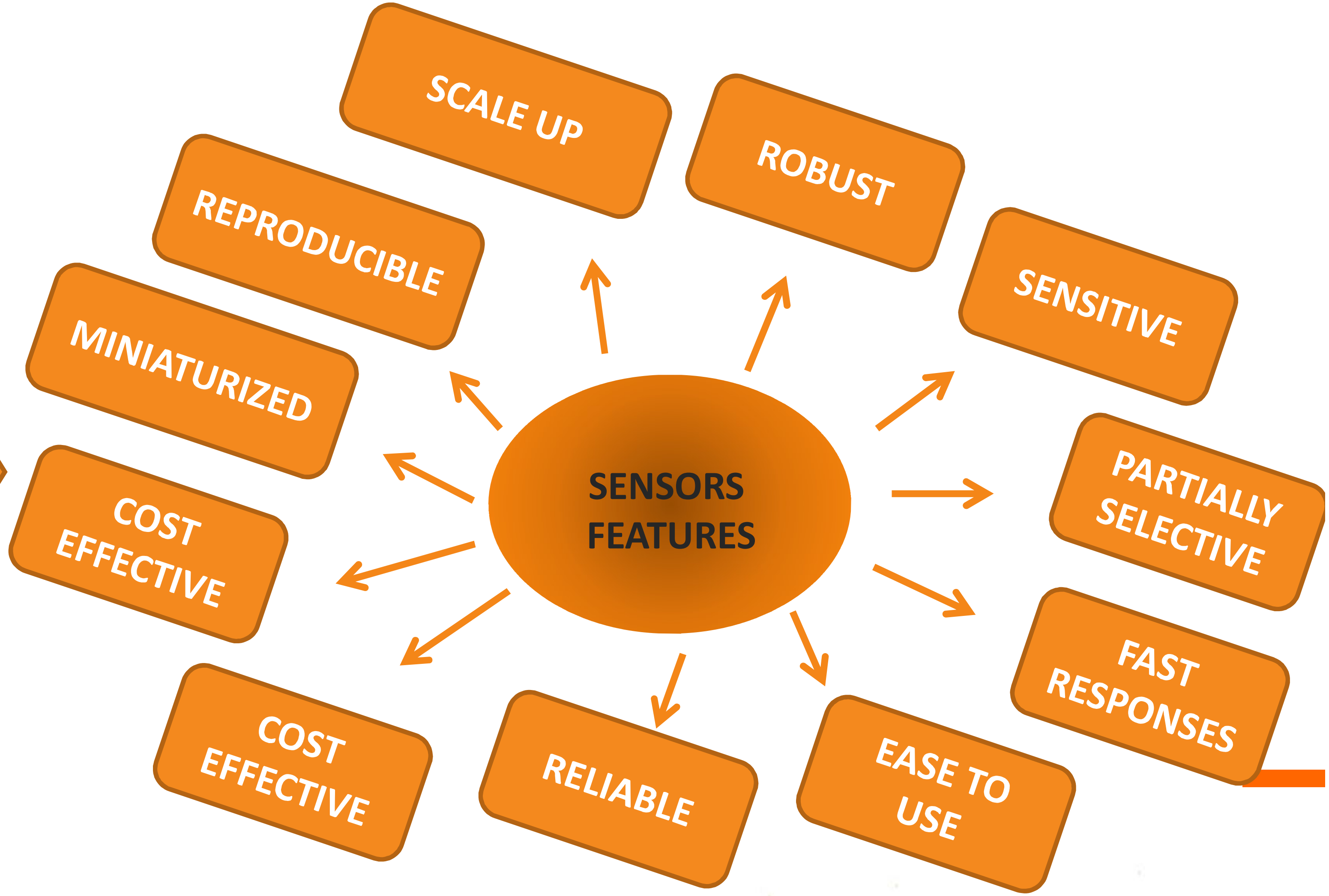






SENSORS EXPECTATIONS

NANOHYBRID MATERIALS
TERNARY AND QUATERNARY COMBINATION



AIM OF THE WORK

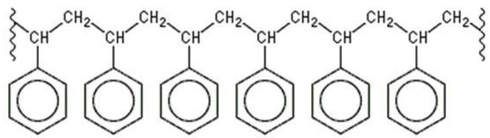
COMBINATION OF SUITABLE NANOCOMPOSITE MATERIALS THAT COULD BECOME "SMART" IN SENSING BY TUNING THE WORKING TEMPERATURE

A quaternary combination of two polymers (**PS, PHB or PP**), a mesoporous graphene nanopowder (**MGC or G**) and a free-base porphyirin (**H_2TPP or Porf**), where selectivity can be thermally driven also by very low-cost miniaturized ceramic heaters

State of Art

WHY DO YOU USE POLYSTYRENE?

RECYCLING



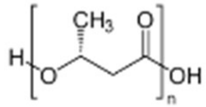
polystyrene

Polystyrene: wide variety of consumer products.
Polystyrene: **automotive, electronics, foodservice, insulation, packaging and more**.
It is a versatile and useful material, but due to the environmental problem caused by **waste** plastic foams, people are evaluating whether to use it or not.

Blending PS with biopolymers induces the biodegradability of the polymer fabrics
Schlemmer et al. 2009

WHY DO YOU USE PHB?

BIODEGRADATION

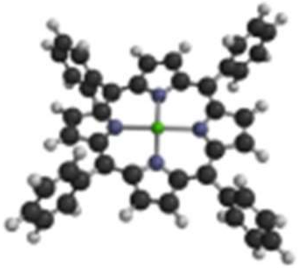


POLYHYDROXYBUTIRATE

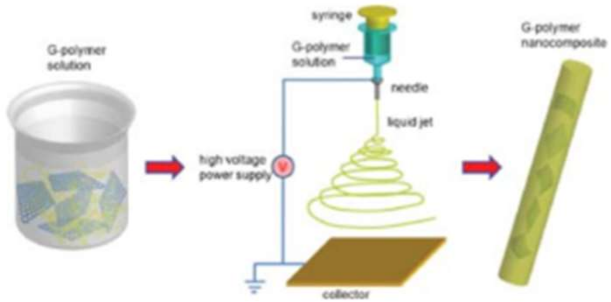
(PHB) is natural thermoplastic polyester **completely biodegradable**

Among the several applications of biodegradable sensors, the monitoring of environmental conditions after ecological disasters would result extremely suitable and environmentally friendly if small **sensors might be dispersed over a wide area without further contributing to pollution**.

The sensing agents: porphyrin and graphene



VOCs/GAS SELECTIVE MOLECULES



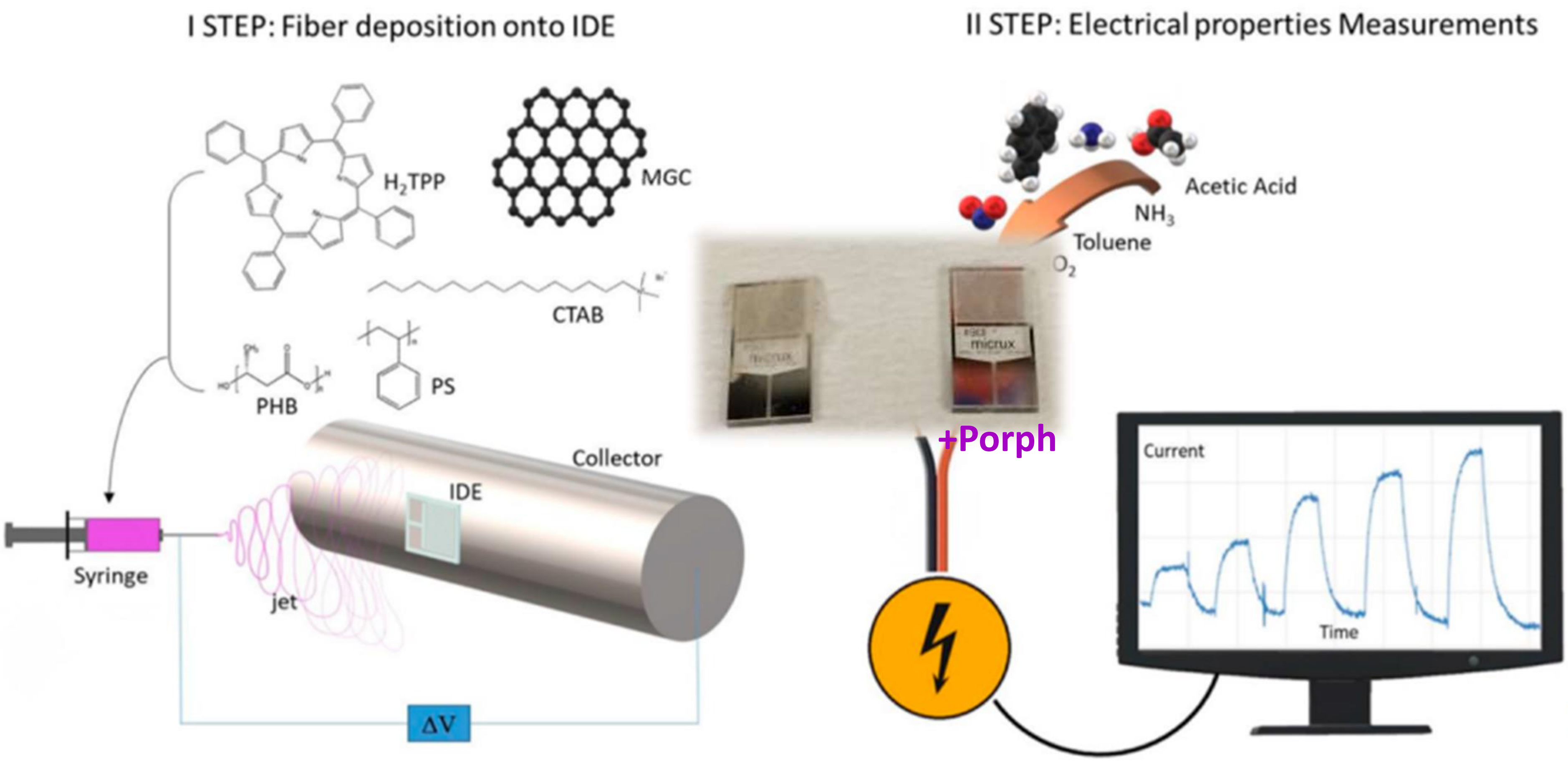
Courtesy by Bao et al. 2010, Adv Funct Mat 20(782–791)

- ✓ Porphyrins belong to an important family of biomolecules: they are used as **sensitive materials** for many different kinds of chemical sensors.
- ✓ The **sensitivity** of these molecules is usually correlated with their structure and in particular with the kind of metal ion, aromatic system, and peripheral substituents.
- ✓ In addition to the single molecule sensitivity, supramolecular assemblies can be endowed with additional properties that can **increase the sensitivity towards selected species**.

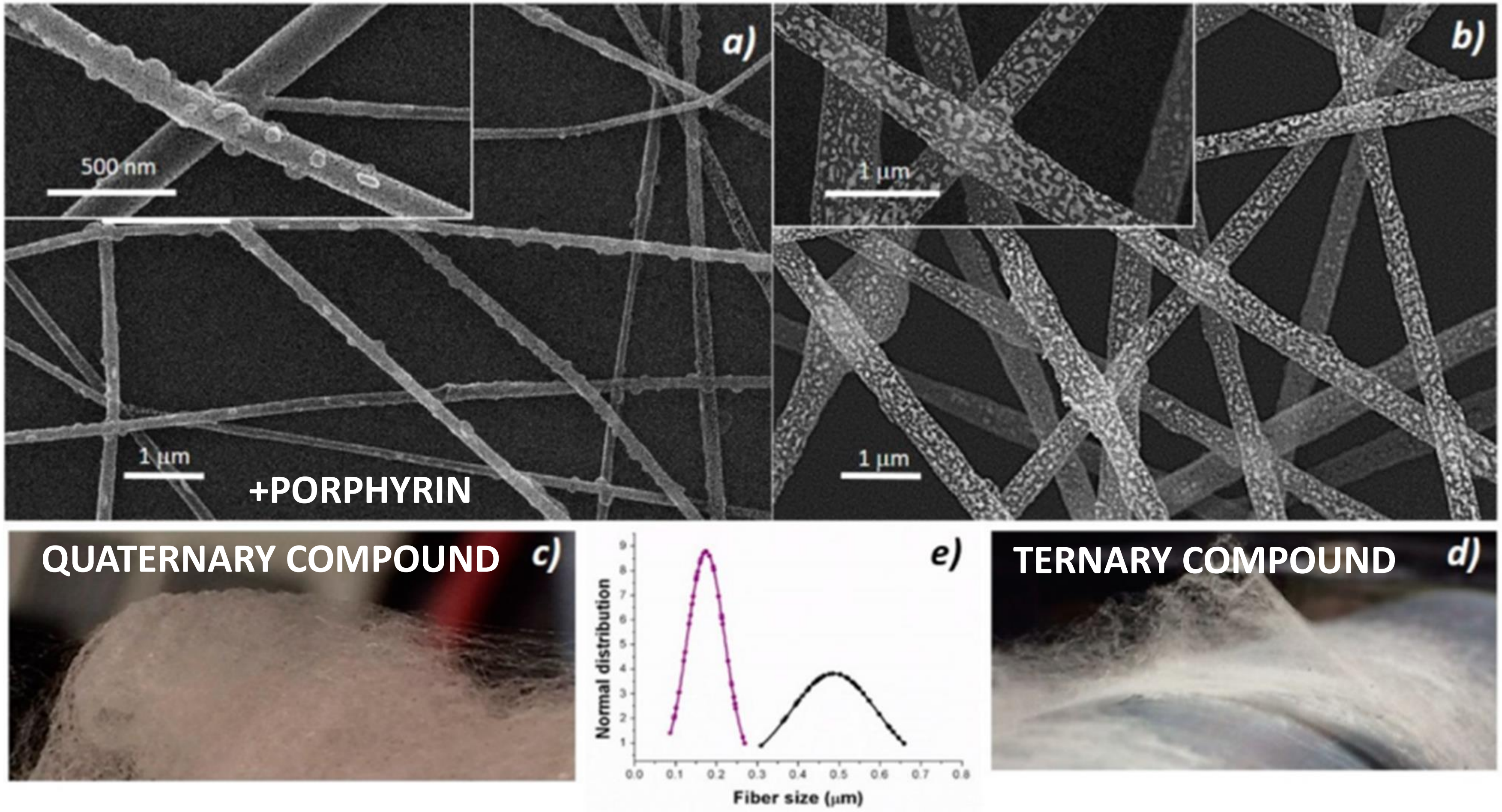
CONDUCTIVE PARTICLES

- ✓ **Graphene (G)**: one-atom-thick 2D nano-crystal of sp^2-hybridized aromatic carbon covalently packed into a continuous hexagonal lattice.
- ✓ G is theoretically a zero-bandgap semiconductor with **excellent r. t. electrical conductivity**, with a charge carrier mobility of about 10^4 cm^2 V^{-1} s^{-1}
- ✓ **Ultrasensitive to oxidizing gases**

SKETCH OF SENSOR FABRICATION



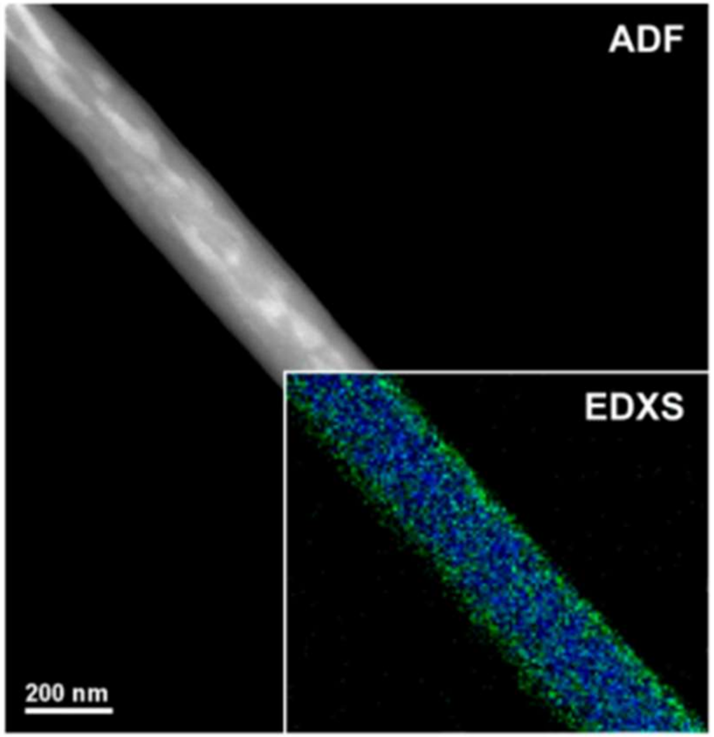
FIBERS CHARACTERIZATION



SEM micrographs of H_2TPP-PsB-MGC (**a**) and PsB-MGC (**b**) and their respective pictures placed under (**c**,**d**). Diameter distribution graph (**e**) of H_2TPP-PsB-MGC (purple) (**a**) and PsB-MGC fibers (black) (**b**).

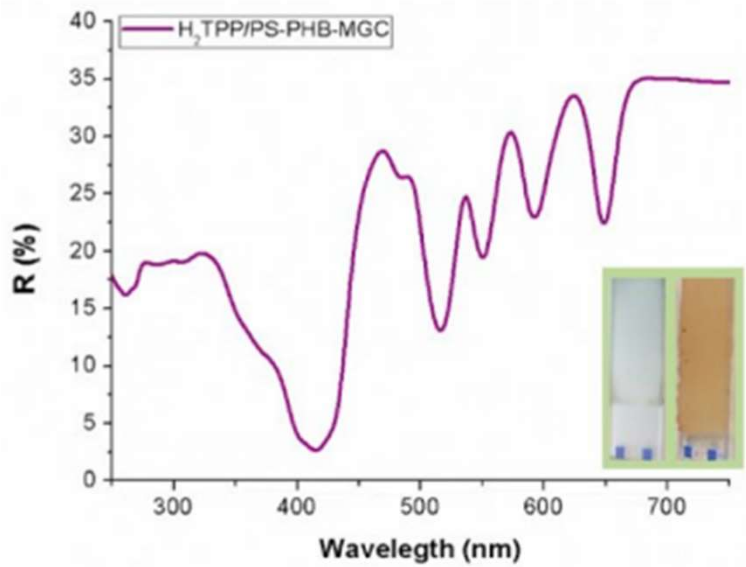
FIBERS CHARACTERIZATION

ADFM-STEM



Annular dark field mode-scanning - transmission electron microscopy image of a porphyrin doped fiber. The inset shows the corresponding energy dispersive X-ray spectroscopy (EDXR) chemical map from carbon (blue) and oxygen (green).

DR-UV-VIS



Diffuse reflectance ultraviolet-visible (DR-UV-Vis) spectrum of a H_2TPP PsB-MGC thick fibrous layer (the orange one in inset). Inset shows also a porhyrin-free fibrous coating (the white-grey one).

Soret (reflectance minimum about 2.5% at 415 nm)
Q bands: VI: 516 nm, R: 13%; III: 550 nm, R: 19%; II: 591 nm, R: 23%; I: 648, R: 22%

FIBERS CHARACTERIZATION-2

nanomaterials

Open Access Article

Electrospinning of Polystyrene/Polyhydroxybutyrate Nanofibers Doped with Porphyrin and Graphene for Chemiresistor Gas Sensors

by Joshua Avossa [1], Roberto Paolesse [1,2], Corrado Di Natale [1,3], Emiliano Zampetti [1], Giovanni Bertoni [4], Fabrizio De Cesare [1,5], Giuseppe Scarascia-Mugnozza [5] and Antonella Macagnano [1,5,*]

Nanomaterials **2019**, *9*(2), 280; https://doi.org/10.3390/nano9020280

- The **bright regions** inside the polymer/porphyrin fiber could be due to Br^-, counterion to CTA^+ (Cetyltrimethylammonium)
- They are supposed to be indirectly related also to **graphene dispersion**
- Due to the poor polymer–polymer miscibility (**solidification in different domains**):
- **Oxygen** is more concentrated at the surface: PHB at surface (carbonyl, hydroxyl and ether groups)
- **Porphyrin** could be fairly dispersed among **PS** chains and **MGC nanofillers** in fiber inner part, and PHB arranged to the outermost part.

frontiers in Chemistry | Analytical Chemistry

Thermally Driven Selective Nanocomposite PS-PHB/MGC Nanofibrous Conductive Sensor for Air Pollutant Detection

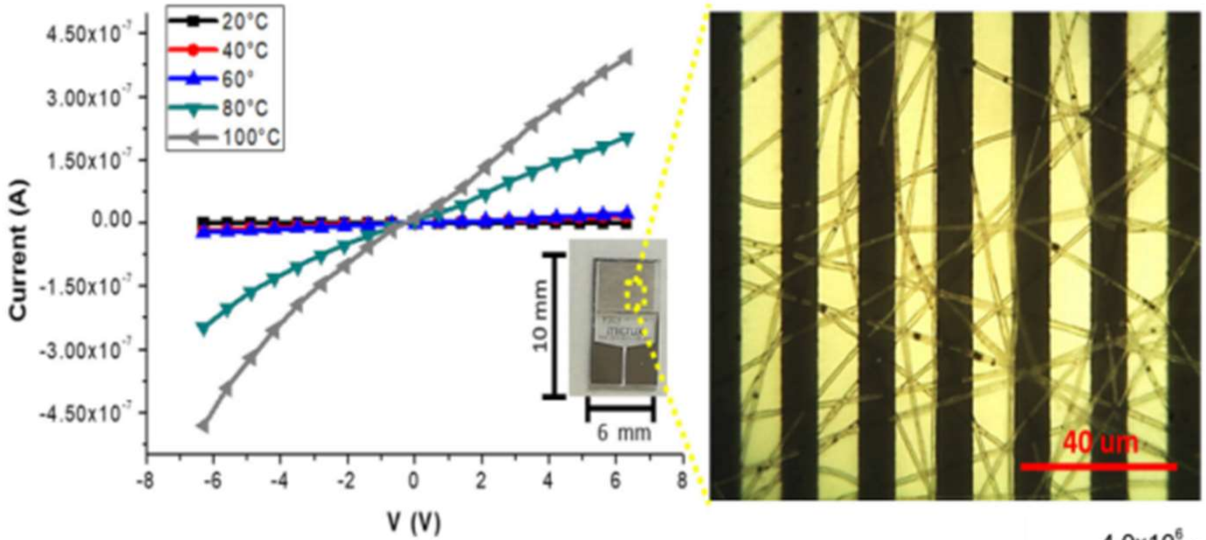
Joshua Avossa[1], Emiliano Zampetti[1], Fabrizio De Cesare[1,2], Andrea Bearzotti[1], Giuseppe Scarascia-Mugnozza[2], Giuseppe Vitiello[3,4], Eyal Zussman[5] and Antonella Macagnano[1,2*]

ORIGINAL RESEARCH ARTICLE

Front. Chem., 25 September 2018 | https://doi.org/10.3389/fchem.2018.00432

ELECTRICAL FEATURES VS TEMPERATURE: G+PP

Current-Voltage curves depending on T_W



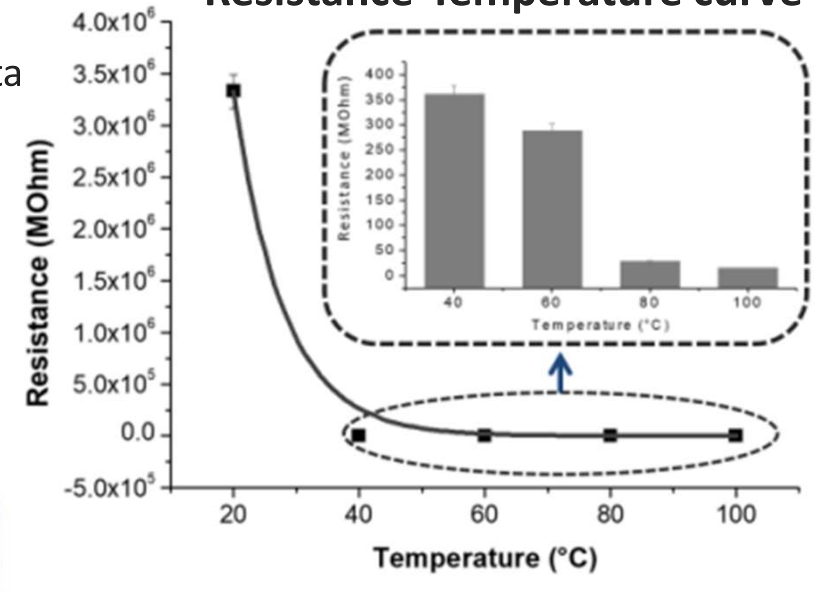
Current-Voltage curves at different temperatures (20, 40, 60, 80, 100◦C) for the fibers coated IDE (inset) are plotted.

On the right, an optical micrograph shows a homogeneous coverage of the transparent fibers onto the interdigitated platinum bars.

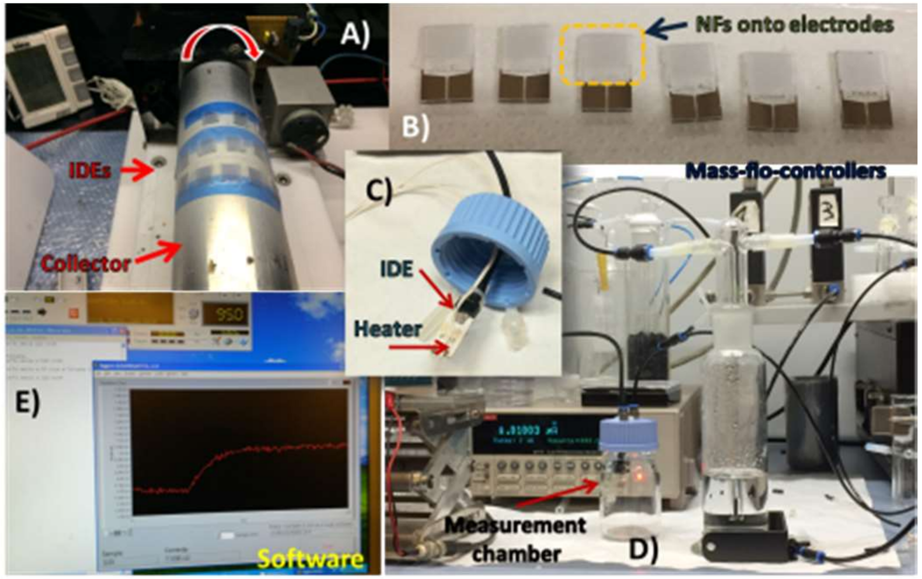
EXPECTED RESULTS:
the gap among nanofillers tends to increase with temperature resulting in a resistivity rise of several decades.

Resistance-Temperature data and corresponding interpolating curve are reported.
The inset shows the resistance values at 40, 60, 80, and 100◦C in a smaller scale.

Resistance-Temperature curve



SENSORS SET UP

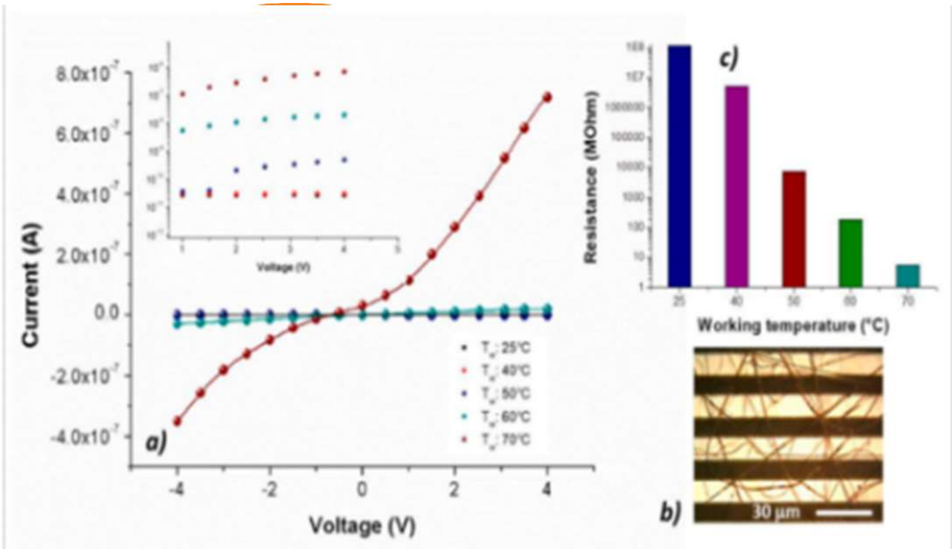


Sensor arrays

Laboratory setup

ELECTRICAL FEATURES VS TEMPERATURE: P+G+PP

a) Current vs. Voltage diagram); **b) optical image of the IDE**); **c) resistance values diagram at 25, 40, 50, 60 and 70 °C**



RESULTS: exponential decreasing of the resistance values to the increasing 10 °C steps:

-phenyl group rotation in polystyrene (polymer backbone chain reorientation;

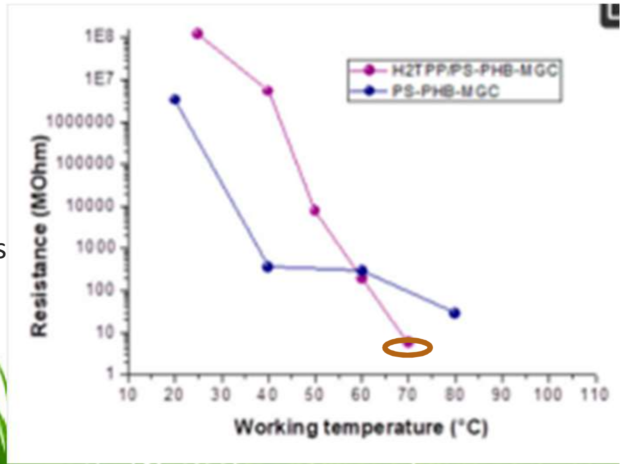
-favoring strong π–π interactions between aromatic organic molecules and the basal plane of MGC

-better distribution of graphene;

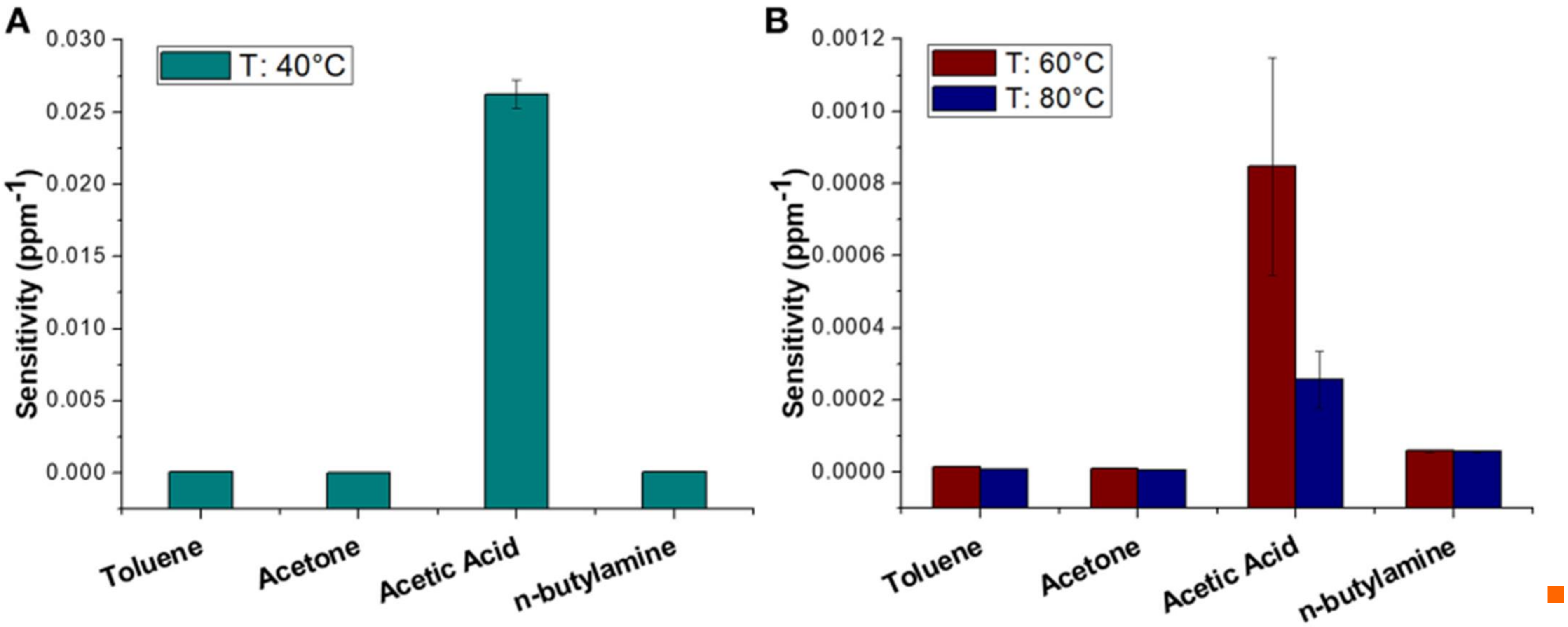
-significant contribution of porphyrin by its aromatic planes

At lower temperature H_2TPP could work as a barrier while at higher temperature it should promote conduction.

Resistance vs. working temperature for H_2TPP-PsB-MGC (purple) and PsB-MGC (blue) fibers

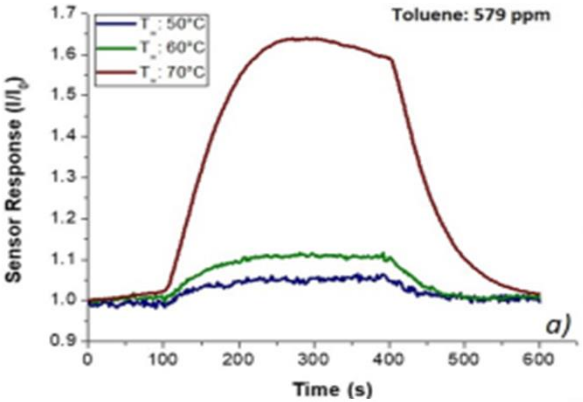


VOCs measurements according to a dynamic mode: G+PP

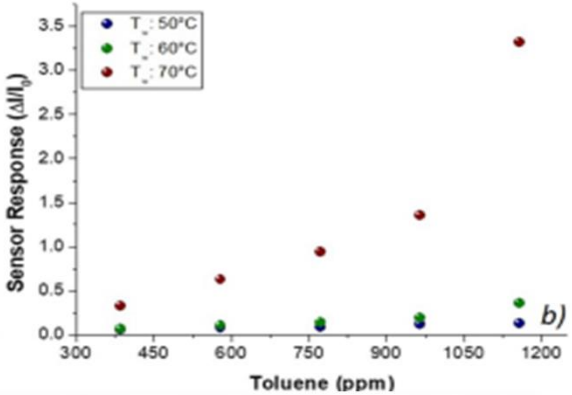


VOCs measurements according to a dynamic mode: G+PP+Porf

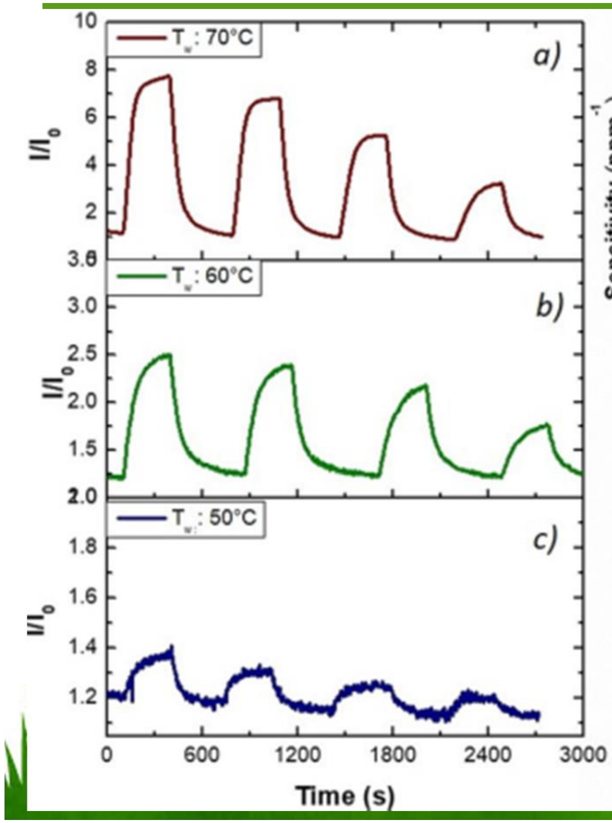
TRANSIENT RESPONSES

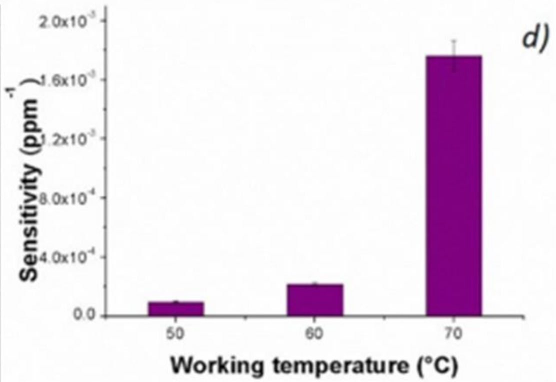


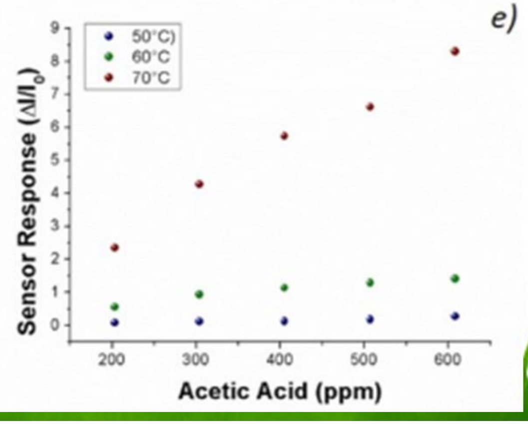
RESPONSE CURVES TO INCREASING T



TOLUENE

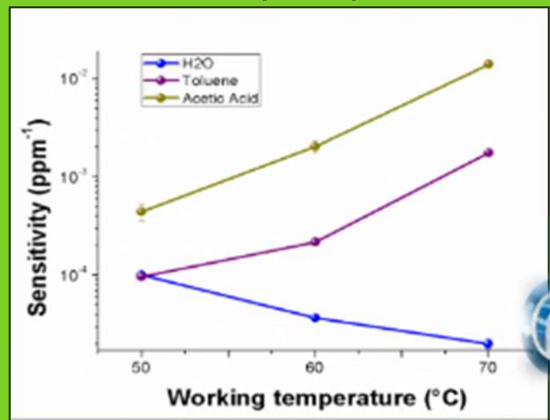






ACETIC ACID

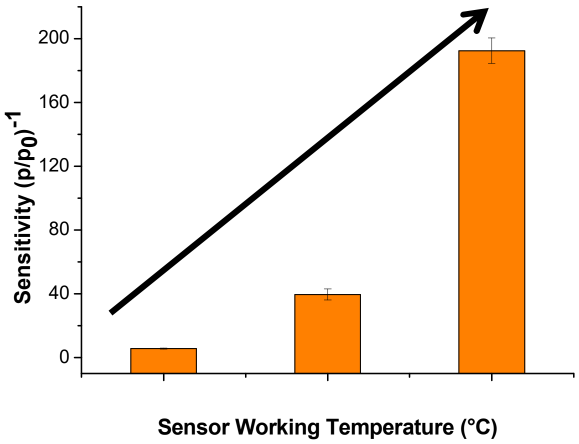
Sensitivity comparison



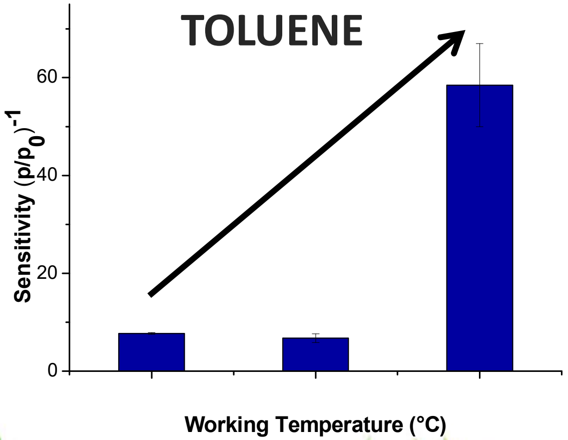
VOCs measurements COMPARISON

G+PP+Porf

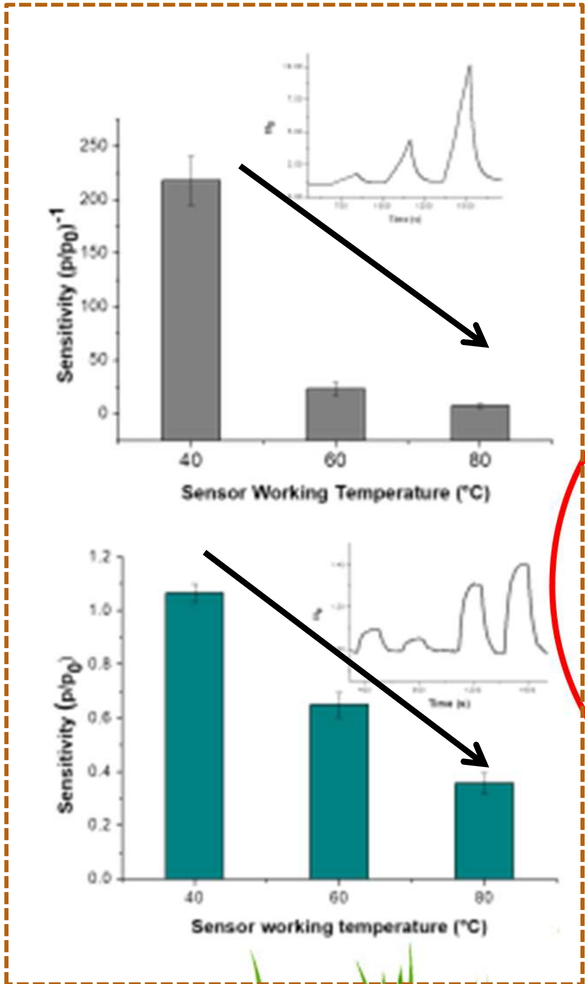
ACETIC ACID



TOLUENE



G+PP



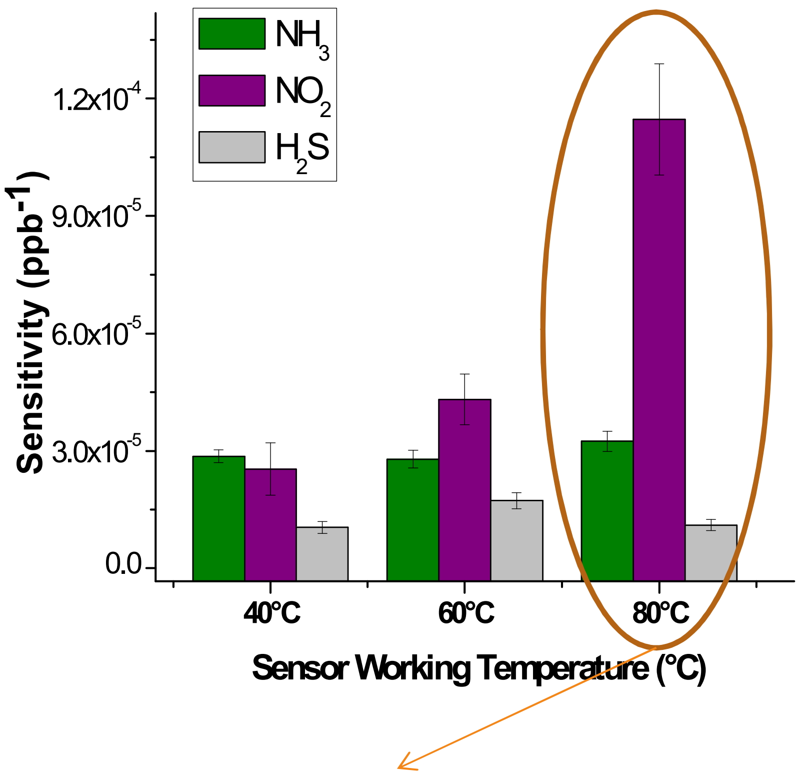
Completely different effects of temperature to VOCs responses:

- ✓ Kinetics
- ✓ Sensitivity values

Temperature looks to favor VOCs interaction when porphyrin is inside fibres

GAS MEASUREMENTS

G+PP



SENSOR SELECTIVE TO NO_2

T=80°C Sensitivity 4 times higher than at 40°C.

The increase in sensitivity could be due to: **redistribution and orientation of graphene** within polymer fibers due to the heating, allowing the gas adsorption onto a larger number of exposed binding sites, despite of the unfavorable energies involved in the phenomena of ad-adsorption.

The $LOD_{80°C}$ (defined as 3 * standard deviation of the blank) has been calculated to be ~**2 ppb.**

PRELIMINARY CONCLUSIONS

G+PP

- ✓ The high polymer porosity favored the gas diffusion
- ✓ Sensor can be tuned in order to be more selective to a gas (NO_2, 80°C) or a VOC (acetic acid, r.t.)
- ✓ The role of the potential interferents in complex environments (VOCs, and RH) can be significantly lowered.
- ✓ Sensitivity to NO_2 comparable to commercial devices

G+PP+Porf

- ✓ H_2TPP within PS-PHB-MGC fibers has a key role: makes the sensor more conductive and sensitive to VOCs, expecially to aromatic hydrocarbons (LOD: 3 ppm)
- ✓ Temperature improves such a selectivity
- ✓ H_2TPP within PS-PHB-MGC fibers makes the sensor less sensitive to NO_2 and other gases

PROSPETTIVE FUTURE

NANOFIBRE + REGOLAZIONE TEMPERATURE + Me-PORFIRINE

-sensori altamente sensibili
-selettivi
-stabili e robusti
-miniaturizzabili e modellabili
-utilizzabili da soli o in array con altri sensori -costi contenuti
-commercializzabili e riproducibili in larga scala
-applicabili in ambienti complessi
-da includere nel sistema finale di monitoraggio sia su QCM che su IDE
-…primo approccio allo sviluppo di dispositivi *eco-friendly*

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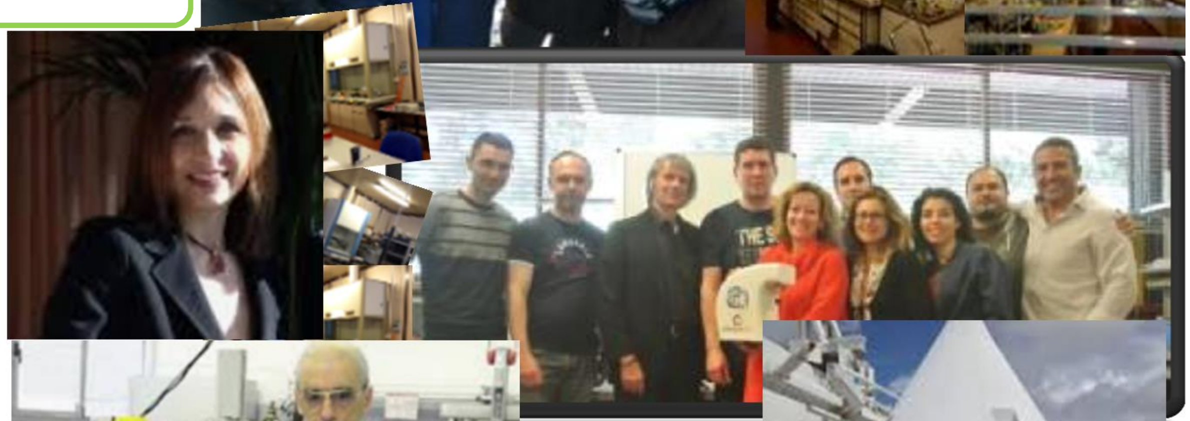
Dr. G. Tranfo

Eng. Emiliano Zampetti
Dr. Joshua Avossa
Dr. Andrea Bearzotti
Dr. Paolo Papa
Dr. L. Ragazzi
Mr. Alessandro Capocecera



Dr. A. Cecinato
Dr. C. Balducci

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