One dimensional, single-chain polymers for gas sensors through high-pressure technology (SCENT)

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ABSTRACT

The SCENT project has targeted the realization of polymeric chains with molecular diameter in a configuration suitable for gas sensing. In particular, we used high-pressure technology (≈ GPa) to promote the polymerization of guest 1D chains inside the nanometric pores of the host zeolite. Specifically, we used VFI and poly-phenylacetylene (PPhA) as target zeolite and polymer, respectively. Our approach was found to be suitable to induce the polymerization of PPhA inside the VFI pores and, with respect to literature reported PPhA, the SCENT prototype gas sensor featured improved gas sensing performance in terms of limit of detection and partial specificity.

Keywords: high-pressure technology; 1D polymers; gas-sensors.

1. INTRODUCTION

The societal demand for efficient and low-cost gas-sensors has largely increased in the last years owing to requests arising from medical, environmental, automotive fields, to name but a few. Nonetheless, in the trillion of sensors roadmap envisaged by 2025, gas sensors play a minor role due to the functional limitation suffered by actual gas-sensor technologies, in particular at the level of individual gas sensor units [1]. In this scenario, SCENT aims at facing gas-sensors' drawbacks concerning selectivity, reproducibility and limit of detection, which are at the basis of current gas-sensors limitations. Gas-sensors literature suggests that the use of nanostructured materials may be an effective solution for these drawbacks, with performance increasing with decreasing the size of the elementary nanostructures with nanowire morphology, but the challenge remains about the realization of nanowires with molecular diameter, i.e. with true 1D character [2].

In the SCENT project, we targeted this goal through the use of host-zeolites featuring an ordered structure of nm- and sub-nm sized pores to template the preparation of guest polymeric chains with true 1D character. High pressure technology is the key factor to achieve this result.

During the project timeframe, the SCENT consortium seeded this new technology by: (i) synthesizing poly-phenylacetylene (PPhA) chains with molecular diameter inside the pores (diameter of 1.2 nm) of the VFI zeolite; (ii) integrating these materials into Quartz Crystal Microbalances (QCMs) gas sensors and testing these devices against basic chemicals. Our results indicate that the prepared materials exhibit a lower limit of detection (LOD) and a different sensing mechanism with respect to PPhA literature.

2. STATE OF THE ART

Gas sensing is an active field of research that attracted an increasing interest due to the widespread range of applications demanding portable and low-cost instrumentation suitable to properly detect target volatiles. Examples includes environmental monitoring, safety and security, in which sensors are required to detect the presence of harmful gases, or medicine and food quality control and processing, in which the volatile

phase of the target samples contains suitable information about the status of the sample itself.
Though literature results suggest that the performance of gas sensors will improve through the use of nanostructures with wire-like shape and narrower diameters [2], the realization of materials with a true, unperturbed 1D character and their exploitation in low-cost devices is still an unfilled challenge in nanoscience and nanotechnology. Indeed, nanostructures such as carbon nanotubes (CNTs) suffer strong reproducibility issues arising from poor control over their features such as chirality, single- and multi-wall structures [3]; inorganic nanowires feature synthesis challenges and disorder drawbacks as the diameter is shrunk down to the nm and sub-nm scale [4]; conjugated polymers, despite their intrinsic 1D nature, suffer strong chain-chain interactions causing aggregation in bundles and the loss of the pure 1D character [5]. Moreover, if the use of individual nanostructures or ordered arrays is hindered by expensive, serial nano-manipulation techniques, being parallel processing methods such as dielectrophoresis still not satisfactory [6], disordered networks offering simpler preparation methods present serious reproducibility issues [7]. As a result, despite the large societal demand for gas-sensors arising from medical, environmental and automotive fields in the trillion of sensors roadmap envisaged by 2025, gas-sensors still play a minor role due to such intrinsic functional limitation.

3. BREAKTHROUGH CHARACTER OF THE PROJECT

The project SCENT is aimed at realizing one-dimensional polymeric nanostructures suitable as gas-sensors. The goal is to realize devices featuring improved detection limit, selectivity and reproducibility with respect to state-of-the-art gas-sensors.

Tab. 1. Comparison between SCENT composite materials and state of the art materials for gas sensing in terms of production costs, limit of detection (LOD), selectivity (Select.), Reproducibility among nominally identical sensors (Repr.), Power consumption (Power cons.). The effectiveness of each technology/material is scored as good (✓), normal (-) or not good (×).

Gas-sensor type/material	Costs	LOD	Select.	Repr.	Power cons.
Polymers	✓	-/✓	×	×	✓
Networks of metal oxides	✓	-/✓	×	×/-	×
Networks of CNTs	✓	-	×	×	✓
Single CNT or metal oxide nanowire	×	-/✓	×	-	✓
SCENT composite materials	✓	✓	✓	✓	✓

Polymer-based gas sensors are unspecific sensors, in the sense they respond to several compounds. As a consequence, gas sensors are typically considered components of more sophisticated sensing systems rather than complete sensing systems by themselves. The electronic nose (EN) is probably the most typical among these sensing systems. It is based on an array of unspecific sensors, each one showing its own partial selectivity, and a pattern recognition software that classifies the smelled atmosphere by comparing the array response with a pre-stored dataset of responses. As discussed in Section 2, current limitations of gas-sensor technologies, including ENs, are mainly arising from limitations of their sensor components.

The three key elements to prepare the SCENT materials are:

- The development of a composite material with host-guest structure;
- The use of host-zeolites featuring an ordered structure of nm- and sub-nm sized pores to template the preparation of the polymers;
- The exploitation of high-pressure technology to induce the polymerization of these guest-nanostructures inside the host-zeolite.

With reference to Tab. 1, the expected improved performances will arise from the following features of the SCENT materials:

- Limit of detection (LOD): true 1D character of the guest polymer and large surface area provided by the host zeolite structure;
- Selectivity (Select.): combination of guest-1D nanostructures with guest-zeolite;
- Reproducibility (Repr.): ordered structure of the zeolite pores and lack of aggregation/network.

Low power consumption (Power cons.) arises from room temperature operation, an intrinsic feature of polymers, and reduced costs from the synthesis method, which do not require nanomanipulation techniques.

4. PROJECT RESULTS

SCENT aimed at exploiting high-pressure technology to prepare materials featuring a true 1D character in a configuration suitable for gas sensors.
More in detail, during the project, the SCENT consortium has achieved the following results:

(i) Synthesis of prototypes of isolated, densely packed, 1D polymeric chains at lab scale. Considering the instability of 1D polymeric chains owing to their intrinsic tendency to aggregate into ropes, polymers with true 1D character were prepared as guest materials inside host zeolites. In particular, after a screening of materials, we synthesized the SCENT composite material using ad-hoc prepared VFI zeolites as the host [8] and poly-phenylacetylene (PPhA) as the guest. We performed the polymerization of PPhA inside the nm pores of the

VFI zeolite in diamond anvil cells (DACs), which allows the maximum flexibility to explore the optimal synthesis conditions;

(ii) Preparation of prototypes of isolated, densely packed, 1D polymeric chains through setups for large scale production. Considering the low production rate of DACs (about 0.001 mm^3/week), which may hinder any effective technological exploitation, the procedure was further adapted to work with large volume devices, featuring a production rate of about 1 cm^3/week. A schematic representation of the prepared host-guest material is shown in Fig. 1;

(iii) Verification of the true 1D character of the guest polymer. The polymerization of PPhA inside the zeolite cavities was proven through the combined analyses by means of Raman, FTIR, NMR spectroscopies and XRD. Several experiments were carried out at synchrotron sources: Elettra (Trieste, Italy) and SOLEIL (Saint-Aubin, France) facilities, respectively. Full details about the synthesis process and characterization of materials are available in literature [9];

(iv) Development of gas sensors. Gas-sensor devices were realized by dispersing powders of the VFI-PPhA composite material prepared using a large volume apparatus over the surface of Quartz Crystal Microbalances (QCMs). Comparing the results recorded with our samples (an example is reported in Fig. 2) with literature results about PPhA, we identified two properties that could be reasonably attributed to the particular structure of our composite material: 1) in the literature, PPhA is mainly investigated as humidity sensor and the SCENT composite material featured a response to humidity that is about 10 times larger than those reported in literature [10]; 2) polymer-based sensors, including PPhA, are generally reported in literature to sense different vapours through the same mechanism, which makes them to exhibit similar partial selectivity when tested against different chemicals [11]. This strongly limits the performance of polymer based electronic noses. The impression from our results is that the SCENT material sense vapours according to a mechanism that differs from the one reported in literature for polymers. Full details are available in literature [9]. This would be beneficial in view of a possible phase 2 of the SCENT project, which will target the preparation of different materials for the realization of a complete sensing system prototype, in particular an electronic nose.

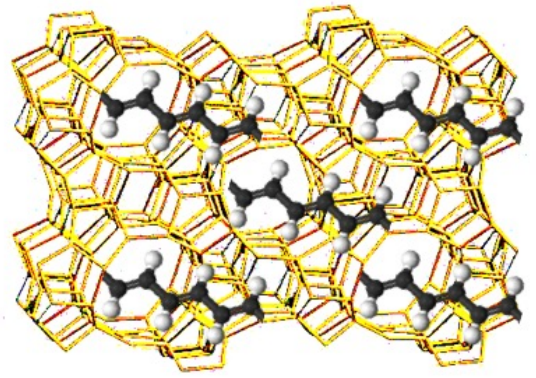

Fig. 1. Schematic representation of the structure of the SCENT composite material: polymeric chains are synthesized individually inside the nm pores of the host zeolite.

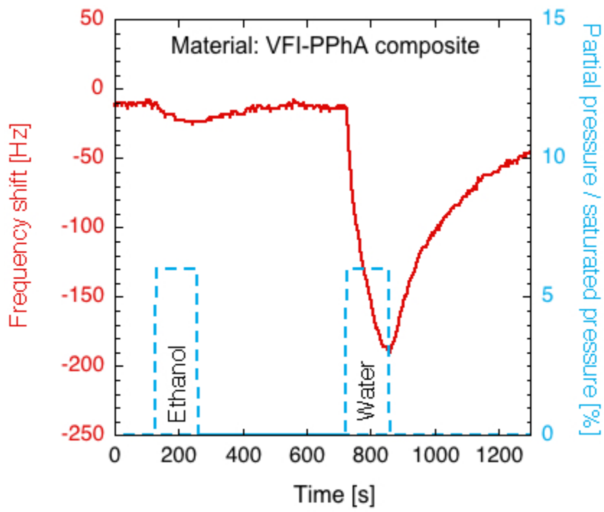

Fig. 2. Sensor response (frequency shift) to ethanol and humidity vapours recorded in a dry air background with QCM sensors functionalized with VFI-PPhA powders. Both vapours are tested at a partial pressure of 6% of the respective saturated vapour pressure.

5. FUTURE PROJECT VISION

During the ATTRACT phase 1, the SCENT consortium has developed the first prototype of gas sensors based on an array of individual polymeric chains with molecular diameter and tested these against basic chemicals. Our results confirmed the suitability of high-pressure technology to synthesize these materials and their potentialities in gas sensing. Nonetheless, this can be considered only as the first step for the development of a sensing technology based on these materials. Its development will be further addressed in an eventual phase 2 through two main objectives:

- Establishment of a consortium to produce at an industrial level these sensors;
- Development of a complete sensing system, an electronic nose, and the demonstration of its effectiveness in a real application.

5.1. Technology Scaling

The full development of the technology means the development and testing of an EN prototype, which will be addressed through the following steps:

- Preparation of at least other 3-4 sensing materials obtained as zeolite/1D-polymer composites through HP technology;
- Optimization of the synthesis parameters for the sensing materials, with particular attention to the intra- and inter-batch reproducibility;
- Optimization of the process to integrate the sensing materials into the sensor substrate, with particular attention to reproducibility;
- Test and validation of the EN prototype in a real application. Determination of the shelf-life of fresh foods, such as meat or fish is envisioned as a reasonable target application matching the potentialities of the envisioned EN and societal needs.

With this tentative research program, we foresee to develop our technology (EN) to a TRL of about 5-6.

5.2. Project Synergies and Outreach

To realize the aforementioned research program, we will integrate the SCENT consortium with partners having the following profiles:

- a company producing the SCENT materials at an industrial level. We envisage is a company expert in production of materials using HP devices;
- a company collaborating with us to engineer the SCENT sensors increasing their TRL;
- a partner with expertise in agri-food field that will drive us in the development of the sensing system toward such an application. It may be either a company, an agency or an institution.

Dissemination and communication of results will be carried out through different channels to reach different types of audience:

- High-quality scientific journals and conferences: to disseminate results in the scientific community;
- Specific events related to food and food technology: to raise the awareness of project results in possible stakeholders and establish a network for exploitation of results beyond the ATTRACT phase 2;
- International and national media: to disseminate the results also to a non-specialized audience.

5.3. Technology application and demonstration cases

We plan to apply the developed technology in the agri-food field, in particular to determine properties such as the shelf-life of a given food or to identify the eventual microbial contamination. This is a suitable field for our technology since food odours are typically composed by thousands of molecules, which makes an analytical approach difficult. A pattern recognition method, as adopted in nature by mammals, looks a more effective approach.

The output of the eventual phase 2 will thus address the following points:

- Excellent science: development of polymers with true 1D structure and the related gas-sensing technology;
- Industry and Societal Challenges: (i) development of a new industrial product (gas sensors featuring improved limit of detection, reproducibility and selectivity and the related EN); (ii) development of a portable and low-cost EN suitable for a fast screening of the food target property as a response to '*Food security*' in the societal challenge '*Food security, sustainable agriculture and forestry, marine and maritime and inland water research, and the Bioeconomy*'.

The three additional partners introduced in section 5.2 will be the key actors to properly address the Industry and Societal Challenges.

5.4. Technology commercialization

Our plan to approach the commercialization of the SCENT technology is based on two steps: (i) establishing the capability to produce prototypes at an industrial level; (ii) developing an industrially compatible process to integrate materials into gas sensor substrates. For each step, we plan to involve a dedicated industrial partner (section 5.2), which will be the privileged partners for know-how transferring and commercialization.

5.5. Envisioned risks

Core risks (R) envisaged for the potential phase 2 are listed below together with the related mitigation strategies (M):

R1: difficulties in replicating the DACs synthesis in large volume devices, which do not support the same pressure as DACs / M1: Exploitation of the pressure-temperature-light exposure combination to achieve the synthesis conditions at lower pressure.

R2: Intrinsic low production rate of HP-materials in DACs will inhibit the development of gas- sensor devices / M2: large volume setups are already available at CNRS and will be used to adapt the synthesis procedures for large scale production.

5.6. Liaison with Student Teams and Socio-Economic Study

In the eventual phase 2, liaison with students will be carried out through the following actions:

- Delivery of seminars to the pool of MSc and PhD students of the universities involved in the project.
- Master thesis related to the project are also planned for a more direct training of students to the new technology.

Concerning the socio-economic study:

- in collaboration with our industrial partners, we will provide information about the market potential of the SCENT technology;
- we will involve our MSc and PhD students as well as eventual stakeholders in interviews and questionnaires aimed at understanding how the impact of our technology is perceived outside the consortium.

6. ACKNOWLEDGEMENT

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