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A wearable flexible graphene biosensor for environmental toxicity monitoring

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Toxic gases are responsible for the loss of many human lives around the world, which is increasing every year. Toxicity can have various biological aspects on the human body. The exposure to its gases leads to harmful consequences for the organism, which leads to metabolic reactions and even death. For this purpose, the initial step is to detect these gases with miniature flexible structures and solid progressed estimation methods using a simulation software tool. The studied sensor is based on the frequency characterization of an RF Planar Resonant Structure, in which the active element is a patch of radiating graphene printed on a polyimide film (Kapton). The objective of this work is to use our Graphene-Kapton sensor for non-invasive testing applications. In our case, the device is tested to detect and recognize several dangerous and toxic gases such as Fluorine azide (F2N), Hydrogen Iodide (HI), Nitrogen (N2), Methane (CH4), and Carbon monoxide (CO). The simulation results indicate that the Graphene-Kapton flexible sensor exhibits an important sensing performance. The sensor is able to detect all the tested gases with a good sensitivity depending on each gas. As well as, the sensor shows a high sensitivity (0.1± 0.01)* 106 [ppm]-1 (0.1 [ppt]-1) of methane (CH4) gas with detection limit of (9±0.1) *10-6 ppm (9 ppt).

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1. Introduction

Nowadays the high death rate from toxic gas dissipation is increasing day by day. The first example that comes to mind is carbon monoxide (CO), which causes a slow and silent death, and spares neither children nor adults [1-2]. Even more alarming is that CO is one of the dangerous toxic gases among many that are colorless and odorless. Toxicity can have various biological aspects on the human body, exposure to its gases leads to harmful consequences for the organism which leads to physiological and metabolic reactions and even death, the most important effects and clinical signs of intoxication concerning each organ are presented in Table 1 [3-4-5-6]. Therefore, the development of a multitude of fast and reliable sensors to detect different toxic gases has become a necessity, many research for gas sensors of different materials and types were been initiated to discover the sensor that combines the fastest response time, good reproducibility, stability, and lower cost [7,8,9].

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Table 1 .effects and clinical signs of intoxications in relation to each organ or system [1-3-4-5].

Clinical signs and effects	Systems and organs
Irritation	eye, skin, digestive system, respiratory system
Corrosion	eye, skin, digestive system, respiratory system
Abnormal Heartbeat	cardiovascular system
Depression	central nervous system
Neuropathy	peripheric nervous system
Breathlessness	respiratory system
Carboxyhemoglobinemia	blood system
Miles	very dark urine or blood in urine

The sensing of gas molecules is critical to environmental monitoring. To overcome these problems, it is important to look for access arrangements. To this end, the initial step is to detect these gases with miniature structure and solid progressed estimation methods. Broad investigations have been performed on the gas detecting issue as a result of its wide applications in assorted fields: environmental protection, toxic and non-toxic gas detection, emission control, and observing of the air contaminations gases. Especially, it is a significant assignment to detect and identify toxic gases [10]. Electronics (bio) sensors are considered as delicate identification devices that have pulled in huge consideration of mainstream researchers inferable from their simple design, quick reaction, favourable portability, high affectability, and selectivity in complex networks [11].

Flexible sensors are getting huge interest in the gas sensing industry in the last years due to their portable electronic products, potential applications in wearable and their great capacity of adaptation to small and irregular surfaces. Several techniques have been developed for their fabrication, such as screen and inkjet printing [12-15]. At times the flexibility of the sensor takes precedence over its capacity when we see all the advantages it offers, in this work we aim to combine flexibility and excellent sensing capacities.

Recently, graphene is considered to be a promising material for gas detection because its physical and electronic properties are strongly affected by the adsorption of foreign molecules. Graphene-based materials have also been investigated in flexible sensor technologies and have become one of the most readily used materials in wearable sensing technology due to their unique properties of lightweight, ultrahigh carrier mobility, good environmental stability, and robust mechanical flexibility [16].

In particular, the detection of industrial toxic gases such as CO, Nitric dioxide (NO_2), and Ammoniac (NH_3) is very important for many industries. As a basic segment of wellbeing checking frameworks and the interface to the human body, sensors, including wearable and implantable sensors, can identify and quantify different signals or examinations with high explicitness and affectability [17]. For sure, because of the mechanical crisscross between the human skin (delicate natural tissues) and traditional inflexible graphene-based sensors, mechanical flexibility is notably essential for these invasive or non-invasive sensors. Additionally, a few requirements including biocompatibility, dependability, strength, comfort, miniaturization, and expenses, and befouling should also be considered [18].

In the present study, the graphene-Kapton biosensor is a miniaturized sensor for a high value of conductivity, and more flexibility and processability. The aim of this study is to provide a concise using a purpose model simulation in order to test the detection of the most harmful gases to human health such as CO, Ozone (O3), Fluorine azide (F_2N), Hydrogen Iodide (HI), and Methane (CH4).

2. Experimental

2.1. Sensor model presentation

In this section, a Planar Resonant Structure (PRS) is used to explain the principle of operation of the sensor. The PRS contains four elements: a radiation patch, a dielectric substrate, a ground plane, and a transmission feed which is shown in Fig.1.

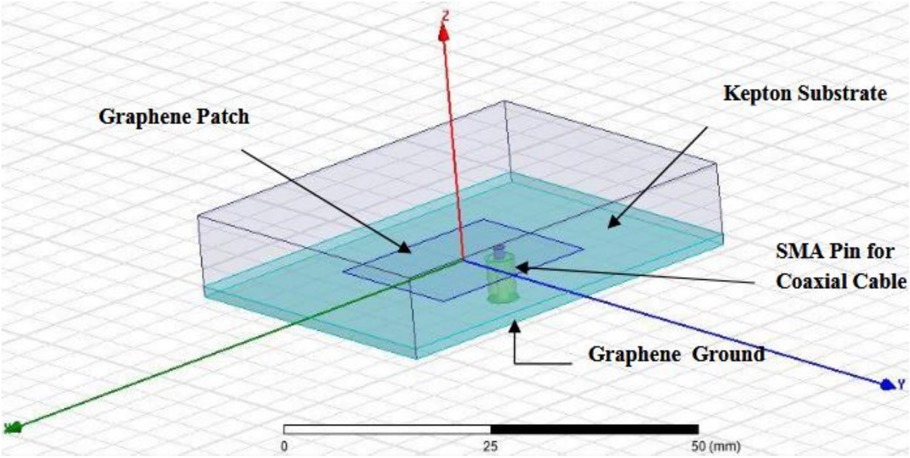

Fig. 1. Grephene-kapton-sensor-structure.

As we mentioned before the sensor is made with two materials, for the conductive one, we opted for graphene for the patch and the finite ground plane with 2.29mm*1.9mm and 5mm*4mm as dimensions respectively. The Kapton substrate is chosen as dielectric material with 0.125mm of thickness, and 5mm, 4mm for length and width respectively. The coaxial feed was placed at -0.575 mm from the x-axis.

2.2. Gas sample modelling

2.2.1. Mathematical approach

Our work has for objective to make a simulation with the EM HFSS software of a single PRS with pure air in order to extract the resonant frequency and the reflection coefficient (S_{11}). These parameters are taken as reference values when the sensor is exposed to pure air. Then, we add a superstrate over the patch which is the tested gas sample to be detected. The last step is to calculate the unknown dielectric parameters (permittivity and loss factor) of a gas sample with an empirical calculation.

This empirical approach we have proposed consists in the following mathematical development. Starting from the shift on the measured resonance frequency compared with the empty resonance of the wearable biosensor. The effective permittivity is obtained by using the following formula [19]:

$$\epsilon_{\mathrm{eff}} = \varepsilon_{0\mathrm{eff}}\left[1 + \frac{2\Delta f}{f_1}\right] \tag{1}$$

with:

$$\varepsilon_{0eff} = \frac{\varepsilon_{sub}+1}{2} + \frac{\varepsilon_{sub}-1}{2\sqrt{1+12\frac{h}{W}}} \tag{2}$$

f_1 is the resonance frequency of the sample fundamental mode,
Δf is the frequency shift between the reference frequency and the gas sample frequency,
W and h are the width of the patch and the thickness of the substrate respectively.

When $W / h >> 1$ and the metal thickness negligible, the effective permittivity can be calculated as suggested in [19]:

$$\varepsilon_{eff} = \frac{\varepsilon_{sub}+\varepsilon_{sup}}{2} + \frac{\varepsilon_{sub}-\varepsilon_{sup}}{2} \cdot \frac{1}{\sqrt{1+12h/W}} \quad (3)$$

ε_{sub}, ε_{sup} are respectively the substrate and the superstrate permittivities.

Then, the superstrate permittivity is deduced by the relation:

$$\varepsilon_{sup} = \frac{2\epsilon_{eff}-\epsilon_{sub}(1+A)}{1-A} \quad (4)$$

with:

$$A = \frac{1}{\sqrt{1+12h/W}} \quad (5)$$

The loss factor can be calculated using the quality factor and is given by the following formula [19]:

$$\mathrm{tg}\,\delta = \frac{1}{RC\omega_0} = \frac{L\omega_0}{R} = \frac{1}{Q} = \frac{\epsilon''}{\varepsilon'} = \frac{\Delta f}{f_0} \quad (6)$$

3. Results and discussion

In this section, we present the results that we obtained during this work, in order to discuss them and come out with relevant conclusions. The simulations were made on electromagnetic (EM) simulation software based on the finite element method (HFSS 13.0). We tested our sensor on pure air, to observe his reflection coefficient (S_{11}) between frequency ranges from 79 GHz to 81 GHz, the result is presented in Fig.2, which was better than expected -57.6550 dB compared to what has been presented in previous works [20-21].

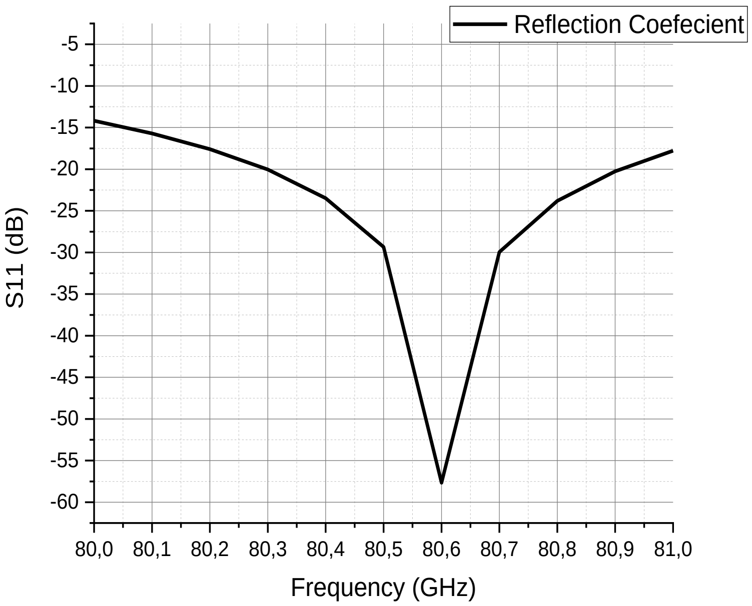

Fig. 2. Biosensor-Graphene-kapton-response-in-pure-air.

Then, we introduce the namely toxic gases in the air-box as: NO, CO_2, F_2N, O3, and CO to test if it is a change in the shift in the sensor's reflection coefficient S_{11} in the presence of gas by comparison with pure air. In Fig.3 we present the variation of the S_{11} parameter as a function of frequency for the graphene-kapton biosensor toward air and the toxic tested gas. The frequency is ranged from 79 GHz to 86 GHz to cover all reflections coefficient S_{11}. As can be seen from the figure, we can observe more precisely that the sensor is able to detect all the test dangerous gas.

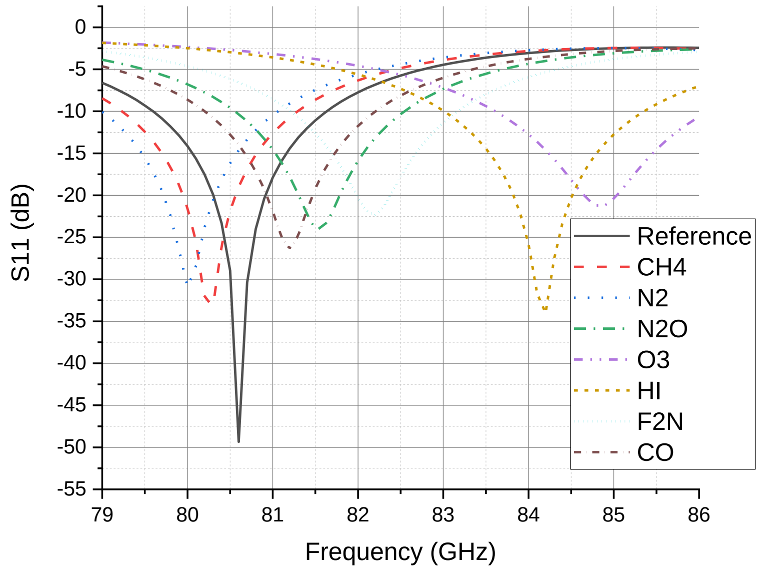

Fig. 3. Variation-of-the-S_{11}-parameter-as-a-function-of-frequency-of-the-graphene-kapton-biosensor-in-environment-infected-by-toxic-gases.

In Table 2, we present the value of the S_{11} parameter, the frequency, and the quality factor of the graphene-kapton biosensor in air and toxic gases. It is clearly visible in (Fig.3 and Table 2) that the shifts in value of S_{11} is well appeared in the presence of the detected gas and the pure air (reference). As well as, we can note also that all the sensor parameters are affected differently for each toxic gas. We can conclude that, our sensor up to detect the presence of various toxic gases mentioned previously in this paper with excellent results compared to the literature [22-23].

Table 2. Variation of the S_{11} parameter as a function of frequency and the quality factor of the graphene-kapton biosensor in environment infected by toxic gases.

Gases		Parameters			
Gas name	Gas signe	S_{11}(dB)	f(GHz)	Δfr/fr (%)	Q Factor
Pure air	*	-49.3367	80.600	*	
Carbon monoxide	CO	-26.5778	81.200	0.7444	1.66
Ozone	O_3	-21.2202	84.100	4.3424	0.28
Fluorine azide	F_2N	-22.3674	82.200	1.9851	0.62
Hydrogen Iodide	HI	-34.0298	84.200	4.4665	0.27
Nitrogen	N_2	-30.9427	80.000	0.7444	1.66
Nitrous oxide	N_2O	-24.0299	81.500	1.1166	1.11
Methane	CH_4	-33.0896	80.300	0.3722	3.33

The usual way to make gas sensors is to use the sensitivity of the material. For that many materials have been used beyond graphene [24-27], and very good sensors have been developed with heterostructures for ultrasensitive gas detection with the effect of van der Waals semiconductors to improve the sensitivity and–detection limit [28-33] of the gas sensing. In this work, we wanted to propose an original method, breaking the gas detection codes and using the electromagnetic fields and their sensitivity instead of the material's sensitivity itself, where the sensor detects changes in the electromagnetic field when a new element is integrated.

The resonant bandwidth of the PSR can be defined as the range of resonant frequencies at a given return loss, e.g., at −10 dB. In theory, all of these radiation parameters can be used to convert a physical quantity (strain, temperature, pressure, pH level, the concentration of an aqueous solution, etc.) into a measurable radiation parameter which leads to a resonance frequency shift. For this suggest, the sensitivity of our flexible sensor is defined as the rapport of a resonance frequency shift (Δf_r) when the sensor is tested towards gas and a resonance frequency (f_r) in pure air.

In order to investigate our sensor performances, we have chosen to make several simulations to detect methane (CH_4) gas. In Fig.4, we have presented the variation of the sensibility towards different gas concentrations of CH_4. The device has a good sensing capability for low gas concentration. The sensor exhibits 5.7 responses towards 27 10^{-6} ppm of CH_4 gas. As well as, the flexibles gas sensor detects methane gas with a detection limit of 9 10^{-6} ppm. The literature reports many graphene based on flexible substrates [10-13]. However, our Graphene-Kapton sensor detects the lowest gas concentration with a good response.

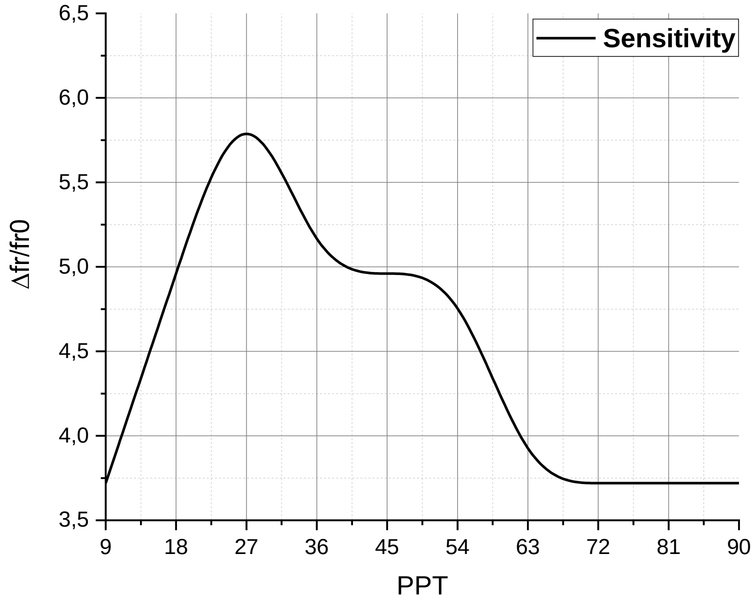

Fig. 4. Sensor's sensitivity curve for Methan (CH_4).

One of the keys to the development of gas biosensors is high selectivity. Sensor sensitivity is when it is specifically sensitive to one gas or other compounds that may be present in the testing atmosphere. For this case, we have exposed in Fig.5 a histogram of the toxic gases detected by our sensor. We can confirm that the response of our graphene-kapton sensor is related strappingly and selectively to the gas nature present in the atmosphere. And can be concluded that, this kind of device is generally proposed as electronic nose.

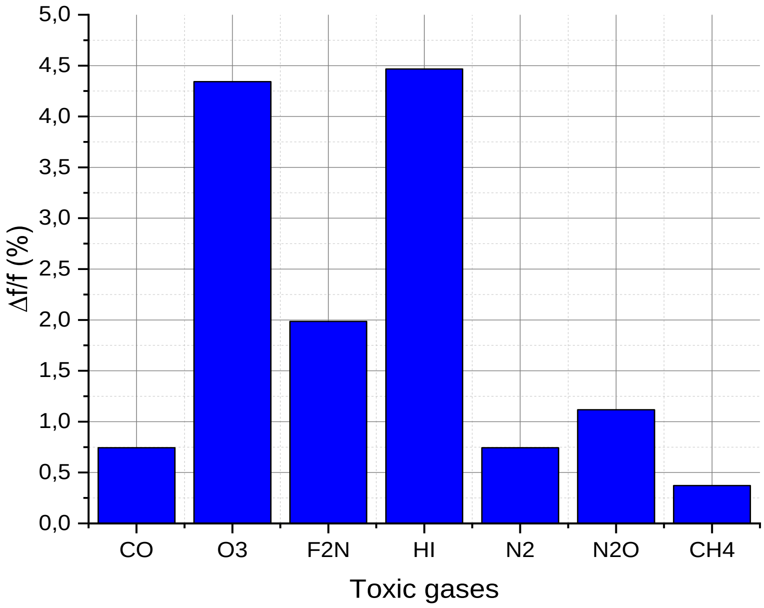

Fig. 5. Toxic gases histogram.

4. Conclusion

The main objective of this work was to discuss the simulation results presented by graphene-Kapton's biosensor to judge its efficiency for the detection of various toxic gases. Our PRS Graphene-Kapton used for non-invasive testing applications for environmental monitoring gives good results for sensing gases and selectivity of several dangerous gases. The effect of the relative frequency ($\Delta f_r/f_r$) and the S_{11} are the predominant parameters for the determination of the sensing performances of our biosensor. The detecting CH_4 gas by our device exhibits a good sensor response at a lower gas concentration as reported in the literature with a detection limit of about (9±0.1) $*10^{-6}$ ppm. The outcomes given by graphene-Kapton's biosensor in the detection and the identification of different poisonous gases are fulfilling and clear, which drives us to infer that the sensor introduced in this study suggests a selective device, precise, and dependable in bio-environmental applications.

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