



ÉCOLE POLYTECHNIQUE DE LOUVAIN

REDUCTION GRAPHENE OXIDE AND LEAD
SULPHIDE HYBRIDS MATERIALS FOR NO₂
CHEMIRESENSITIVE GAZ SENSORS

Master de spécialisation en nanotechnologies

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DEDICATION

A
MA MAMAN



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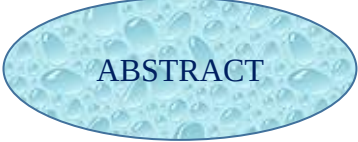
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ABSTRACT

The aim of this work is to manufacture and test the performance of a chemiresistive sensor based on a hybrid PbS/rGO material for the detection of NO₂. To do this, we first synthesize the hybrid material using a simple method and then evaluate its characteristics. The morphology and size of the crystallites of the hybrid material are characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD) while the electronic properties are determined by measuring electrical resistance as a function of temperature. The results obtained show that rGO provides a favorable surface for the nucleation of PbS nanoparticles with a crystallite size of about 7.5-15nm. These results also show that this material is a semiconductor type with an activation energy of 0.13eV or the dominant transport mechanism is of the Mott type (VRH-2D and VRH-D). Performance testing is performed by exposing the sensor to a concentration of 500ppb at room temperature and a relative humidity of 53-62%. The sensor shows sensitivity of 75 to 85% for seven out of 8 pixels tested with an average response and recovery time of 4.6min and 41min respectively. The sensor shows reproducibility over three adsorption/desorption cycles.

Keywords: chemiresistive sensor, hybrid material, reduced graphene oxide, nanoparticles

RESUME

Ce travail a pour but de fabriquer et tester les performances d'un capteur chimiresistif à base d'un matériau hybride PbS/rGO pour la détection du NO₂. Pour se faire, nous faisons d'abord la synthèse du matériau hybride par une méthode simple, puis évaluons ses caractéristiques. La morphologie et la taille des cristallites du matériau hybride sont caractérisées par la microscopie électronique à balayage (SEM) et la diffraction des rayons X (XRD) tandis que les propriétés électroniques sont déterminées en mesurant la résistance électrique en fonction de la température. Les résultats obtenus montrent que le rGO fournit une surface favorable pour la nucléation des nanoparticules de PbS avec une taille des cristallites d'environ 7.5-15nm. Ces résultats montrent également que ce matériau est un type semi-conducteur avec une énergie d'activation de 0.13eV ou le mécanisme de transport dominant est de type Mott (VRH-2D et VRH-D). Les tests de performances sont effectués en exposant le capteur à une concentration de 500ppb à température ambiante et à un taux d'humidité relative de 53 à 62%. Le capteur montre des sensibilités de 75 à 85% pour sept pixels sur 8 testés avec un temps réponse et de récupération moyen de 4.6min et 41min respectivement. Le capteur montre une reproductibilité sur trois cycles d'adsorption/désorption.

Mots clés : capteur chimiresistif, matériau hybride, l'oxyde de graphène réduit, nanoparticules

GENERAL INTRODUCTION

Air quality has become a major concern due to its direct effects on human life and the environment [1]. Urban growth, the intensification of road traffic and industrial activities have significantly increased the level of pollutants in the atmosphere [2] [3]. According to the World Health Organization's 2021 report, pollution is responsible for about seven million deaths per year [4]. This observation shows the urgency of working to reduce pollution in all sectors of activity, mainly industry. Several traditional sensors were initially developed to monitor the concentration of polluting gases in the air. Among others, atomic emission spectrometry analysis, high-performance liquid chromatography (HPLC) [4], gas chromatography (GC) [6] have been developed with various performances including those related to sensitivity, selectivity, response time, recovery time, operating temperature, reproducibility and limit of detection (LOD) [6]. In concrete terms, these tools measure the concentration of gases of interest (CO_2 , NO_2 , CO , CH_4 , H_2S) in the air [7]. However, these sensors were generally considered expensive and cumbersome. This compromises their use in real time since they must remain immovable on specific sites despite their high sensitivity. These sensors have difficulty meeting the current needs of mapping gaseous pollutants due to their size, cost and are unsuitable for real-time measurements [8].

To overcome the limitations mentioned, traditional pollution measurement sensors and chemical sensors have been developed. These sensors can be used to monitor air quality and toxic gases due to their unique features including cost-effectiveness and compatibility with other devices [9]. These sensors also have the advantage of mapping the concentrations of various pollutants within a given geographical area more accurately [10].

Among the most widely used materials for the design of chemiresistive sensors, semiconductor metal oxides have shown high sensitivity to many gases [11] [12]. However, these semiconductor metal oxide-based sensors have significant limitations: low selectivity, high operating temperature [13]. For these reasons, these sensors have difficulty finding applications in real atmospheres and research aimed at improving them is currently focused either on reducing the operating temperature to save energy and to simplify sensor design, or on the development of new sensitive and selective layers [13].

Recent work from the bibliography mentions the interest of the use of nanomaterials for the development of new sensors with new sensitive layers [14]. These layers are made up either of

nanomaterials such as graphene and its derivatives or carbon nanotubes, or by the association of a semiconductor material and nanomaterials forming hybrid materials [10] [11]. This leads to gas-sensitive layers operating at room temperature [12].

This is of undeniable interest compared to "classical" devices made only of metal oxide, which generally operate at high temperatures [15] or rGO, which suffers from low selectivity [16]. As an illustration, Schedin et al [16], fabricated a pure graphene-based NO₂ sensor operating at room temperature but with only a maximum sensitivity of 30%. In the same logic, Hwang, I. et al fabricated a NO₂ sensor using a highly sensitive SnO₂/rGO composite material that operates at high temperature (100°C) [17]. J. Liu et al, on the other hand, manufactured an NO₂ sensor based on graphene modified by the highly sensitive indium oxide with a concentration of the order of ppm at 75°C. Thus, these state-of-the-art results for the detection of NO₂ show that no NO₂ sensor with a sensitivity in the ppb range has so far operated at room temperature. Since NO₂ is a major pollutant emitted by heat engines, fossil fuel power plants and various industrial processes and is therefore highly toxic even at very low concentrations [11], its rapid detection is a necessity, especially since it can cause respiratory disorders, aggravate lung diseases and the formation of acid rain [18]. Hence the interest is rising for research work on designing a NO₂ sensor that could operate at room temperature while maintaining the best detection performance (sensitivity, selectivity, response time) as well as a cheap cost.

The objective of this work is to explore a hybrid material that could fit all these needs: rapid, accurate and selective detection of NO₂ for the preservation of air quality as well as industrial safety. To do this, the present work is organized as follows:

- Chapter 1: We present the general information on gas sensors, their operating principle, especially for chemiresistive sensors, and their characteristics. Then the physicochemical properties of sensitive materials in particular PbS, rGO then sensitive layers coupling semiconductor materials and graphene-based nanomaterials.
- Chapter 2: We describe the experimental method, and the techniques used for this work.
- Chapter 3: We describe the physicochemical properties of the hybrid material synthesized for the sensitive layer for the detection of NO₂.
- Chapter 4: We evaluate the performance of hybrid layers for NO₂ detection. The detection results obtained for this compound will confirm or not the possibility of developing hybrid layers that are very sensitive to NO₂ at room temperature.





CHAPTER I : LITERATURE REVIEW

In this chapter we describe the general information about gas sensors, including the working principle of a chemiresistive gas sensor, their elaboration methods and the possibility of using hybrid materials for their development. The properties of sensitive materials will also be described.

I.1. GENERAL INFORMATION ON GAS SENSORS

I.1.1. Definition

Chemical gas sensors are typical devices that receive a stimulus and transform it into an electrical signal [18] [19]. A chemical sensor consists of two main parts, namely a sensitive layer allowing the recognition of the gas with which it interacts and a transduction system transforming the interaction between the gas and the sensitive element into an electrical signal. Figure 1 shows the general operating principle of a chemical sensor.

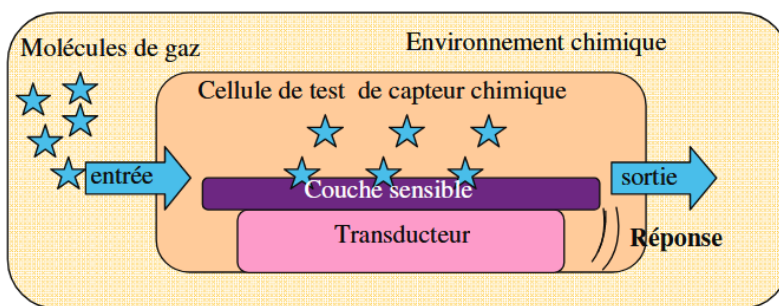


Figure 1 : Principle of operation of a chemical sensor.

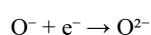
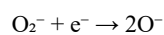
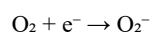
The operating principle is followed: a gas molecule that meets the sensitive layer in a chemical environment, forces the latter to adsorption, which can be either physical (physisorption) or chemical (chemisorption) [20]. Physisorption occurs when the sensitive material forms weak Van der Waal-type bonds of the order of 0.1eV and this is usually the case when there is a low affinity between the sensitive material and the gas molecule. Chemisorption occurs when the sensitive material and the gas molecule form the covalent bonds of the order of 1eV [7] and this is usually the case when the sensitive material and the gas have a high affinity. In terms of applications, physisorption is the most desired case because it does not affect the surface of the sensitive material.

I.1.2. Applications for gas sensors.

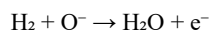
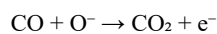
Gas sensors are used to detect and identify volatile compounds, whether in materials or in ambient air, based on the concentration of the gases in them [7]. For this reason, research and studies have been carried out continuously to develop different types of sensors according to the different physical phenomena on which they are based. Among these sensors, we can mention electrochemical sensors, which are based on an oxidation-reduction reaction, infrared sensors, which are based on the absorption of infrared radiation [21] and chemiresistive sensors, which are based on the variation of electrical resistance [22]. The latter is the subject of this work. Our study will focus more on chemiresistive sensors based on semiconductor nanomaterials.

I.1.3. Principle of operation of a chemiresistive sensor

The operating principle of a chemiresistive sensor is based on changing the electrical resistance of the semiconductor sensitive layer in the presence of a gas [23]. Indeed, in the presence of gas, an adsorption phenomenon occurs in the interaction of gas molecules with the sensitive layer, which leads to the variation of the electrical resistance of the sensitive material due to the adsorption of the gas molecule. Adsorption is defined as the ability of an adsorbate (atoms, ions or molecules) to attach to adsorbent surfaces [24]. There are two types of semiconductors (n-type and p-type) and these two types allow us to have four different reaction mechanisms: In the case of an n-type semiconductor, oxygen from the air is adsorbed and picks up free electrons. This causes an increase in the resistance of the sensor, thus leading to a decrease in the flow of electrons inside the sensing material [25]. The different reactions for this stage are:



In the presence of reducing gases, the reducing gas reacts with the adsorbed oxygen and the electrons retained by the adsorbed oxygen are released into the sensing material. As a result, the resistance of the sensor decreases. This is illustrated by the following equations.



The electrons ceded as observed on these equations will be captured by the sensitive material, thus increasing the density of the charge carriers and therefore the consequence is the decrease of the electrical resistance [10]. For oxidizing gas, it's the opposite. In the case of a p-type semiconductor, oxygen from the air adsorbs to the surface of the sensitive layer as an electron acceptor. This oxygen adsorption accumulates charge carriers on the surface of the sensitive material, which decreases the electrical resistance of the material and forms an accumulation zone following the same reaction mechanism as for an n-type semiconductor. Figure 2 shows the summary of the conduction mechanism for an N- or P-type semiconductor material [26].

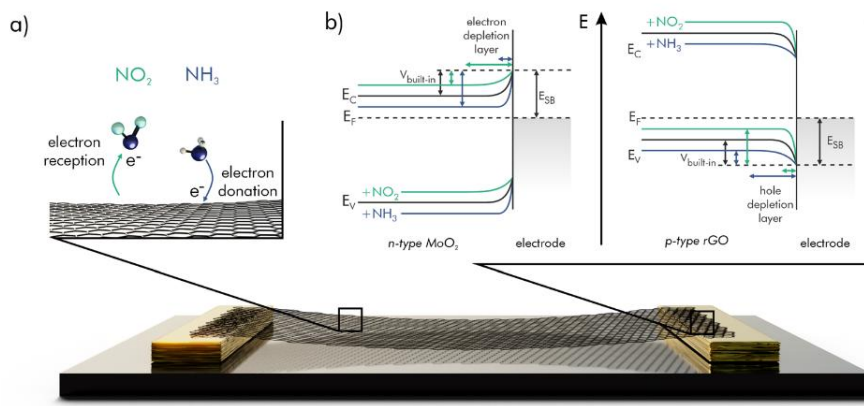


Figure 2: Conduction mechanism for a semiconductor material for the detection of a gas [26]

I.1.4. Characteristics of a gas sensor

The performance of a gas sensor depends on its characteristics: sensitivity, stability, selectivity, response time, recovery, reversibility, reproducibility and detection limit among others. In general, we will examine these characteristics in our work apart from the selectivity that we have not been able to meet the necessary conditions for its realization.

I.1.4.1. Sensitivity

The sensitivity of a chemiresistive sensor is the variation of the physical parameters of this sensor such as conductance or resistance in the presence of a gas on the sensitive layer. This sensitivity is estimated by the percentage change in the resistance of the sensor when exposed to the target gas compared to its resistance without the target analyte [18]. It is defined by the following formula according to the nature of the sensitive material:

- $S (\%) = \left(\frac{R_{air} - R_{gaz}}{R_{air}} \right) * 100$ (Type-n)
- $S (\%) = \left(\frac{R_{gaz} - R_{air}}{R_{gaz}} \right) * 100$ (Type-p)

where S is the sensitivity, R_{gas} is the electrical resistance, R_{air} is the resistance in dry air. For this sensitivity, the value 100% (i.e. the strength of the material is negligible compared to the air resistance) corresponds to the ideal while 0% (i.e. the material and the air have the same resistance) corresponds to the case where the sensor does not work. ideally, you should have a sensor such that low gas concentration leads to a significant variation in the measured parameter, i.e. resistance. The sensitivity of a sensor can be influenced by certain external factors such as relative humidity, sensor temperature, and the time the sensor is exposed to the gas [21]. We should therefore take these external parameters into account in the manufacture of our sensor, especially if we want it to work in a real environment (ambient temperature, relative humidity).

1.1.4.2. Selectivity

A sensor operating in real-world conditions is exposed not only to the gas of interest, but also to other gases that can be absorbed by the sensor and change its sensitivity. Selectivity is therefore the ability of a sensor to react with a single gas in the presence of other gases [21]. A sensor is selective if its sensitivity to one gas is minimally affected by the presence of another gas. This is the most important parameter to ensure the reliability of measurements in environments where gaseous species may be present simultaneously, such as in air [12]. **Figure 3** shows the selectivity of a graphene and functionalized graphene-based sensor.

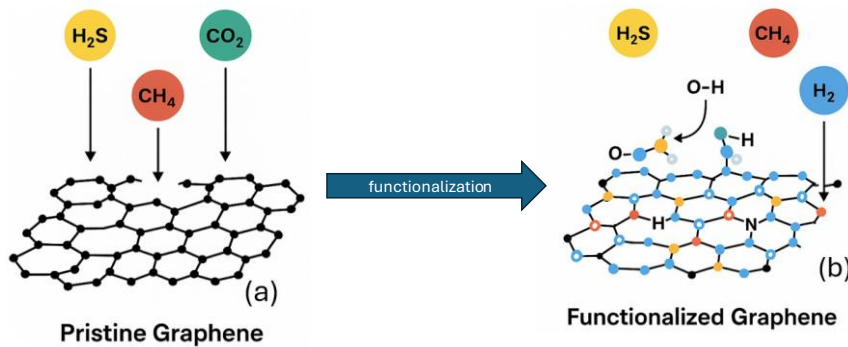


Figure 3 : Selectivity of a graphene-based sensor.

Figure 3(a) shows a representation of pure graphene where several gases are present and can adsorb to its surface. This shows that pure graphene is not selective. In contrast, in (b), pure graphene underwent chemical functionalization that created sites that could attract or recognize a single type of gas, for example, H₂. In this case, the others have no adsorption sites or weak adsorption sites [22]. As a result, the sensor delivers a specific signal to H₂. Experimentally, selectivity is measured by exposing the sensor to different gases, at the same concentrations, and under the same conditions, and then analyzing the differential responses. For a gas A and B, selectivity is defined by:

$$\text{Selectivity}_{A/B} = \frac{R_{\text{gas A}}}{R_{\text{gas B}}}$$

Where $R_{\text{gas A}}$ and $R_{\text{gas B}}$ are the responses of gas A and gas B, respectively. If this ratio is much greater than 1, the sensor is considered selective for gas A

1.1.4.3. Response time and recovery time

Response time is the time it takes for a sensor to react to an event, such as a change in the concentration of a gas in a medium. Recovery time is the time it takes for the sensor to return to the initial configuration once the event has disappeared [27]. In practice, response time is the time it takes for the signal to reach 90% of the maximum variation after exposure to the gas, while recovery time is the time for that signal to return to 90% of its initial value after gas exposure has stopped [28]. Figure 3 illustrates the response and recovery time of a gas sensor after exposure to gas.

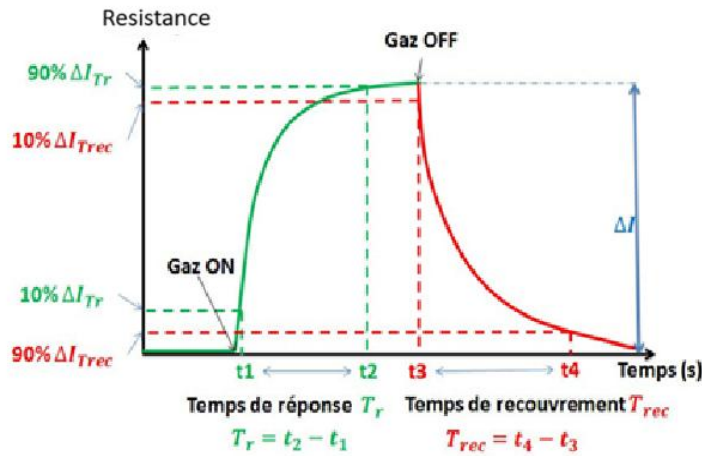


Figure 4 : Illustration of the response and recovery time of a gas sensor.

In this figure, we can identify the response time $T_r = t_2 - t_1$. Here, the response time is the speed at which the sensor reacts in the presence of a target gas. The longer this time, the slower automatic decision-making [7]. On the other hand, the recovery time observed in Figure 3 is the difference between t_3 and t_4 ($T_{rec} = t_4 - t_3$). Response and recovery time is very important because after each exposure, the parameter (Resistance) must return to its initial state for a new gas cycle [23]. The shorter this time, the better the sensor will be able to detect the gas continuously and regularly.

1.1.4.4. Stability

Stability is the ability of a gas sensor to reproduce the same responses over time, this includes in addition to response, preservation of sensitivity, selectivity towards the same gases and recovery time.

1.1.4. Factors Affecting the Operation of a Gas Sensor

The operation of a sensor can be influenced by factors related to environmental conditions such as operating temperature and humidity.

1.1.4.5. Temperature

The temperature of the sensitive layer plays a key role in the operation of chemiresistive sensors, as it directly affects the sensitivity, electrical behavior of the sensitive layer, and thermal effects [29]. Indeed, when the sensitive material is a semiconductor as in the present work, the available thermal energy is insufficient to overcome the activation barriers between

the adsorption and desorption of gas molecules on the sensitive layer at low temperature. This results in a poor signal response. On the other hand, as the temperature increases, the interaction between the sensitive layer and the gas. This increases the variation in electrical resistance due to gas adsorption [1] and thus improves sensitivity to an optimal value.

1.1.4.6. Humidity

Humidity is one of the factors affecting the redox reactions that take place on the surface of the sensitive sensor material. Humidity influences the sensitivity of the sensor because it reacts like a reducing gas, which leads to impacting the performance of the sensor and distorting the measurements. The influence of humidity can affect the sensor in two ways:

- The first is the adsorption of water molecules by the sensitive layer, which leads to the reduction of the number of adsorption sites, thus infecting the adsorption of oxygenated species on the surface of the semiconductor.
- The second is the presence of moisture which can behave like an electron donor, which leads to the modification of the resistance of the sensitive layer.

1.2. PRESENTATION OF THE SENSITIVE LAYER

To develop a gas sensor based on hybrid material, it is necessary to understand the fundamental characteristics of each constituent material. First, we present the physical and structural properties of PbS, as well as those of rGO by highlighting their complementarity in detection devices. Next, we will discuss the different methods of synthesis of the PbS/rGO composite.

1.2.1. Lead sulfide (PbS)

Lead sulfide (PbS), also known as galena in its natural mineral form, belongs to the class of lead chalcogenides which are the type IV-VI semiconductors of the periodic classification table. These chalcogenides typically crystallize in the face-centered sodium chloride (NaCl) cubic system.

1.2.1.1. Synthesis

Great efforts have been made over the past three decades to create viable synthetic techniques to produce high-quality, crystalline semiconductor nanocrystals with tunable physical and chemical characteristics. The synthesis routes reported in the literature are often classified into four types, depending on the conditions of the reaction medium: vapor phase, solid phase, liquid phase and two-phase approach [30].. However, vapor phase and solid-phase

synthesis are often characterized by poor control of nanoparticle size and shape, making them unsuitable for accurate and reliable synthesis. On the other hand, the liquid-phase approach has proven to be an effective method [31]. Thus, solution-phase synthesis based on a two-step process such as nucleation and crystal growth, allows the size, shape and density of particles to be controlled by adjusting the concentration, temperature and reaction time. One of the advantages of this method for the synthesis of PbS is that it is reproducible, inexpensive, and carried out in an aqueous medium and at room temperature, and therefore environmentally friendly [32]. But to control the size of the nanocrystals and avoid aggregation and imperfections and the localization of charge carriers in the nanoparticles, it is necessary to use a surfactant. As with any chemical synthesis, it is necessary to investigate the influence of reaction parameters. To do this, Mishra et al studied the parameters and their results reveal that the size and growth of nanoparticles are controlled by temperature while shape is a function of the ratios between the reactants and the reducing agent [33].

1.2.1.2. Properties of PbS nanoparticles

Lead sulfide is a chalcogenide semiconductor characterized by a low direct band gap of about 0.4eV, a high charge carrier mobility of $0.44\text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ and a large exciton Bohr radius of 18nm, implying strong quantum confinement of electrons and holes at relatively large sizes [22]. The structural, thermal, optical, and electrical properties of lead sulfide are size-dependent, meaning that by switching from a 3D system (bulk PbS) to a 0D system (quantum dots, QDs), it is possible to tune these properties to make PbS structures suitable for a wide range of applications. One of the most interesting aspects of reducing the size of lead sulfide down to the nanoscale is the opening of the electron and optical gap, which completely changes the absorption spectrum and conductivity of the system [34].

1.2.2. Graphene oxide

1.2.2.1. Generalities

Graphene oxide is a graphene nanomaterial containing oxygenated functional groups such as hydroxyl (-OH), carbonyl (C=O), carboxyl (O-C=O) and epoxides (C-O-C) [26]. **Figure 5** shows the structure of graphene oxide according to the Lerf-Klinowski model with the modifications made by Gao and Szabo [26]. Like pure graphene, graphene oxide also contains a significant amount of sp^3 carbons depending on the degree of oxidation of the material on which the functional groups are distributed in a non-uniform manner.

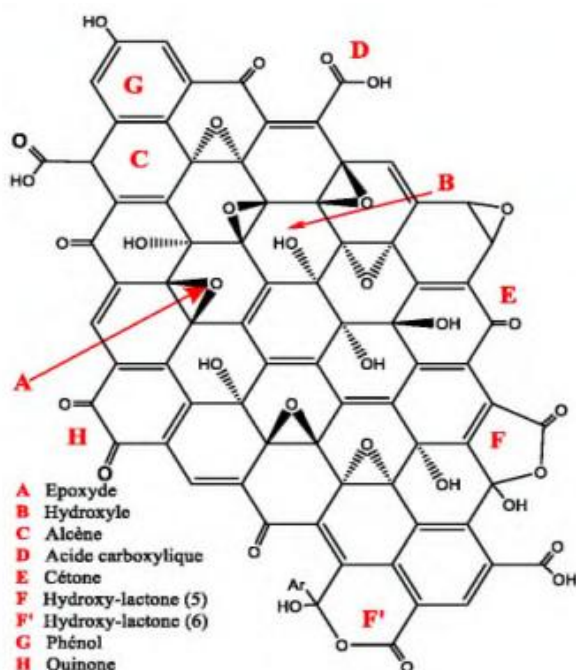


Figure 5 : Schematic representation of graphene oxide according to the Lerf-Klinowski model modified by Gao and Szabo [27]

1.2.2.2. Reduction strategies

Graphene oxide reduction is an operation that aims to transform insulating graphene oxide into reduced graphene oxide with electrical properties close to those of pure graphene. It is accompanied by a partial restoration of the sp^2 structure of the carbon lattice and a significant improvement in electrical conductivity. Several methods have been developed for the reduction of the latter to prepare graphene nanosheets in large quantities with high structural quality and high thermal stability. These include thermal reduction, chemical reduction, and hydrothermal reduction.

- **Thermal reduction:** Thermal reduction is one of the direct methods of obtaining reduced graphene oxide. It is a strategy that exploits the thermal decomposition of oxygenated functional groups on GO sheets to partially restore the conjugated SP^2 structure of pure graphene. The principle of thermal reduction is based on the stability of C-O bonds, which are energetically less stable than C-C bonds. Thermal reduction of GO can be performed in a variety

of atmosphere, pressure, and temperature conditions. Possible heating sources are microwaves, laser, plasma, and electron beam lithography [35]. At higher temperatures, the rate of deoxygenation is lower and complete oxygen removal is difficult. Indeed, C.Botas et al [36] have shown that at temperatures greater than or equal to 1100°C, little percentage of atomic oxygen is still measured due to the absence of oxygen, which becomes a limiting factor. It should be noted that the elimination of oxygen functionalities occurs easily by the loss of carbon (CO and CO₂ detected between 130-150°C) which creates the carbon gaps in the structure of the GERD obtained. Figure 4 shows the principle of the thermal reduction of GO to rGO.

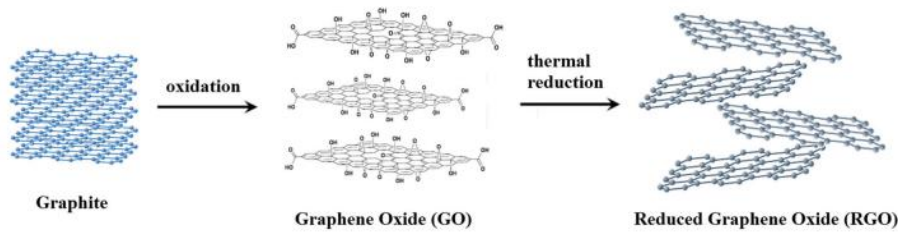


Figure 6 : Reduction of GO by the thermal method Chemical reduction

1.2.2.3. Physicochemical properties

One of the advantages of graphene oxide is its ease of dispersion in water and other organic solvents, due to the presence of oxygen functions. Due to the breaking of the conjugation and the formation of sp³ bonds, the oxide is an electrical insulator [37]. To recover the electrical conductivity, it is necessary to eliminate the oxygen groups by reduction of the graphene oxide either chemically, thermally, by a hydrothermal method, or by a combination of a chemical and thermal method which is the method used in the present work.

1.2.3. Synthesis of graphene oxide-nanoparticle hybrid materials

Graphene oxide is a basic precursor for the manufacture of graphene-based devices. In fact, the abundant presence of oxygenated groups in its structure gives it a hydrophilic character and ensures good distensibility in water or in protic solvents such as aliphatic alcohols [38]. These oxygen groups, being polar, will facilitate the formation of nanoparticles on its structure [28]. Like graphene, GO has a large specific surface area, which will promote the formation of a large quantity of nanoparticles on its surface and thus give hybrid materials with promising properties. To prepare the hybrid materials Graphene oxide and semiconductor or metal oxide, two strategies can be used:

- Pre-form nanoparticles by other techniques to control their size and shape before the formation of the hybrid material with GO by direct chemical deposition. This method allows the hybrid material to be prepared in two steps, which is self-assembly [29].

- Forming the hybrid material directly and in one step. In this case, the co-precipitation of GO with one or more metal salts in solution. This allows the formation of nanoparticles directly on the GO and obtain the hybrid GO-based materials. This last approach is the one envisaged for the synthesis of the hybrid material synthesized in the present work.





CHAPTER II : EXPERIMENTAL METHODS

In this chapter, we first describe the synthesis and physicochemical characterizations of the hybrid material (Section II.1). Then we describe the fabrication and characterization of the gas sensor using the hybrid material synthesized Section I as a sensitive layer for the detection of NO₂ (Section II.2).

II.1. SYNTHESIS AND CHARACTERIZATION OF HYBRID MATERIAL

II.1.1. Chemical

Table I presents the chemicals used for the synthesis of hybrid material.

Table I : chemicals used for the synthesis of hybrid material.

Chemical	Chemical Formula	Supplier	Additional information
Milli-Q water	H ₂ O	-	
Lead(II) nitrate	Pb(NO ₃) ₂	Sigma-Aldrich	99.999% trace metals basis, water soluble
Sodium sulphide	Na ₂ S	Sigma-Aldrich	Water soluble
2-Mercaptoethanol	C ₂ H ₆ OS	Sigma-Aldrich	14.3 M (pure liquid), Reagent grade
L(+)-Ascorbic acid	C ₆ H ₈ O ₆	VWR Chemicals	99.0-100.5% USP
Graphene oxide	-	Graphenea	Powder

II.1.2. Synthesis of hybrid material (PbS/GO)

In the literature, several different methods have been used to synthesize PbS/GO. In the papers [1], the authors used the 170°C hydrothermal method for 6h where GO and PbS were synthesized separately before being mixed and homogenized. In the papers [11], the authors used the chemical precipitation method to synthesize PbS and GO separately. These synthesis methods are indirect since PbS and GO are synthesized separately.

Unlike previous methods, our synthesis approach, illustrated in Fig. 1, consisted of the direct synthesis of PbS/GO, i.e. the synthesis of the PbS/GO composite was carried out in water at room temperature, without additional heat treatment. This direct method potentially has many advantages in terms of process simplicity and energy saving. Specifically, to synthesize PbS/GO nanocrystals, graphene oxide (GO), lead nitrate (Pb(NO₃)₂), sodium sulfide (Na₂S)

was used respectively as a source of graphene oxide (GO), lead (Pb), sulfur (S), while 2-mecaptoethanol was used as a surfactant [3] [4].

To prepare 0.2M of GO, we dispersed 13.68mg of GO in 60ml of deionized water using the Band ultrasound at 80W and 37kHz for 1 hour at room temperature. Then we prepared 0.1M of $\text{Pb}(\text{NO}_3)_2$ by dissolving 1.5g of it in 50ml of distilled water in an 80ml beaker. The volumes 25ml of GO and 25ml of $\text{Pb}(\text{NO}_3)_2$ are first taken and mixed in a sonication plastic flask for 5 minutes at 40W and 37kHz to have a homogeneous dispersion, then transferred to a round-bottomed tricol flask which will serve as a reaction medium throughout the synthesis. In our case, the mixture was left under magnetic stirring for one hour (Solution A). Then a 2-mecaptoethanol solution with a concentration of 0.1M was added drop by drop via a decanter bulb.

In the same way, a 0.1M solution of Na_2S was prepared by dissolving 360mg of Na_2S in 50ml of distilled water. Once this solution was prepared, it was added drop by drop using an automatic syringe to solution A. The final mixture is left under rigorous stirring until the colour turns completely black. In our case, this colour was obtained after 3h. This black staining marks the presence of PbS/GO. The black solution was centrifuged by an ALC PK120 centrifuge at 6000rpm for 15 minutes to isolate the PbS/GO from the other components of the reaction (NaNO_3). A black precipitate was thus obtained corresponding to our target material PbS/GO.

Note that the concentration of GO must be higher than that of the other reactants. This is because GO acts not only as a support on which PbS nanoparticles disperse to prevent their agglomeration, but also because it has many oxygen functions (hydroxyl, epoxide, carboxyl groups), which in solution will react with Pb^{2+} and S^{2-} ions. A high concentration of GO would increase the availability of functional sites and consequently improve the growth of PbS nanoparticles [1] [5]. The next step considered was to wash the precipitate with distilled water. This wash did not yield the expected results due to the high solubility of PbS/GO in water. We therefore opted to keep the solution (PbS/GO + water) in a plastic bottle and kept it in the fridge. Figure 7 shows the different stages of synthesis of the target material.

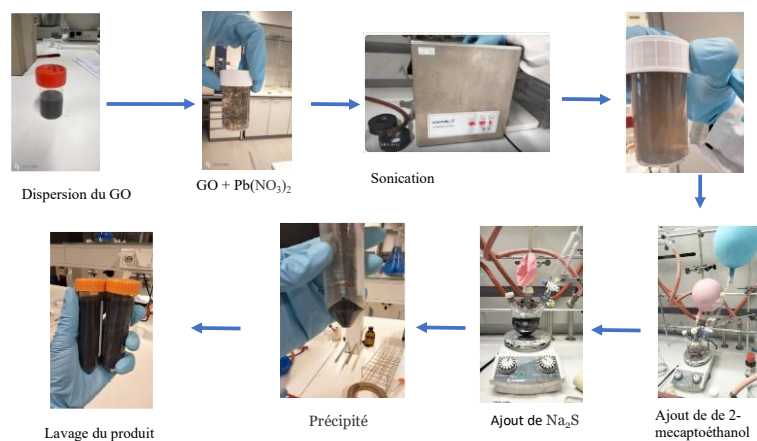


Figure 7 : Schematic representation of the synthesis of PbS/GO nanocomposites.

II.1.3. Thermal annealing and chemical reduction of PbS/rGO

The treatment of the hybrid material, namely PbS/GO, consists of improving the structure of the material for the optimization of its structure and a reduction of oxygen atoms on the surface of the GO to improve the physical, chemical and electronics properties. It was carried out in two stages: thermal annealing and chemical reduction.

II.1.3.1. Thermal annealing.

Once the sensitive material was deposited on the interdigitated electrodes, the substrate was placed in a vacuum chamber for thermal annealing. The vacuum vessel consisted of an Edwards XDS10 dry scroll vacuum pump, ultimate vacuum = 6.10^{-2} mbar) and a turbomolecular pump (Pfeiffer Balzers TPU 240, PMP 01 330, ultimate pressure 10^{-9} mbar). An infrared lamp (64635 HLX, Osram), powered by a laboratory power supply unit (72-2925 Single Output Laboratory DC Power Supply, Tenma) positioned above the transparent cover to heat the substrate to the desired temperature and monitor using a thermocouple. Variations of resistance of the sample are recorded by a Keithley digital multimeter, all connected to a computer, allowing the evolution of the electrical resistance of the device to be monitored. Figure 8 shows this experimental set-up designed by Dr. F.M. Fernandes.

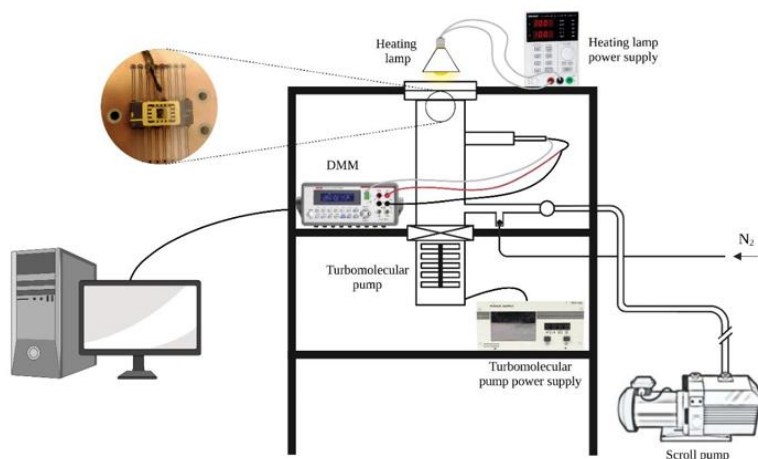


Figure 8 : Schematic Representation of Thermal Annealing Treatment Station [34] Once the principle of the method has been described, the procedure followed is as follows:

- The first step is to heat it to 348K for 20 minutes to evaporate the residual solvents and stabilize the initial structure of the material.
- The second step consists of heating from 383K for 20 minutes: at this temperature the, therefore the resistance will increase or decrease depending on the nature of the material, - desorption of water meniscus and improvement of the contact with the substrate and the metallic electrodes –
- The third step is to heat to 423K for 30 minutes: at this temperature more significant changes in the crystal structure can occur. This can help reduce surface defects and consequently the variation in strength.
- The fourth step is to heat to 433K for 20 minutes: this temperature allows us to check if a slightly higher temperature can have an improvement in the structure of the material without damaging it.
- The fifth and last step consists of heating to 153K for 30 minutes: at this temperature thermal degradation phenomena can begin to occur. This temperature can also improve the crystal structure of the material. All this thermal process is ment for activating the sensitivity of PbS by improving the crystallinity and changing the chemical composition of the surface. It is also used to determine the nature (metallic, insulator or semiconductor) of the material. Figure 9 shows simultaneously the variation of temperature (red) and resistance (Blue) during thermal annealing as a function of time.

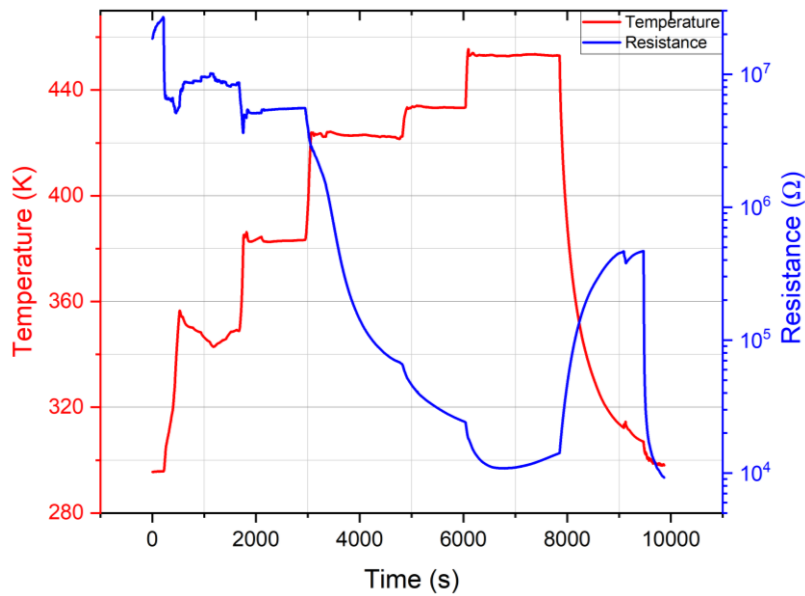


Figure 9 : Variation of temperature and resistance during thermal annealing.

To determine the nature of the material, we extracted data from the temperature and resistance at constant time at each step. Then we drew the resistance curve as a function of temperature. This curve is shown in Figure 10.

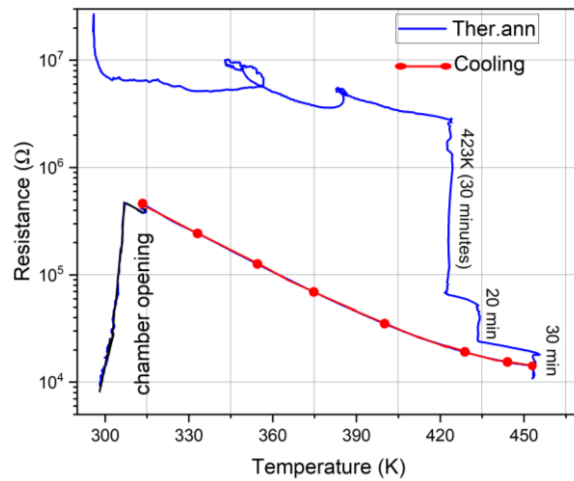


Figure 10 : Variation of the resistance as a function of temperature.

From this curve we can see that the resistance decreases linearly with temperature. This is typical of the behavior of semiconductor materials [6].

II.1.3.2. Chemical reduction.

After the thermal annealing, the next step was chemical reduction. For this, ascorbic acid was used as a reducer. First, a mass of 7.05g of ascorbic acid was dissolved 50ml of distilled water in an 80ml beaker and then transferred to a hydrothermal chamber. The substrate was added to the resulting solution and the whole thing was placed in the oven. The temperature of the furnace gradually varied from 298K to 363K (about 1 hour to go from 298K to 363K) where the furnace was left for 3h (time needed for reduction). Finally, the temperature gradually reduced to 323K. At this temperature, the sample was extracted from the chamber and washed first in acetone to remove any particle residue, then in isopropanol to remove traces of acetone on the substrate and finally in distilled water. The remaining product was dried at 323K for 1 hour. Figure 11 illustrates the material reduction step.

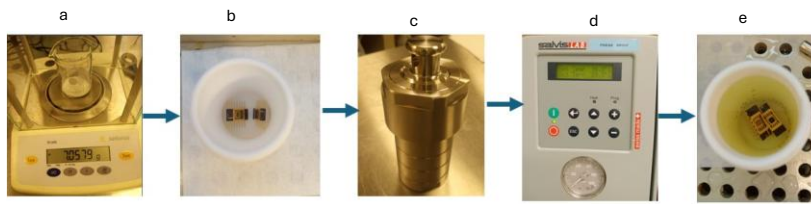


Figure 11 : illustration of the chemical reduction steps.

II.1.4. Characterization techniques

In this part, we will describe the different analytical techniques that will allow us to understand the materials and devices developed in this work for the purpose of reproduction. The aim is to highlight the contribution of specific techniques to the development of graphene-based gas sensors. We will focus on the following analytical techniques: scanning electron microscopy for morphological analysis, X-ray diffraction for crystallographic analysis, Raman microscopy for structural and chemical analysis.

II.1.4.1. Scanning electron microscopy (SEM)

Scanning electron microscopy is a method for studying the surface condition of materials by direct observation of high-resolution images and the determination of surface roughness. Unlike light microscopy, scanning electron microscopy is a technique that uses

electrons rather than visible light, resulting in a much higher resolution. Its resolution is between 5-20 nm [39]. It is an observation technique that allows the morphology of materials to be studied. SEM consists of scanning a selected area of the sample with a beam of focused electrons.

The principle of SEM is based on the interaction between the atoms in the shell and the accelerated, focused electron beam that sweeps the surface of the sample. The primary electrons from the electron gun impact the surface of the sample and are elastically or inelastic scattered. The acceleration voltage therefore depends on the energy of the incident electrons in the SEM varies between 500V and 30 kV [40]. The surface topography is observed through the imaging of secondary electrons which have a low energy of the order of 50 eV. Because this energy is low, only the secondary electrons emitted on the surface of the sample have a chance to escape the material and reach the detector [12]. Figure 6 shows the schematic principle of the SEM.

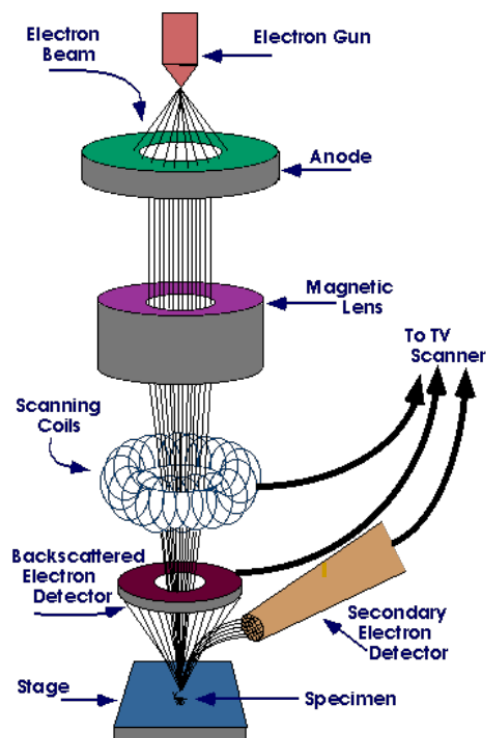


Figure 12 : operating principle of the SEM [41]

The application of the SEM for the case of graphene and its derivatives makes it possible to identify the presence of graphene sheets [42]. Since we have synthesized graphene oxide-based hybrid material, we expect to see graphene flakes and PbS nanoparticles. It should be noted that SEM imaging is highly dependent on excitation parameters such as acceleration voltage, working distance, and magnification [3].

For the current work, the images were obtained using the Zeiss-type scanning electron microscope shown in Figure 13, with an acceleration voltage of 5.00kV to 15kV, a working distance of 3.9mm, at different magnifications (17.08kX-300.00kX) and InLens signal.



Figure 13 : Reel image of SEM we used (WINFAB).

II.1.4.2. X-ray Diffraction (XRD)

X-ray diffraction is a non-destructive technique, that provides information about the phase, the preferred orientation of the crystal and the structural parameters such as the average size of the crystalites, crystallinity and structural defects [43]. Its principle is based on the interaction of monochromatic X-rays with the material. Specifically, when the incident beam bombards the sample and interacts with the electron cloud of atoms, several types of interactions can occur, but only interactions without loss of X-ray energy are exploited [44]. When this incident beam interacts with the material, the rays are scattered in all directions of space. The wavelength of X-rays is less than 2Å (order of magnitude of the interatomic distance) in crystal lattices. The rays scattered by the atoms of the crystal lattice produce destructive and constructive interference at specific angles. Its constructive interactions occur when Bragg's law is satisfied [43].

$$2d\sin\theta = n\lambda$$

Where, d is the distance between two crystallographic planes, θ is the angle between the incident beam and the diffracting planes, n is the order of diffraction (integer) and λ is the wavelength of the X-rays used. Figure 14 shows the general principle of XRD.

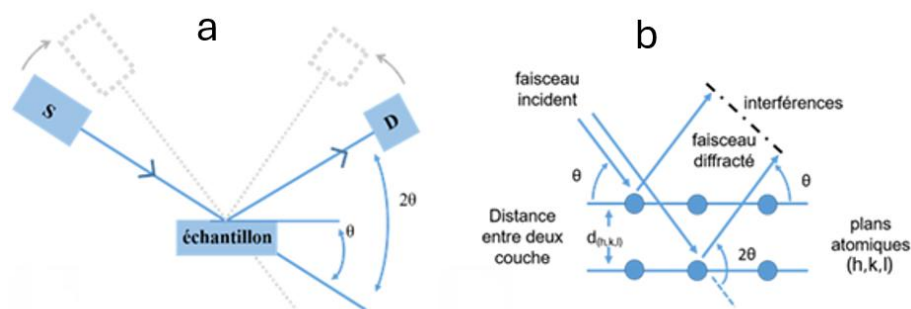


Figure 14 : θ - θ -type Bragg-Brentano set-up (a) and X-ray diffraction principle (b)

From the above, it is possible to relate the width at mid-height of the diffracted lines to the size of the crystallites using Scherrer's equation [45].

$$D = \frac{K\lambda}{B \cos \theta}$$

D is the size of the crystallites

K is Scherrer's constant ($K = 0.91$ for cubic systems)

B is the bandwidth at mid-height of the diffraction peak

λ is the wavelength of the X-rays used

θ is the angle between the incident beam and the diffracting planes.

For our case, we used a Bragg-Brentano diffractometer with X-ray emitted from the $K\alpha_1$ line of copper, which has a wavelength of $1.5405\text{\AA}$. The angles of the source and the detector were recorded over an interval of 5° to 90° . This technique allowed us to identify the phases of our material as well as to estimate their average size. The measurements were made at the Institute of Condensed Matter and Nanosciences (IMCN), Molecular Structural Analysis (ASM) laboratory of the Catholic University of Louvain (UCLouvain).

II.1.4.3. Raman spectroscopy

Raman spectroscopy is an essential analytical technique for the study of carbonaceous materials, including graphene [46]. Its principle is based on illuminating a sample with a monochromatic laser and analysing the light scattered in return. When the laser beam interacts with the surface of the sample, a fraction of the incident photons exchange energy with the electrons of the material being examined [47]. These photons are then scattered with a modified wavelength. The frequency difference between the incident photon and the scattered photon corresponds to a specific vibrational transition that serves as the chemical signature of the excited molecule and the material being analyzed.

For graphene and its derivatives, the Raman spectrum is characterized by three bands, allowing to quantify defects or disorder on functionalized sp^2 carbons (D-band) and sp^3 carbons (G-band) or the number of layers (2D band) [48]. Figure 10 shows an example of the Raman spectrum of graphene oxide and graphene oxide reduced with the D, G and 2D bands [19].

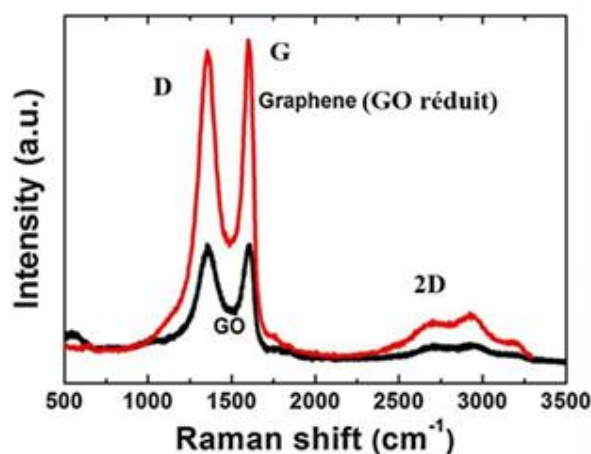


Figure 15 : Example of the Raman spectrum of graphene oxide and reduced graphene oxide [49]

In more detail, the D-band observed around 1350cm^{-1} is characteristic of the presence of structural defects in graphene as well as C- sp^3 carbon bonds [47]. The G-band around 1580cm^{-1} is associated with the vibrations of sp^2 hybridized carbon planes. As for the 2D band, it appears around 2700cm^{-1} and yields information on the number of layers. This curve will allow us to make a comparison with the different samples [50]. This technique will allow us to identify

not only the characteristic bands of the GO, but also to highlight the effect of the surface treatment on our material. To do this, our measurements were carried out at room temperature, using a Horiba Jobin-Yvon microspectrometer (i.e. a Raman spectrometer coupled with an optical microscope), with a green laser with a wavelength of 514nm. Different objectives were used for measurements to visualize the surface on which the laser will focus. (10X, 50X and 100X for numerical apertures of 0.25, 0.7 and 0.9 respectively, allowing a laser spot size of about $1\mu\text{m}^2$). The calibration of the device was performed on a standard silicon sample by checking the position of the peak at 0 cm^{-1} as well as the position of the characteristic band of silicon at 512cm^{-1} [51].

Once the hybrid material has been synthesized and characterized, we will now use it as a sensitive layer for the manufacture of the sensor

II.2. FABRICATION OF GAS SENSING

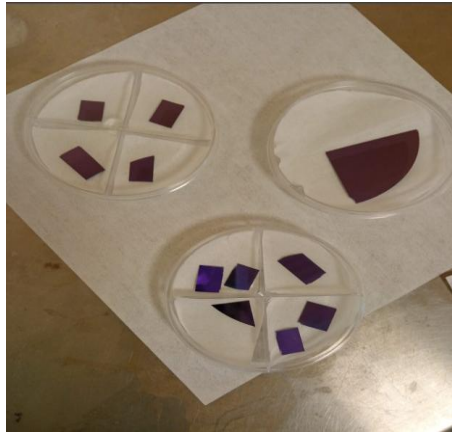
II.2.1. Deposition of the material on the substrate

II.2.1.1. Substrate preparation

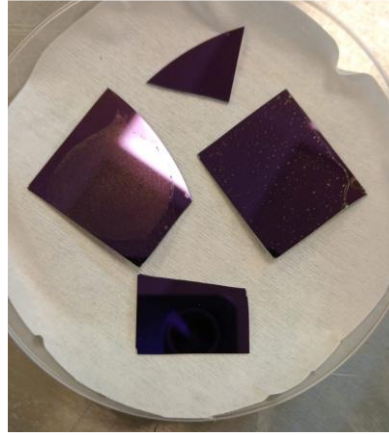
For the characterization and fabrication of the final device, we used two types of substrates: Silicon/Silica (Si/SiO₂) Substrates and CMOSEnvTM Substrates (VOCsSens).

- **Silicon/silica substrates (Si/SiO₂)**

For the substrate (Si/SiO₂) we used: a Si/SiO₂ wafer polished on one side only, with a diameter of 10.6cm, a central layer of 500-550 μm for physicochemical characterizations. To facilitate the manipulation, this wafer was cut into small samples of about 1cm^2 (Figure 16), then cleaned in acetone for 5 minutes to remove all organic contamination, then in methanol to remove all traces of acetone and finally rinsed with deionization water.



a) Clean



b) Deposition material

Figure 16 : image of the substrates used for physicochemical characterizations.

- **CMOSEnvi™ Substrates (VOCsSens)**

For this substrate we used microchips developed and patented by VOCsSens. They were used in this work for the electrical characterizations and the fabrication of the final device. They are made from a 400 μm thick silicon layer, a 300nm thick SiO_2 insulating layer on which Ti: Au metal lines (200 and 2000 $\text{\AA}$ thick) have been deposited by photolithography. These metal lines are made up of a width of 2 μm and are spaced $5 \pm 1\mu\text{m}$ apart.

CMOSEnvi™ Substrates (VOCsSens) are structured with several types of interdigitated electrodes. Figure 17 is a schematic representation of a CMOSEnvi™ die and its interdigitatedelectrodes (IDE) [Fernando and Valentina [Ref.Master thesis]].

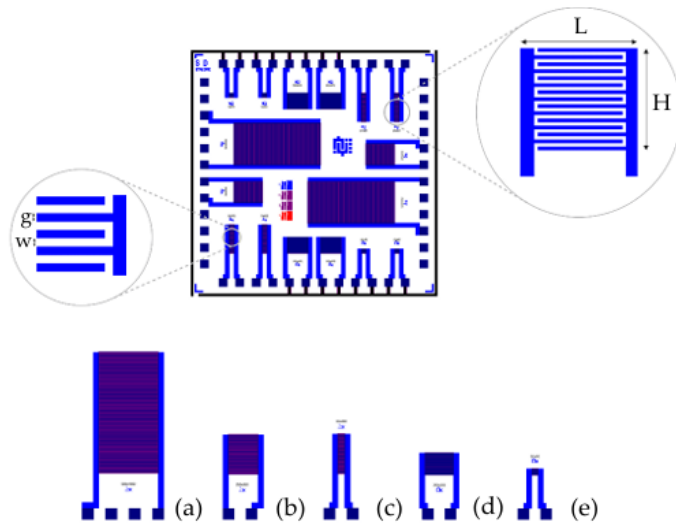


Figure 17 : Schematic representation of a CMOSEnvi™ die and its interdigitated electrodes (IDE). On the left, detail of the electrodes with the width (w) of the metal fingers and the spacing (g) between them. On the right, the length (L) and height (H) of the active zones of the electrodes.

Table II presents in detail the geometric characteristics of the different interdigitated electrodes.

Tableau II : Details about the interdigitated electrodes (IDE).

Electrodes	Number of fingers	Length (L)[μm]	Hight (H)[μm]
a)	150	500	1050
b)	50	250	350
c)	50	500	350
d)	50	200	250
e)	15	50	60

II.2.1.2. Deposition technique

The deposition of the sensitive material was carried out by the drop casting, which is a drip deposition method. Alternatively, to make manual deposition by pipetting, an automated microsyringe connected to a computer was used. The system is made up of several elements described as follows:

- ❖ *A benchtop stereomicroscope* is used to accurately observe the deposition area and ensure optimal alignment between the microsyringe and the substrate. It is equipped with a movable stage, allowing the substrate to be positioned and moved with finesse, to precisely target the area to be treated.

- ❖ *Two adjustable lamps* provide localized and adjustable lighting, ensuring good visibility during operation.

- ❖ *A ceramic heating element* (temperature between 85°C and 90°C) located in the center of the station serves to maintain a controlled temperature on the substrate, thus promoting the evaporation of the solvent and the proper fixation of the deposited materials. The substrate is held in place on the heating plate using a conductive agent paste, thus ensuring good thermal contact.

- ❖ *A microsyringe, with a volume of 0.1ml* connected to a computer, which controls the system via dedicated software. This software allows precise control of the injection speed and volume of each drop, ensuring a reproducible and controlled deposit. The needle used has a diameter of 0.25 mm, which allows the deposit of drops from a few microliters to several hundred nanoliters.

- ❖ *A power supply unit (RSPD 3303C) and a digital multimeter* visible on the side provide temperature control via a thermocouple connected to the heating element. Figure 4 presents the schematic of the experimental deposition of the sensitive layer materials.

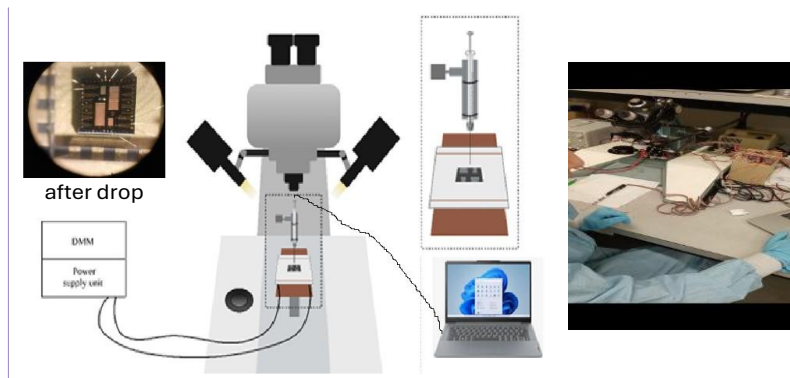


Figure 18 : Schematic representation of drop casting used.

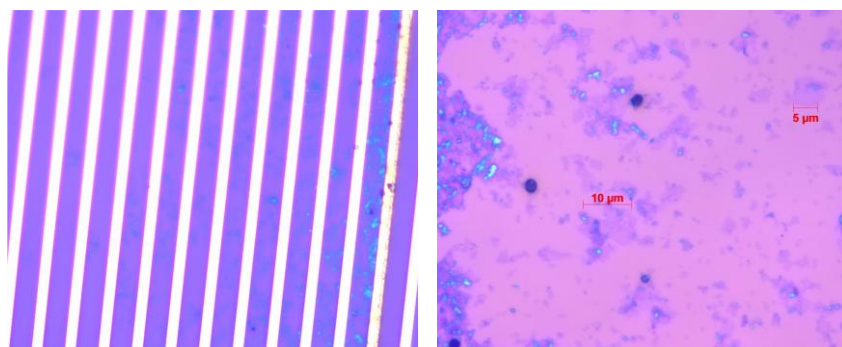


Figure 19 : optical image of sample after drop casting

Deposition of the sensitive material on the electrodes

Since the sensitivity of the sensor will be determined by the thin films of the sensitive material (PbS/GO) on the interdigital electrodes, the next step was to create these thin films on the substrate. To do this, the solution was taken out of the fridge, then sonicated at 40W and 37KHz for 10 min to break the large PbS/GO particles. Then, filtration was done using a filter at 5μm (Whatman Puradisc 13), then at 2.7μm to isolate the remaining large particles and to have the thinnest possible layers. Figure 20 shows the different aspects of the solution.

Commenté [BH1]: ce serait bien d'avoir plus d'images au microscope optique des IDE avec les gouttes déposées



Before sonication



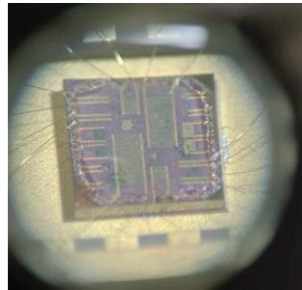
After sonication



Filtration 5µm



Filtration 2.7µm



Deposition material in the interdigitated electrodes

Figure 20 : material preparation and deposition by drop casting.

II.2.1.3. Gas testing

This is used to evaluate the performance of the developed sensor, i.e., the response of the sensor to the target gas, sensitivity, selectivity, reproducibility, and response and recovery time. For this purpose, a test bench is used to vary the sensor's environment by exposing it to varying concentrations or injecting the gas in series from the target gas, but also to interfere with gases at different temperatures and humidity. Figure 21 shows a diagram of the test bench [6] used for gas exposure at the Electronics Laboratory (Welcome platform) at

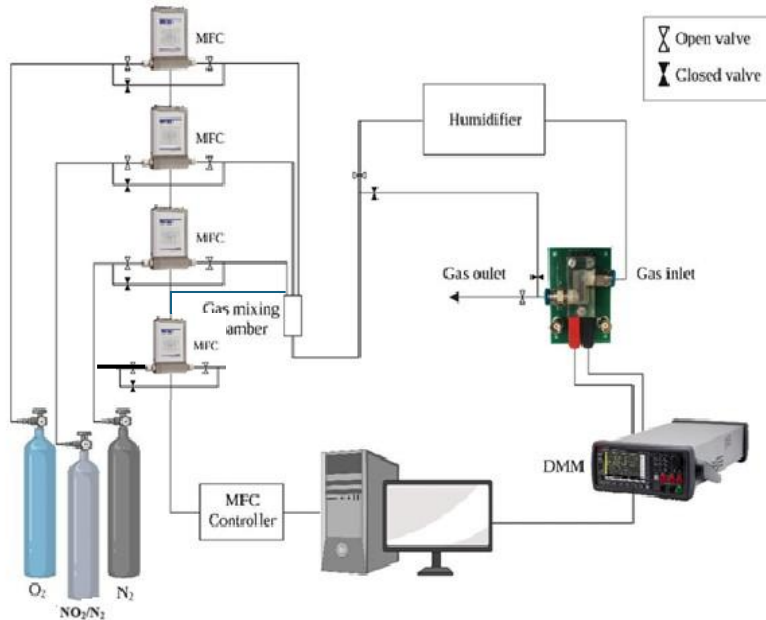


Figure 21 : Schematic representation of the laboratory gas sensor measurement facility [6].

To evaluate the performance of our sensor we performed the gas test at room temperature (25°C), atmospheric pressure (1atm), 43% relative humidity and a gas injection rate of 2000ml/min. The test protocol is based on a repeated series of sequences alternating the test gas and a recovery phase in a synthetic airstream. Expositions were carried out in three repetitive sequences described as follows:

- ❖ 420 sccm O₂ + 580 sccm N₂ + 1000 sccm synthetic air for 2h30min, to stabilize the baseline of the resistance.
- ❖ 420 sccm O₂ + 200 sccm N₂ + 380 sccm NO₂ + 1000 sccm of air hang for 30 minutes for NO₂ exposure.
- ❖ 420 sccm O₂ + 580 sccm N₂ + 1000 sccm of air for 2h30 min to allow a complete recovery.

Table 3 presents all the test sequences in detail. It should be noted that we used a commercial mixture of NO₂ in N₂ with a concentration of 2.63ppm, and after mixing in the

lines we obtained a test concentration of $2.63 \times 380 / 2000 \approx 0.5 \text{ ppm}$. It should also be noted that the sum of the flow rate must be equal to 2000ml/min.

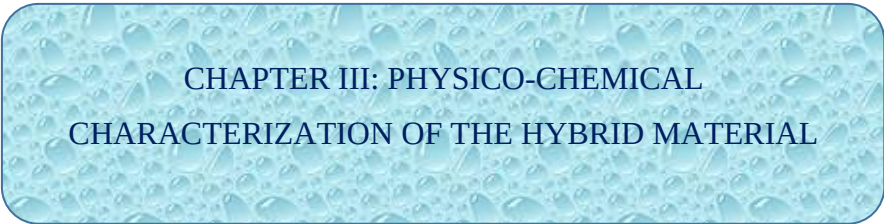
Table III: Details sequences in gaz testing

Stage	But	Time(min)	O ₂ (sccm)	N ₂ (sccm)	NO ₂ (sccm)	Air(sccm)
Initiale Stabilization		150	420	580	0	1000
Cycle 1	Exposition in NO ₂	30	420	200	380	1000
	Recovery	30	420	580	0	1000
Cycle 2	Exposition in NO ₂	30	420	200	380	1000
	Récupération	30	420	580	0	1000
Cycle 3	Exposition in NO ₂	30	420	200	380	1000
	Recovery	30	420	580	0	1000
Full recovery		150	420	580	0	1000

Table description

Initially, the sensor is subjected to dry air (without pollutants) at a constant temperature and relative humidity for a long enough time to allow a stabilization of the baseline. This is to deduce the initial resistance (R_0). Then the sensor is exposed to NO₂ for 30 minutes. At this stage, there is a variation in the strength of the sensitive material. Finally, we move on to a recovery phase for 30 minutes under air to allow the desorption of the NO₂ molecules on the sensitive material. This exposure and retrieval step is repeated three times to ensure the reproducibility of the sensor. Finally, the sensor is subjected to a long recovery time to observe the tendency of the sensor to stabilize once the cycle is complete





CHAPTER III: PHYSICO-CHEMICAL CHARACTERIZATION OF THE HYBRID MATERIAL

In this chapter we present and discuss the results of the physico-chemical analysis performed on the hybrid material, i.e. PbS/rGO: scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) and Raman spectroscopy. Then, we focus on the transport mechanism, through the analysis of electrical resistance measurements performed on PbS/rGO in different experimental conditions.

III.1. PHYSICO-CHEMICAL CHARACTERIZATIONS

III.1.1. Scanning Electron Microscopy (SEM)

To visualize the morphology of the synthesized hybrid material, we performed scanning electron microscopy. **Figure 15** shows the SEM images of the raw hybrid material, a hybrid material after thermal annealing under vacuum followed by chemical reduction in an aqueous medium by ascorbic acid in a hydrothermal chamber and GO with the same thermal and chemical treatment.

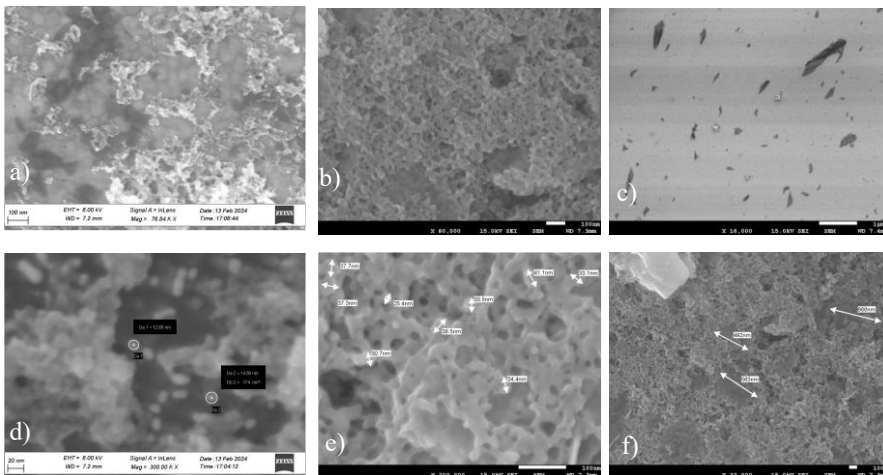


Figure 22 : SEM images of the hybrid PbS/GO material: (a) raw material and in (d) the morphological size nanoparticles estimate 10-20nm of the raw material; (b) target material (e) morphological size of target material with the same magnification in (d); (f) morphological size of the rGO; (c) rGO.

Typically, in (a), we observe a highly disordered structure, consisting of agglomerated particles. This agglomeration is probably the result of a nucleation of PbS nanoparticles on the GO sheets [11]. The material has a dense, heterogeneous texture with a non-uniform surface.

In (b), after annealing, a porous structure is observed with a good improvement in the dispersion of PbS nanoparticles uniformly on the rGO sheets. This annealing has increased the specific accessible surface area, which could be considered as active sites for gas molecule adsorption. This constitutes a good sign for gas detection. Image (c) shows the GO alone that has undergone the same surface treatment as the hybrid material. In contrast to the hybrid material (a) and (b), a planar structure with non-porous GO sheets is observed. The absence of PbS nanoparticles therefore confirms that porosity is highly dependent on nanoparticles. In images (d) and (e), we can see an increase in the particle size after treatment (thermal annealing plus chemical reduction). It is revealing that the individual particles grew during the annealing, and tend to merge, forming a network, where rGO flakes are intimately integrated. This could be justified by the fact that during heat treatment, PbS nanoparticles migrate together and fuse to form larger organized and thermodynamically stable particles. In addition, this observation is in agreement with literature showing that heat treatment has been shown to increase the size of PbS nanoparticles [52].

After annealing, we can estimate the length of the rGO layers in the range of a few hundred nm [Fig. 15(f)]. Overall, the size of the PbS nanoparticles evolves from 10-15 nm to 20-40 nm after annealing. The hybrid material with its porous structure exhibits a large surface-to-volume ratio, offering channels for efficient and rapid gas diffusion, which certainly enhances the potential of our hybrid material for gas detection applications [12].

III.1.2. Dispersive Energy Spectroscopy (EDS)

The EDS was used to complete the information observed by the SEM to determine the chemical composition of our hybrid material, we performed the EDS analysis on the final sample, i.e. the samples that first underwent heat treatment and then chemical reduction on a SiO₂/Si substrate. **Figure 16** shows the EDS spectrum of the hybrid material after surface treatment. The presence of silicon from the substrate is observed; oxygen from either the substrate or the GO; carbon from GO, lead and sulfur from PbS.

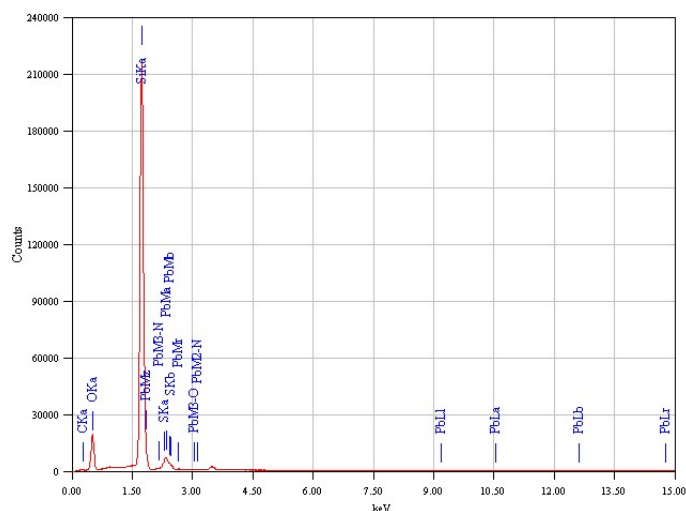


Figure 23 : EDS spectrum of hybrid material (PbS/rGO).

Table III presents in detail the chemical composition in mass and atomic percentages of each element present in the material.

Table IV : Chemical composition of the hybrid material after surface treatment

Element	Mass %	Atomic %
C	4.74	9.55
O	22.48	34.01
Si	63.25	54.51
S	1.29	0.97
Pb	8.84	0.96

From this table, we can see that the atomic percentage of silicon and oxygen is 54.51% and 34.01% respectively. This strong dominance of silicon and oxygen suggests that the layer of deposited material on the substrate is relatively thin. It is also noted that the atomic percentages of sulfur and lead are practically identical, which constitutes a good sign of a successful formation of stoichiometric PbS nanoparticles. The elementary mapping of PbS shows an identical spatial distribution of lead and sulfur atoms as we can see in **Figure 17**. This confirms that we have a homogeneous distribution, further supporting the formation of PbS particles. The dispersion effect and uniformity play a major role in the response properties of the gas [53].

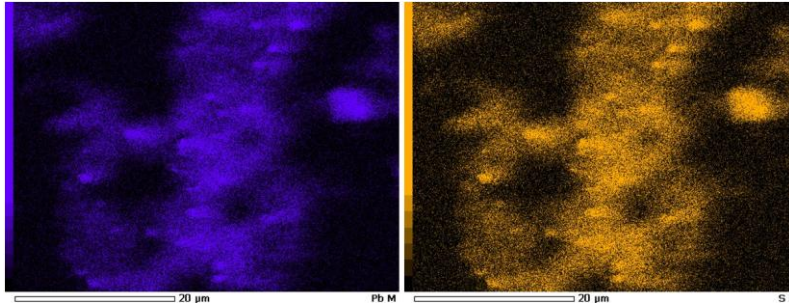


Figure 24 : Elementary PbS Mapping – Pb on the left and S on the right (thermal annealing plus chemical reduction).

III.1.3. X-ray diffraction (XRD)

X-ray diffraction analysis was used in this work to determine the nature of the different phases and the size of the crystallites. **Figure 18** shows the diffractogram of the PbS/GO composite material before treatment (thermal annealing and chemical reduction) obtained after data was processed by the profex software, subsequently by OriginPro2024 software.

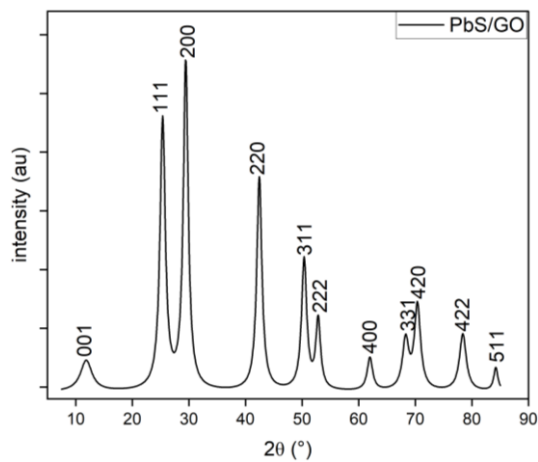


Figure 25 : Diffractogram of the hybrid material PbS/GO

In this figure, we can see that the peaks are well defined, indicating a good crystallinity of the material [43]. We see a first low intensity diffraction peak around $2\theta = 11.64^\circ$. According to the literature [44], this peak represents the diffraction plane of (001) of the hexagonal structure of GO. Due to a low intensity of the GO diffraction peak, the synthesized material

(PbS/GO) has a similar PbS pattern, so the phase corresponds to galena [54] [55]. According to the ICDD PDF-4 card No. 00-005-0592 the angles 26°; 30.1°; 43.1°; 51°; 53.5°; 62.6°; 68.9°; 71°; 79°; 84.9° correspond respectively to the diffraction planes (111), (200), (220), (311), (222), (400), (331), (420), (422), (511) of PbS [55]. These results corroborate those found in the literature for pure PbS [55]. Based on these results, the average size of the PbS crystallites was first determined by Profex software and estimated to be 7.5 nm. To confirm this value, we applied Scherrer's equation [45] to the dominant and sharp peaks that indicate the crystallinity of the particles that make up our material.

$$D_{hkl} = \frac{K\lambda}{B_{hkl} \cos \theta}$$

Where, D_{hkl} is the size of the crystallites, K is Scherrer's constant, λ is the wavelength of the X-ray, B_{hkl} is the half-height bandwidth of the considered diffraction peak (FWHM), θ is the half-angle of deflection, h , k and l are the Miller indices for each diffraction plane.

Table IV shows the size in nm (D_{hkl}) as a function of the diffraction angle (2θ), the width at mid-height for an excitation wavelength $\lambda=1.54\text{\AA}$. The values of the diffraction angle considered are those of the most intense peaks shown in **Figure 18**, i.e. 26°, 30.1°, 43.1°, 51°, 53.5°. For these values, the results show that the size of the crystallites varies between 7.21 and 7.83 and the average for these values is 7.6nm.

Table V : crystallite size of raw material.

PbS/GO	2θ (°)	hkl	FWHM	D_{hkl} (nm)	Average crystallite size (nm)
	26	200	1.06	7.83	
	30.1	220	1.12	7.47	7.6
	43.1	311	1.15	7.59	
	51	222	1.15	7.78	
	53.5	400	1.27	7.21	

This average crystallite size of 7.6 nm corresponds to the value found after an anisotropic refinement of the raw data with the profex software, which was 7.5 nm. Note that we cannot compare these results with those found by the SEM because the SEM shows an estimate of the morphological size while the XRD gives the size of the crystalline core (size of the crystalline core inside the particle). As mentioned in Chapter II, if we had XRD after surface

treatment, we would expect a shift in the diffraction peak due to $2\theta = 11.64^\circ$ at $\sim 25^\circ$ corresponding to the 001 and 002 planes respectively [56].

III.1.4. Raman spectroscopy

To identify the presence of GO and to evaluate the effect of surface treatment (thermal annealing and chemical reduction) on the hybrid material, we performed Raman spectroscopy, which is a technique commonly used for the characterization of carbonaceous nanomaterials, including graphene and its derivatives. **Figure 19** shows the full Raman spectrum of the raw material (a), after thermal annealing (b) and after chemical reduction (c) while (d), (e) and (f) show the deconvolution spectra of (a), (b) and (c) respectively, on a smaller range of wavenumber.

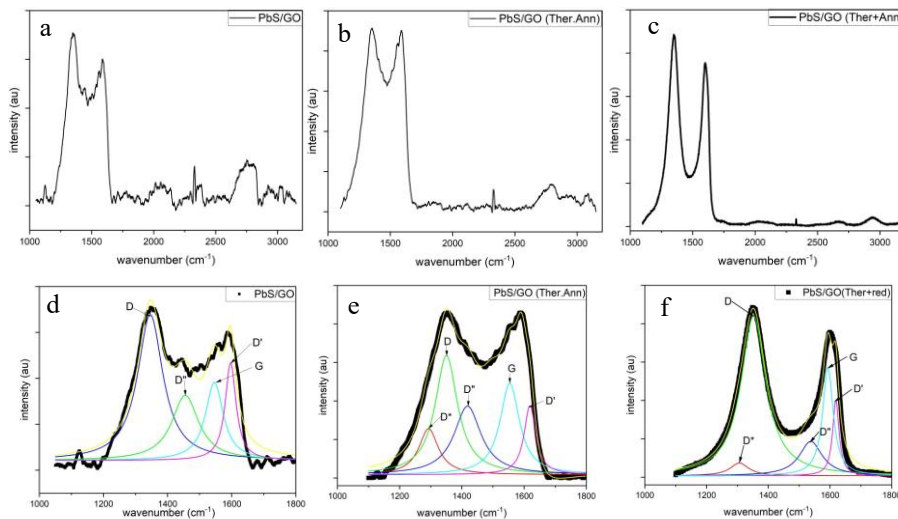


Figure 26 : Raman spectrum of PbS/GO (a) and (d); Heat-treated PbS/GO (b) and (e); Heat-treated and chemically treated PbS/rGO (c) and (f).

According to **Figures 19** (a), (b) and (c), the spectrum shows peaks at the wavenumbers 1345cm^{-1} , 1588cm^{-1} and 2749cm^{-1} for (a); 1351cm^{-1} , 1590cm^{-1} and 2775cm^{-1} for (b); 1351cm^{-1} , 1550cm^{-1} and 2770cm^{-1} in (c). These spectra reveal that we find roughly the same peak components between PbS/GO, heat-treated PbS/GO and heat-treated PbS/rGO followed by chemical reduction. According to the literature, these are the graphene D bands for the peak around $\sim 1350\text{cm}^{-1}$, G for the peak around $\sim 1590\text{cm}^{-1}$ and 2D for the peak around $\sim 2750\text{cm}^{-1}$

[57]. These peaks are characteristic of graphene and its derivatives. The D band centered around 1350cm^{-1} is usually attributed to the disorder induced in the GO sheets [4]. The G-band around 1590cm^{-1} tells us about the vibrations in the plane of the sp^2 lattice of carbon atoms [9]. The very low intensity 2D band around 2750cm^{-1} allows to estimate of the number of GO layers by the I_{2D}/I_G ratio. However, the intensity of the 2D band being very low, the I_{2D}/I_G ratio cannot be estimated efficiently from the full spectrum because the values are close to those of the noise level. Dividing the average noise level by the peak G gives a value of less than 2. According to the literature, a lower I_{2D}/I_G ratio 2 corresponds to several layers [4]. The differences between these spectra are therefore in the intensities and shape of the peaks.

For the raw PbS/GO, a high intensity of the D-band compared to the G-band is observed, reflecting a high density of defects, not only due to the presence of the different oxygenated functional groups, but likely also to the presence of nanoparticles as observed on the morphology. After thermal annealing at 180°C , there is a strong variation in the D band and a change in the shape of the two bands. This suggests a reorganization of the structure of the material. In the literature, the thermal reduction of GO is generally obtained above 200°C and increases with temperature [10]. The thermal annealing having been carried out at 180°C , we can therefore say that there was no reduction of the GO. It is therefore clear that there has been a structural reorganization and not a reduction in the GO.

For the raw PbS/GO, a high intensity of the D-band compared to the G-band is observed, reflecting a high density of defects, not only due to the presence of the different oxygenated functional groups, but likely also to the presence of nanoparticles as observed on the morphology. After thermal annealing at 180°C , there is a strong variation in the D band and a change in the shape of the two bands. This suggests a reorganization of the structure of the material. In the literature, the thermal reduction of GO is generally obtained above 200°C and increases with temperature [48]. The thermal annealing having been carried out at 180°C , we can therefore say that there was no reduction of the GO. It is therefore clear that there has been a structural reorganization and not a reduction in the GO.

On the other hand, for the sample that first underwent the heat treatment up to 180°C and then a chemical reduction (spectrum (c)), we find that the D, G and 2D bands are more intense and well defined, but with an even higher I_{2D}/I_G ratio than that of the heat-treated sample. We can say that because of chemical reduction; new graphitic domains have been created with smaller sizes than those present in the raw material and the heat-treated material.

In order to make a more in-depth analysis, we made a deconvolution of the D and G bands between 1000cm^{-1} and 1800cm^{-1} into several Lorentzian components, in a similar way as ref. [5], namely: the D band around 1350cm^{-1} for the structural defects the D band around 1590cm^{-1} for the graphitic structure, the D' band around 1620cm^{-1} for the secondary defects, the D* and D'' around 1250cm^{-1} and 1500cm^{-1} respectively for disorders related to sp^3 configurations and topological defects [48]. Note that the position of the peaks is kept constant. The spectra obtained are shown in **Figure 19** (a), (b) and (c).

The spectrum of the raw material (PbS/GO) has a superposition of peaks reflecting a high density of defects as discussed above. For the heat-treated PbS/GO spectrum, a superposition of peaks is also observed, but with a clear improvement in the graphitic order (G-band). Finally, for the heat-treated material followed by a chemical reduction, there is a significant refinement of the bands, whatever their nature, confirming a good organization of the structure of the material as observed by the SEM. This refinement of the bands and the increase in their intensity is characteristic of the restoration of the sp^2 network [5].

Observations and analyses of Raman spectra suggest that the combined strategy of heat treatment followed by chemical reduction is particularly effective in restoring the graphitic structure of our material which tends to have the same structure as that of rGO after the same treatment. Figure 6 shows the spectra of rGO and PbS/rGO.

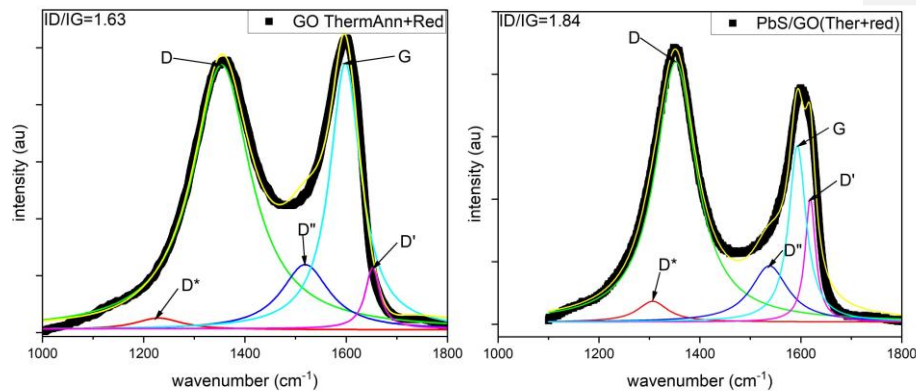


Figure 27 : Raman spectrum of rGO (left) and PbS/rGO (right) after surface treatment.

The spectra collected on the two samples, namely GO and PbS/GO, after heat treatment followed by chemical reduction, have the same appearance and the position of the D and G

peaks are different with the appearance of secondary peaks with different intensities. In Raman spectroscopy, the analysis of the intensity ratios of the D and G bands provides additional elements on the defects present in the rGO. For this reason, we have calculated the intensity ratio I_D to I_G for rGO and PbS/rGO which are respectively 1.83 and 1.64. This is to be expected because the PbS nanoparticles are attached to the surface of the GO, thus increasing the rate of disorder in the structure.

III.2. ELECTRICAL MEASUREMENTS

To understand the electronic behavior of the hybrid material, an analysis on the variation of resistance as a function of temperature was performed. The measurements were performed in two different systems: Progressive heat treatment from 350K to 450K followed by continuous cooling down to 315K in the vacuum annealing chamber, and a continuous decrease in temperature from 340K to 30K and finally a continuous increase in temperature from 17K to 290K in a small closed-cycle cryostat. In all cases, resistance measurements are made in a 2-contacts configuration.

III.2.1. Heat Treatment

To determine the type of electrical transport in the hybrid material, a treatment was carried out by gradually increasing the temperature from 300K to 450K (line at the top in Fig. 21) followed by continuous cooling down to 315K (bottom curve in Fig. 21). We observe the electrical resistance of the material began to decrease very significantly gradually with temperature in the range 420-450 K (see Figure 21), where we stopped the heating ramp.

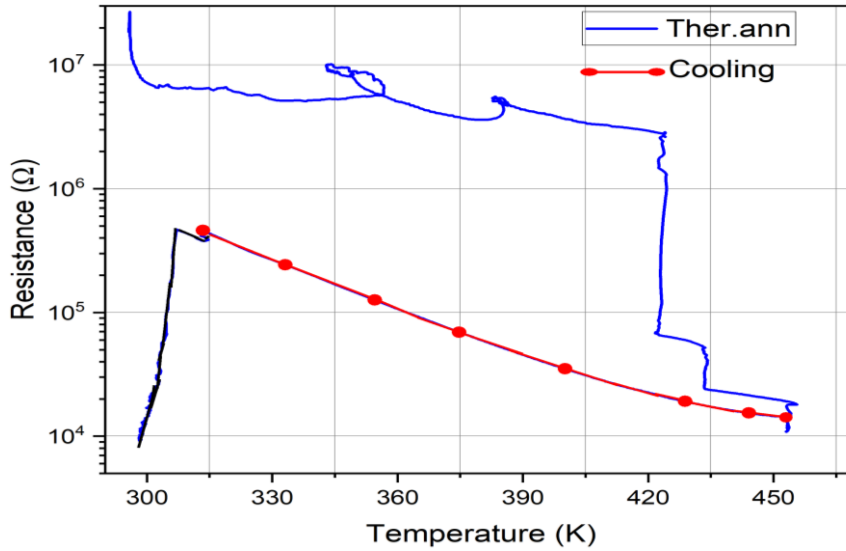


Figure 28 : Variation in the strength of the hybrid material as a function of temperature

In figure 21, we can see several nonlinear discontinuities on the curve at different stages during the heating stage. At first glance, this discontinuity is the result of structural modifications of the hybrid material as observed on SEM but is also related (at lower temperature) to desorption of gases in the UHV environment (e.g. water). In the cooling stage, the resistance increases quite smoothly when the temperature decreases, down to 315 K (nb: below that temperature, the chamber was opened, so there is a contribution of adsorption of gas from the atmosphere). This is typical of the behavior of a semiconductor material [12]. Thus, it is necessary to determine the activation energy and the dominant transport mechanism in the hybrid material given that a semiconductor is characterized by its gap energy or its activation energy [13]. To do this, a restricted range of the temperature is applied according to Arrhenius' law [58]:

$$R = R_0 \cdot \exp(E_a / 2K_B T)$$

Where R is the resistance, R_0 is the pre-exponential factor, E_a is the activation energy, K_B is the Boltzmann constant, and T is the absolute temperature. Applying the logarithm on both sides, we obtain:

$$\ln R = \ln R_0 - E_a / 2K_B T$$

By plotting the curve of $\ln R$ as a function of $1/T$, we determine the activation Energy E_a . The resulting curve is show in **Figure 22**.

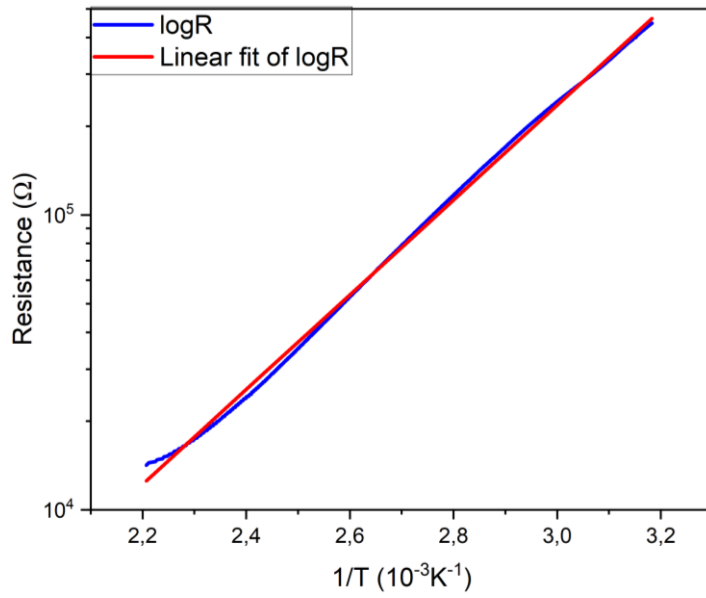


Figure 29 : *Determination curve of the activation energy and the transport mechanism at high temperature.*

From this curve and by linear adjustment, we deduce that the slope of the linear curve corresponds to $E_a/2K_B$. This leads to an energy activation value $E_a \sim 0.13\text{eV}$ compared to 4.9 eV for the GO which is insulating.t. The correlation coefficient $R_2 = 0.9987$ indicates a very good quality of linear fit. Compare

III.2.2. Continuous decrease in temperature

To optimize the performance of the hybrid material in the design of gas sensors, it is crucial to understand the electronic conduction mechanism. The goal is to control the operating temperature of the manufactured sensor. To do this, we measured the dependence of the resistance with respect to a wide temperature range in the decreasing direction from 340K to 30K and in the increasing direction from 15K to 290K. The resulting curves are shown in **Figure 23**.

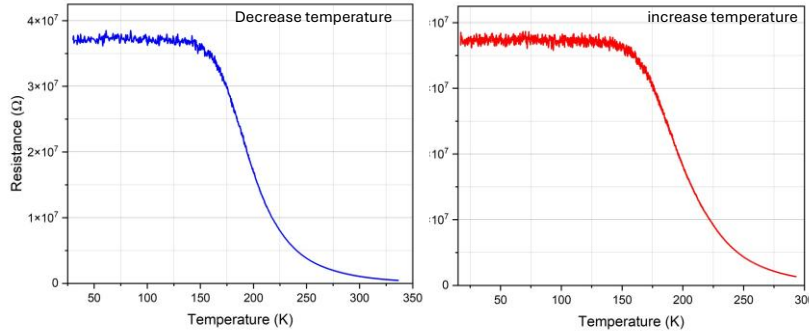


Figure 30 : Resistance as a function of temperature of PbS/rGO plotted in the range of 340K to 30K (blue) and 15 to 290K (red).

From these curves, the resistance behaves in the same way with respect to temperature as during the cooldown of a semiconductor. It is also observed that at very low temperatures ($T < 180K$), the resistance is independent of the temperature: this is very likely to be related to the impedance limit of the measurement system, since the resistance of the sample is becoming very large – it is therefore a measurement artefact. Since several models have been proposed in the literature for disordered materials like ours, we also tested our material on these different models to identify the one that best describes the transport mechanism in our material. These are:

- Arrhenius model which is typical of semiconductors where the resistance or expression is [59]

$$R = R_0 \exp\left(\frac{-E_g}{2kT}\right) \longleftrightarrow \text{Log}R = f\left(\frac{1}{T}\right)$$

- Mott's model for disordered materials where conduction is by VRH [60]

$$\text{Log}R = f\left(\frac{1}{T^{0.5}}\right) \longleftrightarrow 1D$$

$$\text{Log}R = f\left(\frac{1}{T^{0.33}}\right) \longleftrightarrow 2D$$

$$\text{Log}R = f\left(\frac{1}{T^{0.25}}\right) \longleftrightarrow 3D$$

- Shklovskii-Efros model for materials with state density deficiencies around the Fermi [15] level due to Coulomb interaction

$$\text{Log}R = f\left(\frac{1}{T^{0.5}}\right).$$

It has been demonstrated in sections III.1.1, III.1.3 and III.2.1 that the synthesized hybrid material (PbS/rGO) is not only disordered, but also semiconductor. For this reason, all

models were tested to determine the dominant transport mechanism. **Figure 24** shows the results obtained after linear adjustment for each of the models mentioned above.

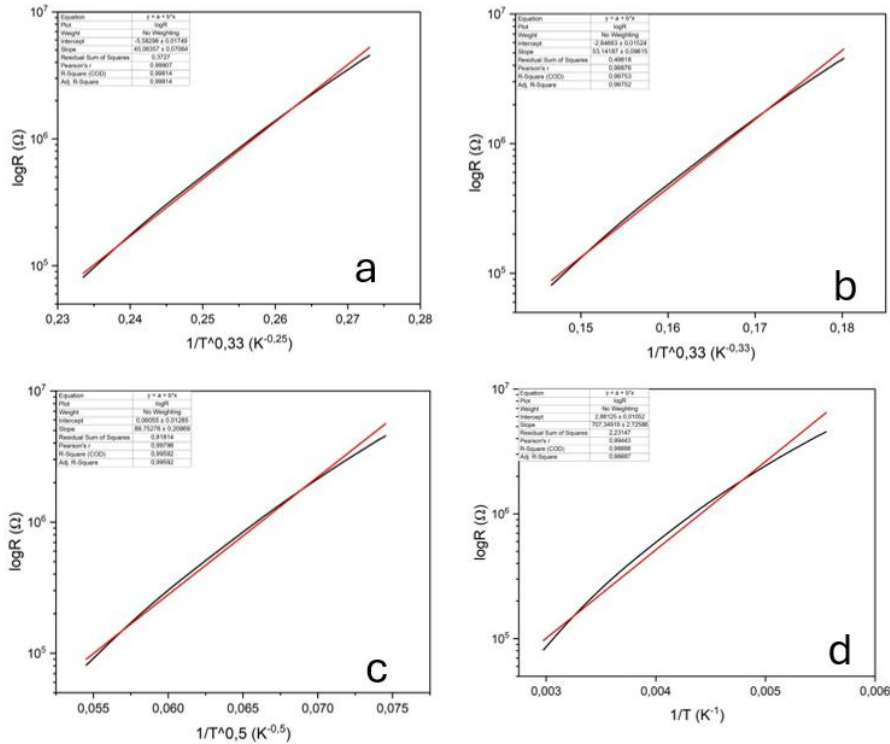


Figure 31: $\log(R)$ as a function of T^{-x} with $x=1/4, 1/3, 1/2, 1$

From this figure and with the statistical analysis on the correlation coefficient, the best correlations ($R^2 > 0.998$) are obtained with Mott's model VRH-2D and VRH-3D (a et b), i.e. a different slope from the one found at higher temperature. This means that the dominant conduction mechanism between room and low temperature in PbS/rGO is variable jump transport in a disordered system formed by semiconducting particles, with a high probability of VRH in 2D or 3D. For the manufacture of gas sensors, a VRH-type conduction indicates that the sensor can operate efficiently at room temperature [61] due to a reasonable range of resistance, to be compared with most metal oxides used in commercial gas sensors which must be heated to operate. Operating at room temperature is a big advantage in terms of energy consumption.

Conclusion

In this chapter, the focus was on the determination of the physicochemical and electronic properties of the synthesized hybrid material, namely PbS/rGO. For this, we used SEM, EDS and Raman spectroscopy for structural properties, while electronic properties were studied by electrical measurement during heat treatment or cryogenic cooling. The SEM results showed that the structure is porous with the rGO sheets decorated by the PbS nanoparticles, as X-ray diffraction showed a strongly crystalline material. The study of the electrical properties revealed a semiconductor-like material with an activation energy of about 0.13eV, as well as a dominant transport mechanism of the Mott-type, i.e. VRH-2D or VRH-3D. Thus, the results obtained are very satisfactory and promising for the manufacture of gas sensors, which is the main objective of our work.

CHAPTER IV: RESULTS AND DISCUSSION OF GAS SENSING PERFORMANCE

As the main objective of this work is to manufacture a NO₂ sensor from a hybrid material PbS/rGO, we present in this chapter the results of the performance test of the manufactured sensors to compare their performance to that of existing NO₂ sensors. The results obtained and discussed in Chapter III allowed us to confirm the formation of the synthesized hybrid material with a promising physico-chemical structure for gas sensing. These results are used in this chapter to discuss sensor performance such as sensitivity, response time, recovery time, reversibility, reproducibility, and stability.

IV.1. OBSERVATION

In this work, we used a substrate containing 8 pixels, schematized in Figure 10 (a), constituted by interdigitated metallic electrodes. The results of the gas test performed on this substrate are given in Figure 10 (b). It shows the variation in resistance as a function of time for 7 out of 8 pixels of the substrate (P2 to P8) that reacted after exposure of the sensor to NO₂ at 500ppb.

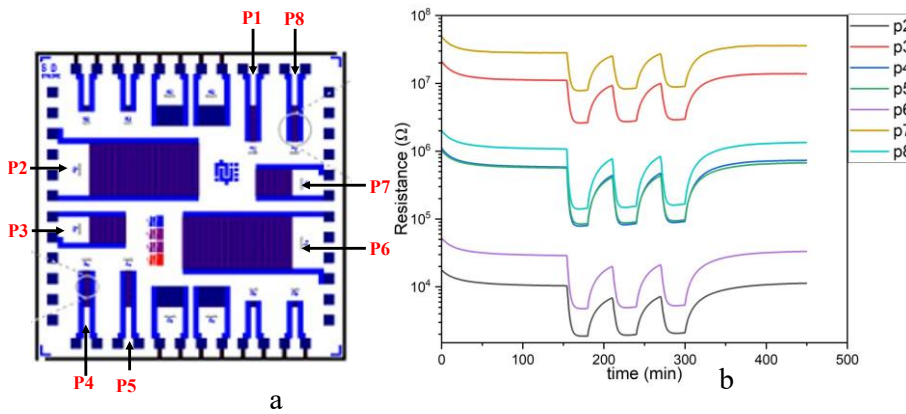


Figure 32 : (a) Schematic of the substrate (the blue regions are metallic), each active “pixel” being indicated as PX (where X = 1 to 8). (b) variation of the resistance of the sensor as a function of time for 8 different pixels – the onset of significant variations of resistance coincides with the introduction of 500 ppb in the atmosphere during 30 min. (b) variation of the resistance of the sensor as a function of time.

In Figure 25 (b), we see that the 7 pixels that reacted to NO₂ have a very similar behavior, marked by a decrease of resistance with a similar relative variation upon the introduction of NO₂. We also notice that pixels with the same device layout (example P2 and

P6) show resistance values of the same order of magnitude ($\sim 2 \times 10^4$ Ohm for P2 and $\sim 5 \times 10^4$ Ohm for P6). Overall, the 7 sensitive pixels give results over 3 orders of magnitude depending on the pixel chosen ($\sim 10^4$ Ohm for P2 and P6; $\sim 10^6$ Ohm for P1, P4 and P5; and $\sim 10^7$ Ohm for P3 and P7). The resistance is therefore a function of the electrode chosen. Having multiple signals on the same substrate is a major advantage for gas sensor design because multiple outputs can be measured simultaneously to confirm in real time whether the gas is present in the atmosphere.

On the other hand, **Figure 25 (b)** also shows that during the first 150 minutes an airflow is injected into the chamber, the resistance is constant for all pixels. At the 150th minute, the resistance drops sharply over 3 to 4 minutes, marking the presence of NO_2 in the atmosphere. After this time, we reach the saturation of the charge carriers, marked by a stabilization of the resistance over the rest of the injection time, i.e. 26 to 27 minutes. The drop in resistance during the injection time of NO_2 is because NO_2 is an oxidizing gas, which acts as an electron acceptor. It therefore adsorbs on the surface of the nanocomposite, then captures the electrons from the lattice matrix. This increases the accumulation of charge carriers (holes), resulting in a significant decrease in the electrical resistance of the sensor [62]. As for stabilization, it would correspond to the maximum concentration of the gas. This would block all the active sites needed for adsorption at 500ppb [1]. The mechanism of NO_2 detection can therefore be summarized as follows:

NO_2 binds to the surface by forming ionized complexes and then captures electrons via interactions with active sites present on PbS/rGO [22]. This assumes that, somehow, nanoparticles/rGO can form a continuous conductive layer. After 30 minutes of NO_2 injection, the injection is stopped, and the resistance gradually increases to its initial value during the NO_2 desorption phase. In other words, a complete phase corresponds to 30 minutes of NO_2 injection followed by 30 minutes of desorption. To attest to reversibility (alternation of phases between adsorption and desorption), the cycle is repeated three times, and the same behavior is observed for all pixels, although the reference resistances are different.

IV.2. SENSITIVITY

The sensitivity of a sensor is the percentage change in the resistance of the sensor when exposed to gas (NO_2) compared to its resistance in the absence of gas. It is defined by:

$$S = \frac{R_{\text{gas}} - R_{\text{air}}}{R_{\text{air}}} \times 100\%$$

Where S is the sensitivity, R_{gas} is the resistance after the sensor is exposed to NO_2 , R_{air} is the resistance in the absence of NO_2 .

Figure 26 shows the results of the sensor's sensitivity as a function of time for the seven pixels that reacted to NO_2 .

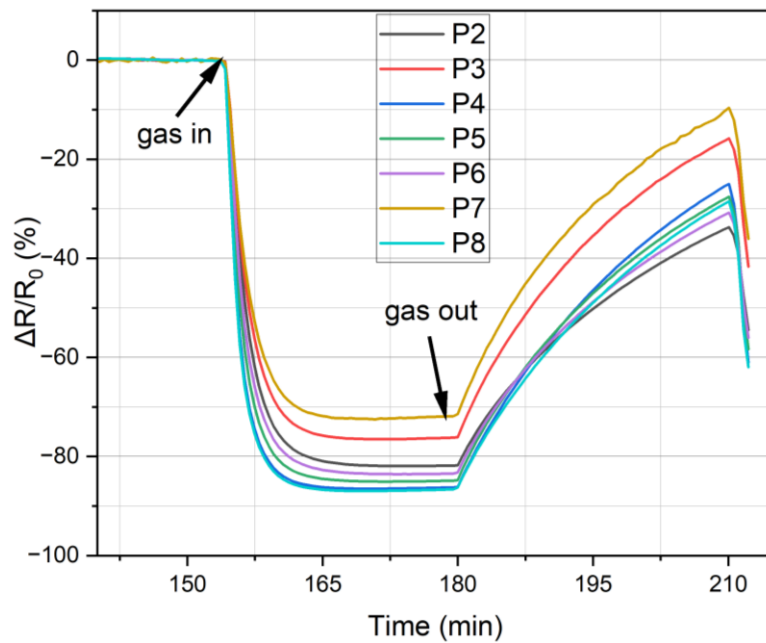


Figure 33 : PbS/rGO sensor response after exposure to 500ppb NO_2

The sensor sensitivity values are between 81 and 86% for pixels P2, P4, P5, P6 and P8. As for the two remaining symmetrical pixels, namely P3 and P7, their sensitivities are 72% and 76%, respectively. Even though some pixels have the same device layout (P3 and P7), they have different sensitivities of about 4%. This may be due to inhomogeneity during the deposition of the hybrid material. To our knowledge, no scientific work in literature using the same substrate has shown such sensitivity to NO_2 , but also the number of signals for a single substrate.

IV.3. RESPONSE TIME

Under experimental conditions, we defined 30 minutes of exposure under NO_2 . This time is sufficient to understand the phenomenon of adsorption. Immediately after the

introduction of the gas, we observe a sudden decrease in electrical resistance, followed by a period during which the resistance remains constant over the exposure time. Considering that the response time of a sensor is required for the variation of the resistance to reach 90% of its total evolution during an exposure to 500ppb of NO₂, the response time (T_{res}) is equal to Δt ($t_2 - t_1$) as indicated in **Figure 27** for a chosen pixel (P4). We use the same principle on all pixels and find an average response time of ~ 4.6 min. After this time, all active sites of the material are occupied.

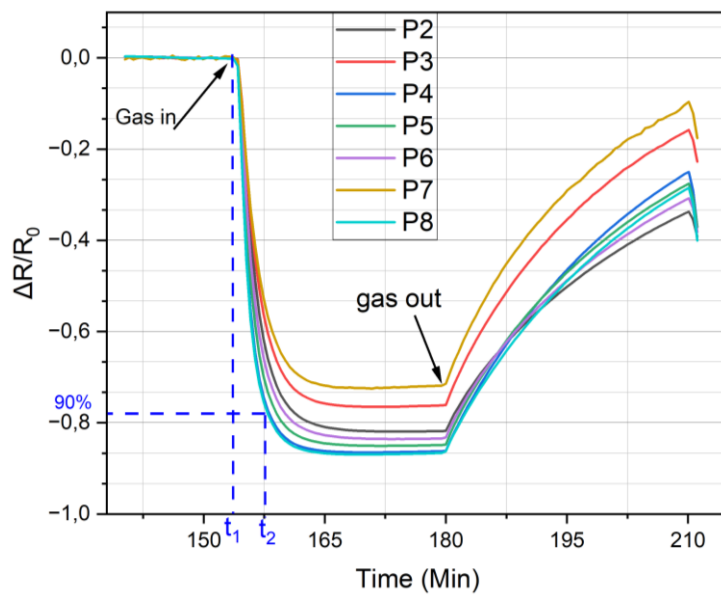


Figure 34 : Determination of the response and recovery time of the sensor at 500ppb of NO₂.

For the technological development of NO₂-specific sensors, such exposure times are long. Therefore, optimization of our sensor parameters to further reduce such response times is necessary.

IV.4. RECOVERY TIME (T_{rec})

Recovery time is the time it takes for the signal to return to 90% of its initial value after stopping gas exposure. This time is determined here after the third exposure or L because the resistor returns to a plateau value for some pixels (3 and 7) as shown in Figure 12. this recovery time $T_{rec} = t_4 - t_3$ is estimated at ~ 41 min for the Pixel 7. For others, pixel it is difficult to determine due to a poor choice of baseline.

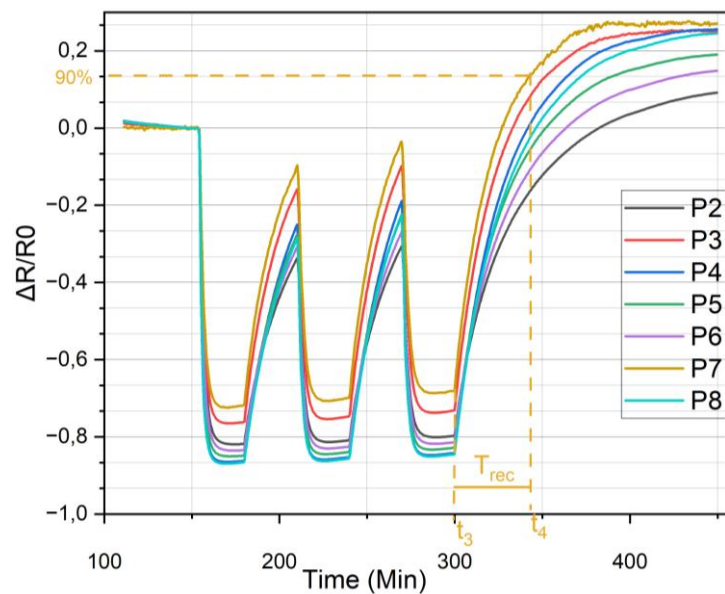


Figure 35 : Illustration of the determination of the recovery time.

With reference to the bibliography, vacuum NO_2 desorption tests have been considered to validate the possibility of NO_2 desorption [1]. In our case, the return to the baseline of the sensor was ensured by the passage of an airflow. Thus, under these conditions, the recovery time at room temperature is well is not ensured after 30 minutes. This is why we cannot determine this time after the first two exposures, because one of us chose 30min of exposure to NO_2 and 30min of air) It would be necessary to use a heater to accelerate desorption.

IV.5. REPRODUCIBILITY

The aim is to check whether the sensitive surface has been chemically modified due to the oxidizing nature of NO_2 . Thus, once the sensor is stabilized under air, we carried out a NO_2 detection for 30min and then we put the sensor back under air flow for 30min. This test was repeated three times. The results obtained are presented in **Figure 29**.

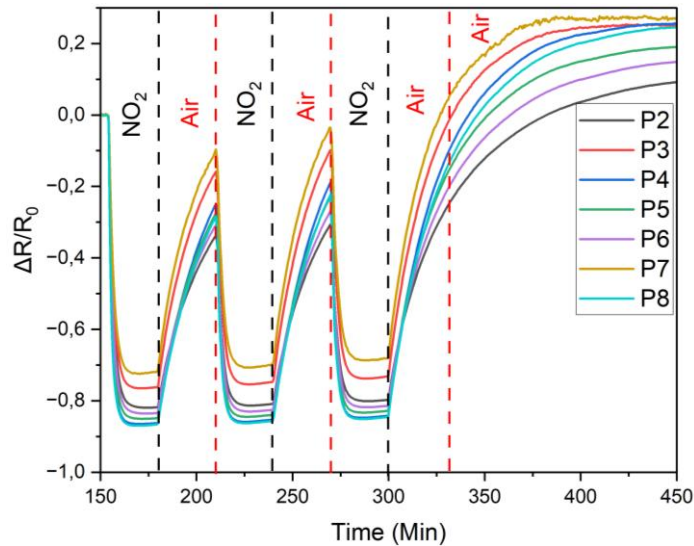


Figure 36 : Reproducibility of the sensor over three exposure cycles

Based on these results, the sensor retains its initial response amplitude without attenuation despite baseline changes for three continuous cycles under the same conditions. this deviation from the baseline could be explained by the fact that all gas molecules remain adsorbed on the surface of the sensitive layer, as shown by Yubing Sun [62], or by the existence of high adsorption energy sites where the molecules desorb very slowly [63]. Despite this drift, the sensor remains reproducible over all cycles.

IV.6. ENVIRONMENTAL FACTORS: TEMPERATURE AND HUMIDITY

To ensure the operation of our sensor in real conditions, it was exposed to room temperature and humidity between 53 and 62%. **Figure 30** shows the curves of temperature (a) and humidity (b) as a function of time. For a chemiresistive gas sensor, temperature and humidity are the factors that typically affect the sensor's response to either adsorption/desorption kinetics or material strength.

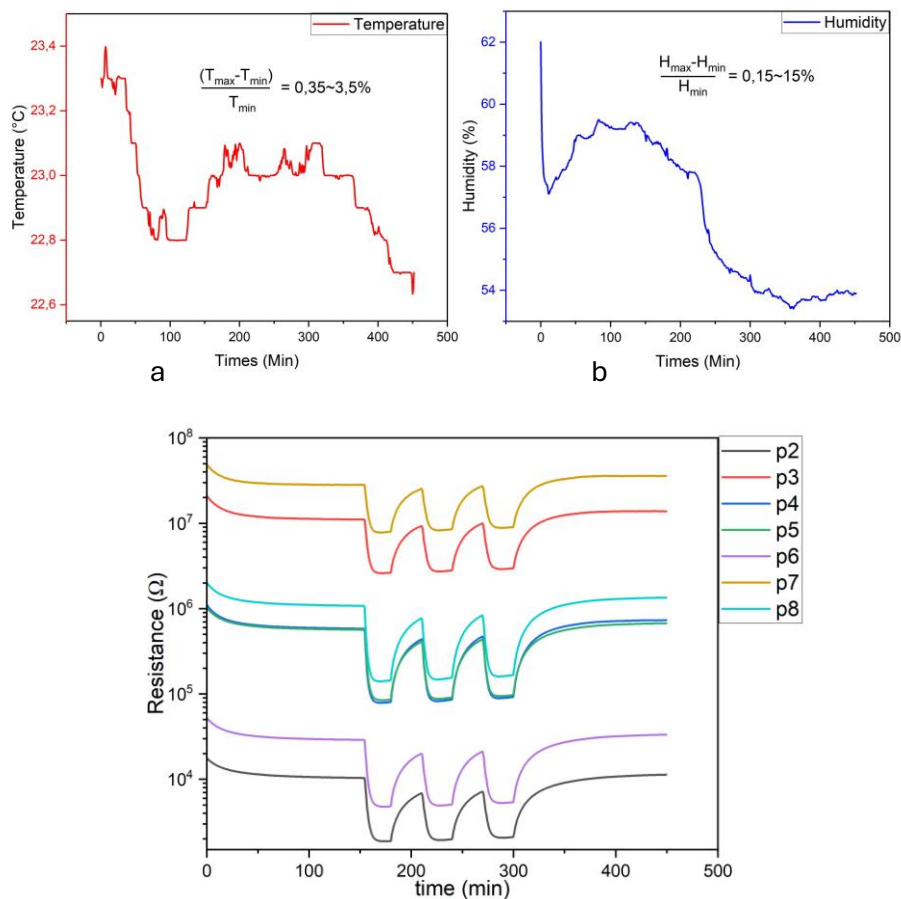


Figure 37 : Factors influencing the sensor response: (a) Temperature, (b) Humidity, (c) Response.

For our sensor, the influence of this parameter can be described in three steps: Before exposure, during exposure and after exposure of the sensor to NO_2 .

Before exposure (0-150 minutes): From Figure 30 (a), (b) and (c), there is a small variation in sensor resistance despite a variation in temperature from 23.3 to 22.9°C and the humidity varies over a much larger range initially (starts above 62% and falls to ~ 57 %, so this is a relative variation of about 10%). This may be related to the initial drop in resistance that is observed between 0 and 50 minutes.

During exposure (150-350 minutes): When the sensor is exposed to gas, there is a sudden drop in resistance to all pixels but no correlation with any of the small temperature or humidity change. This constitutes proof that the observed variation in resistance is only related to the presence of NO₂.

After exposure (350-450): After the three series of exposure of the sensor to NO₂, the resistance returns close to the initial resistance while the temperature and humidity vary in the same way (22.7 to 23.4°C) and humidity varies only around 54%. We can conclude that the variations in resistance are triggered by the same event as the presence of NO₂. To check that it works in "extreme" environments, we will do the tests at 90% humidity to confirm or not the influence of these parameters on the operation of the sensor.

IV.7. STABILITY

To assess the long-term stability of the sensor, we performed the tests on three periods: 7 days (section IV-1), 21 days and 180 days. It should be noted that the sensor was stored in an ambient atmosphere in a box.

IV.7.1. Sensor performance after 21 days

After manufacturing the sensor, the gas test was carried out for 7 days and the performance was determined as previously presented. After 21 days, the same test was performed under the same conditions on the same sample. **Figure 31** shows the results of the change in resistance as a function of time.

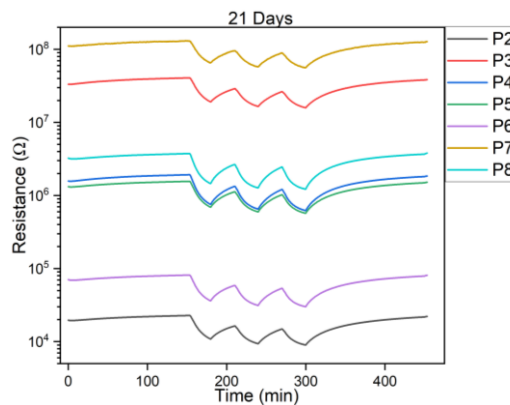


Figure 38 : 21 days sensor response (same conditions as the test in Fig. 10: 500 ppb NO₂ injected during 30 min, separated by 30 min recovery).

As before, we notice that these are the same pixels that react, proof that the sensor remains stable. On the other hand, we observe an increase in the baseline resistance, i.e. by a factor of 10 on all pixels on the one hand, and a modification of the shape of the curves on the other hand. It is also noticeable that the injection of the gas gradually decreases the resistance and no longer reaches saturation during the exposure time. This could be due either to an oxidation of rGO thus reducing its conductivity, or to a PbS oxidation, or to the beginning of degradation of the sensitive material. We also notice, as for the first test, that pixels with the same layout have the same orders of magnitude of basic resistance. That is $5 \cdot 10^4$ Ohm for P2 and P6, 10^6 Ohm for P4, P5 and P8 and 10^8 Ohm for P3 and P7. The different characteristics of the sensor deduced from this curve are sensitivity (**Figure 32**), response/recovery time (**Figure 32**) and reversibility (**Figure 33**).

- **Sensitivity**

Figure 15 shows the results of sensitivity, response and recovery time

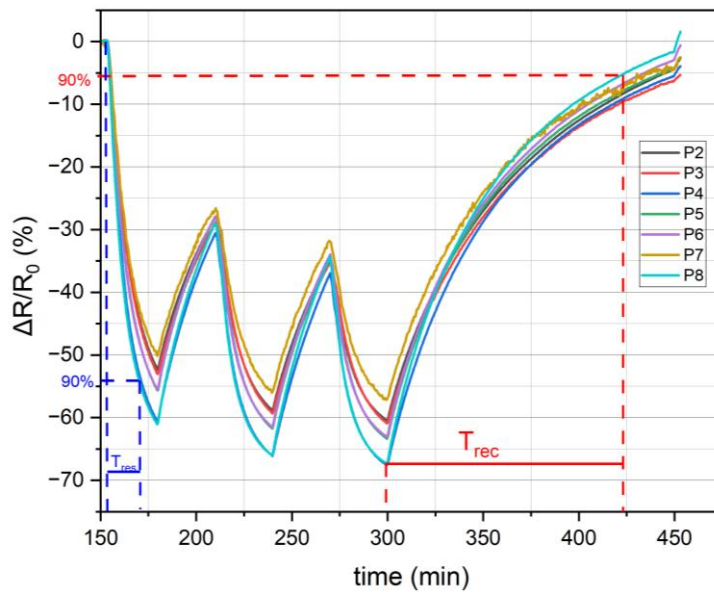
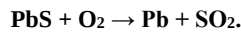
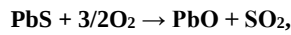
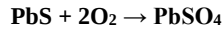
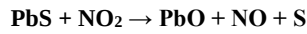


Figure 39 : Sensitivity, Response and Recovery Time

From Figure 32, we notice, the sensitivities are 52, 53, 61, 55, 55, 50, 61% for pixels P2, P3, P4, P5, P6, P7 and P8 respectively. This is lower than the sensitivities obtained in the first test. This can either be due to a degradation of the support by alteration of the PbS-rGO

interface, so the consequence is the loss of synergistic effect, or due to a partial oxidation of the PbS by forming oxides that are less active than the PbS according to the equations [64]



- **Response time**

From the response curve shown in **Figure 32**, we can see that the response time is 17min for pixels 4 and 8, is longer compared to the same pixels at 7 days as well as the recovery time which is even longer (>100min). It is possible that the interaction between NO₂ and PbS/rGO leads to an irreversible chemical reaction. This phenomenon has been observed a lot in the literature by the detection of NO₂ by the nanocomposite ZnO/rGO [27].

- **Reproducibility**

To study the reproducibility of the sensor's response, we carried out three measurement cycles for the same injection conditions, i.e. 30 minutes of exposure, 30 minutes to the airflow. The results obtained are presented in **Figure 33**.

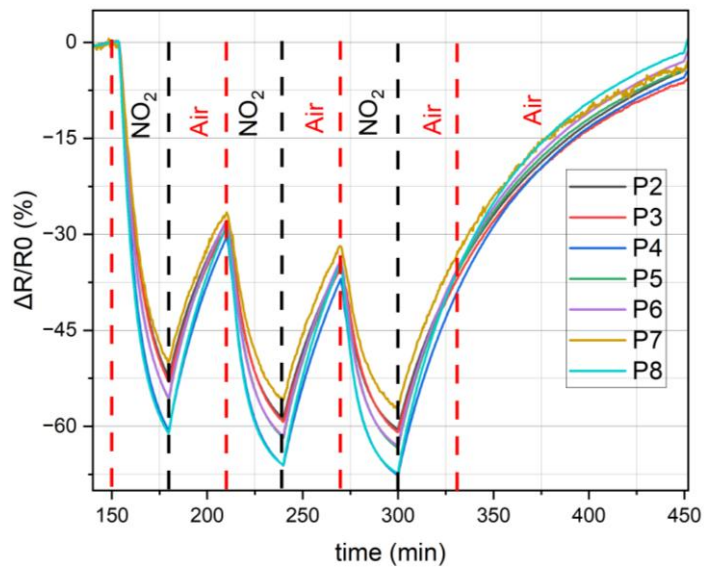


Figure 40 : Sensor reproducibility at 21 days

From **Figure 33**, we can see that the curves show the same relative variations despite the problem of returning the response to the initial value. We can nevertheless emphasize that the sensor remains reproducible with good performance with some drifts such as the response and recovery time that have become longer.

IV.7.2. Sensor performance after 180 days

In **Figure 34**, we plot the sensor response as a function of time under 500ppb of NO₂.

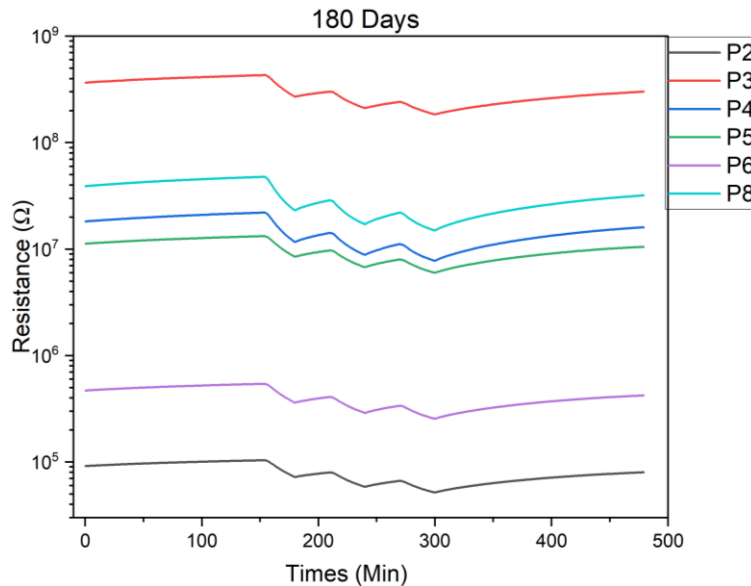


Figure 41 : 180-day sensor response

In **Figure 34**, several observations are made: first, an increase in the baseline resistance. This could mean a change in the electrical properties of the sensitive material. Unlike the other pixels, pixel 7 initially shows an increase in resistance after injecting NO₂. This suggests a different detection mechanism and therefore the origin could be the formation of parasitic oxides such as PbO which unlike PbS which is a P-type semiconductor, PbO is an n-type semiconductor [26] and therefore in the presence of an oxidizing gas such as NO₂, there will be a decrease in charge carriers [6]. There is also a small variation in the signal on the other pixels. No pixel returns to its baseline. Starting from the curve in **Figure 35**, the performance of the sensor is deduced from **Figure 36** which follows from it.

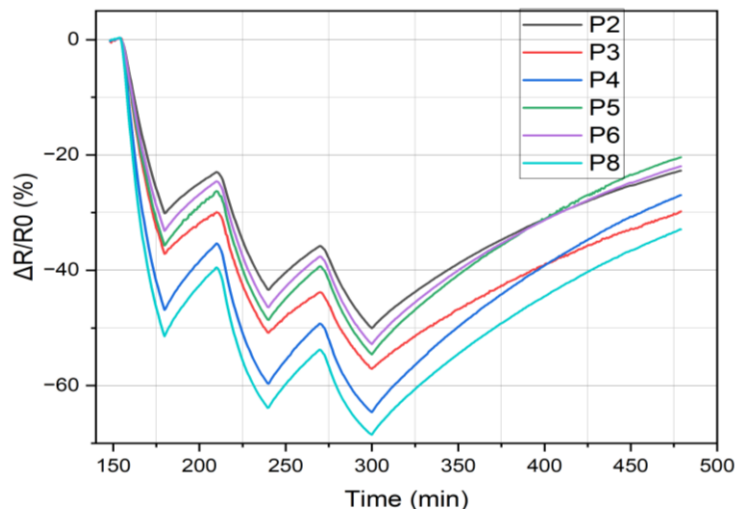


Figure 42 : 180-day sensibility

Here we notice that exposure time strongly influences the sensitivity of the sensor, and the baselines are different due to incomplete recovery. After the first exposure, it is difficult to determine the sensitivity of the sensor. For this we have deduced the sensitivity and the response time which are 29, 35, 47, 34, 33 and 50% corresponding respectively to P2, P3, P4, P5, P6 and P8 for sensitivity and a response time of about 25min for all pixels. Figure 18 summarizes the evolution of the sensitivity of each sensor pixel over 180 days. It should be noted that pixel 7 is omitted because of the unexpected behavior.

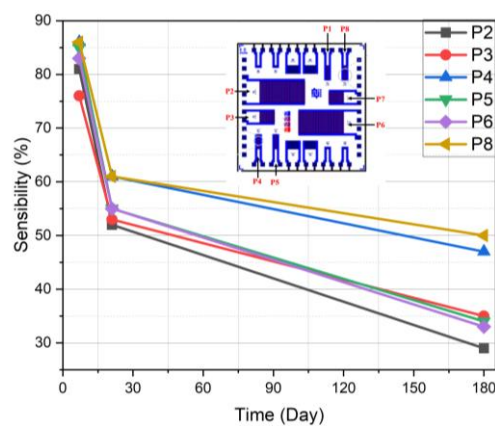


Figure 43 : Temporal analysis of the sensor's sensitivity

In **Figure 36**, there is a general and significant decrease in sensor sensitivity over time, but the data is variable on a pixel-by-pixel basis, within an initial range of ~10% (~75-85% sensitivity after 7 days) increasing to ~ 20% after 180 days (~ 30 to ~50% sensitivity). We also notice that the Pixel 8 has the best sensitivity regardless of the number of days. We also notice that Pixel 2 is affected more overtime.

IV.8. COMPARISON OF OUR RESULTS WITH OTHER HYBRID-BASED NO₂ SENSORS FROM rGO

In this part, we present a comparison between the results obtained by the hybrid material PbS/rGO and other NO₂ sensors based on hybrid materials from rGO. To our knowledge, no NO₂ sensor using the same method of manufacturing the sensor based on hybrid PbS/rGO nanomaterial has been described in the literature. On the other hand, a highly sensitivity PbS/rGO-based CH₄ sensor has already been manufactured [28] [65]. **Table V** compares the results in terms of operating temperature, detection concentration, sensitivity as well as response and recovery times of our PbS/rGO-based sensors with existing sensors.

Tableau VI :

Matériel	Operating Temperature	Concentration	Sensitivity	Response time/recovery	Référence
SnO ₂ /rGO	60	1ppm	12.7%	-/-	[21]
ZnO/rGO	RT	100 ppm	47,4%	6,2/15,5 min	[27]
MoS ₂ /G	200	10ppm	69%	0.7/0.9s	[66]
CuO/rGO	RT	350ppb	25%	10.5/-s	[67]
PbS/rGO	RT	500ppb	72-86%	210s/21min	Current work

From this table we notice that the SnO₂/rGO composite was tested under 1ppm of NO₂ at 60°C. Its sensitivity of 12.7% is very small compared to our sensor at 500ppb (72-85%). In [4], a graphene-based NO₂ sensor modified by indium oxide is manufactured showing a high sensitivity with a concentration of the order of ppm at 75°C. Even though the concentration for the test is higher, the sensor consumes more energy than ours (75°C compared to our sensor which operates at room temperature) [17]. In the [66] a MoS₂/G based sensor operating at 200°C at 10ppm is presented with a sensitivity of 69% and a response/recovery time of 0.7/0.9 shorter than that obtained in the current work. This is not a surprise because at their work they tested

at 10 ppm and in the current work we tested at 500 ppb. The increase of the reaction/recovery time is expected at lower concentrations.

even though our sensors have a high sensitivity and consume less power. By the same logic, a CuO/rGO-based sensor, operating at room temperature but with low sensitivity, is manufactured. Compared to our sensors, the latter is faster in terms of sensitivity and more advantageous in terms of response time. In view of the above, it should be noted that the results obtained on our NO₂ sensors are generally better than the state of the art on rGO-based composites, and this for low gas concentrations than those used in the literature (ppm) despite the longer response and recovery time than those existing

GENERAL CONCLUSION

The aim of this work was the fabrication of a chemiresistive gas sensor based on a hybrid PbS/rGO material for the detection of NO₂ at very low concentrations. To achieve this goal, the hybrid material was first synthesized based on the reagents (PbNO₃)₂, Na₂S and GO. We used SEM, Raman spectroscopy and XRD to characterize its structure, and the study of the variation of resistance as a function of temperature also allowed us to determine its electronic properties. The three structural characterization Methods mentioned above showed that:

- The synthesized hybrid material is porous with the PbS nanoparticles distributed non-uniformly on the rGO.
- The size of the crystallites varies between 7 and 15nm; Chemical heat and reduction treatments effectively reduce the defects of the synthesized material.
- As for the electronic properties, the material is semiconductor with an activation energy of 0.13eV and the dominant transport mechanism is of the MOTT VRH-2D and VRH-3D types.

As these properties were deemed appropriate for the rest of our work, we then fabricated our sensor by depositing the hybrid material on the electrodes interdigitated by the drop casting method. For the performance test, gas measurements made at room temperature and with a relative humidity of 63% to 53 showed a sensitivity of 75% to 85% for 500ppb of NO₂; an average response time of about 4.6min and an average recovery time of 41min. We have also verified that this sensor is reproducible. The 180-day stability tests also showed acceptable performance over 21 days but gradual degradation beyond this time. For example, the rate of degradation of sensitivity is 10% on day 21, 25% on day 180. As for the response time, which is 4.6 minutes on the 1st day, it increases to 8 minutes on the 21st day and 17 minutes on the 180th day.

Although these preliminary results are promising in terms of sensitivity, stability and reproducibility, they also show some limitations of our sensor compared to the state of the art. Mainly, the response and retrieval times obtained are longer (4.6min for this work compared to 30s for the state of the art [9]). Thus, for the continuation of this work, it will not only be interesting to optimize the manufacturing parameters of our sensor (improvement of the synthesis of the hybrid material), but also to conduct more complete tests such as the selectivity test, the detection limit and the high humidity TES that we could not do for various reasons (lack of logistics, lack of time, etc.). This optimization will aim to further reduce response and recovery time. The extreme humidity test will allow us to investigate their influence on the



performance of the sensor. It would also be interesting to study the selectivity of the sensor in an environment interfering with several gases.

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