

1 Lossy Mode Resonance Based 1-Butanol Sensor in the Mid- 2 Infrared Region

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ABSTRACT

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The utilization of nanometric Graphene Oxide / Polyethyleneimine (GO/PEI) bilayers deposited onto SnO₂-coated CaF₂ planar waveguides significantly enhances the sensitivity of Lossy Mode Resonances (LMR) based devices for gas sensing applications. LMR generation in the mid-infrared region, which also contributed to achieve better sensitivities, was accomplished with the aid of fluorinated (CaF₂) planar waveguides. LMR wavelength shift was studied as a function of the number of GO/PEI bilayers. In the particular case of 10 bilayers of GO/PEI, the sensitivity of the device to 1-butanol was 70.4 pm/ppm, which increased by a factor of 5 compared to the device without GO/PEI bilayers. The GO/PEI sensor was also sensitive to other alcohols, like 2-propanol, but it showed negligible sensitivity to other gases, such as CO₂, NH₃ or C₂H₂. The cross sensitivity with temperature was tested at temperatures of 20, 100 and 180 °C during water vapor measurement (1723 ppm), showing that the sensor performance was not affected by the temperature fluctuations.

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9 **1. Introduction**

10 Lossy mode resonances (LMR) may occur when a thin film is deposited on a waveguide fulfilling some
11 conditions. Specifically, if the optical characteristics of the thin-film material match the conditions for LMR
12 generation, some of the modes will shift from being transmitted through the waveguide to being transmitted
13 through the thin film [1]. Basically, the necessary conditions for the LMR to occur are: the real part of the
14 permittivity in the thin film has to be greater than zero and its module greater than both, the module of its
15 imaginary part and the module of the imaginary part of the material surrounding the film [2, 3]. The result is
16 the generation of an attenuation band in the spectrum of the optical signal transmitted through the system,
17 known as LMR. LMRs can be obtained with both transverse electric (TE) and transverse electric magnetic
18 (TM) polarizations, and it is possible to generate multiple attenuation bands in the transmitted spectrum
19 depending on the thickness of the thin film and the refractive index (RI) of the materials. It is possible to
20 describe the behavior of external parameters monitoring the central wavelength of the optical resonance [1].

21 LMRs have been successfully obtained using optical fiber waveguides and thin films of several metal
22 oxides, such as indium tin oxide (ITO) [1], indium oxide [4], tungsten oxide [5], tin oxide [6], zinc oxide [7],
23 aluminum-doped zinc oxide [8], copper oxide [9] and iron oxide nanostructures combined with tin oxide
24 [10]; also, polymeric coatings [11] have been used to generate LMR. Recently, planar waveguides combined
25 with thin film materials have been successfully proposed as an alternative candidate for the fabrication of
26 LMR based devices [12, 13]. Planar waveguide approach is less brittle than optical fiber, facilitates the thin
27 film fabrication processes generally intended for planar surfaces and enables a greater variety in the number
28 of materials available compared with that of optical fiber.

29 LMR effect in fiber optics has demonstrated to be successful for the detection of ammonia [14], humidity
30 [15, 16, 17, 18, 19, 20, 21, 22, 23], ethanol [24] and hydrogen sulfide [25]. Recently, planar waveguides have
31 also been proven successfully for acetone, water vapor and ethanol detection [26]. In this latter work, the

32 material used to generate the LMR was graphene oxide (GO) deposited onto cover slides utilized as
33 waveguide [26].

34 Some of the above-mentioned studies [7, 10, 19, 22] use nanostructures, such as nanorods, to maximize the
35 surface area in direct contact with the gas target and, therefore, improve the sensor's performance. In other
36 works, a sensitive coating containing relevant functional groups is used for the detection of some specific
37 gaseous compounds, as it was the case of GO [24, 26].

38 GO, a non-stoichiometric compound and precursor of graphene materials, contains various types of oxygen
39 moieties, including epoxy, hydroxyl, carboxylic and carbonyl groups. The hydroxyl and epoxide functional
40 groups are located on its basal plane, and carbonyl and carboxyl functionalities on its edges (according to the
41 variations of the Lerf-Klinowski model [27, 28], the most accepted model in the scientific literature). GO has
42 demonstrated its suitability in combination with the LMR effect to design optical sensors (fiber optics and
43 planar waveguides) for the detection of ethanol, acetone, humidity, and ammonia, amongst others [24, 25].
44 However, it is worth mentioning that all these studies have been focused on the visible region of the spectrum,
45 where the sensitivity is lower than that of the mid infrared region (MIR). Moreover, many strong absorption
46 lines can be found in the MIR wavelength region associated to rotational and vibrational changes of
47 molecules [29], which shows significant potential for a new generation of devices in this region targeting
48 applications for breath analysis in medical applications or exhaust gases in industrial sectors [30].

49 Butanol (butyl alcohol) is an aliphatic saturated C₄ alcohol (C₄H₉OH, 74.12 g/mole) with four structural
50 isomers: *n*-butanol, isobutanol, *sec*-butanol and *tert*-butanol. Due to an asymmetric C atom in the secondary
51 alcohol, there are two stereoisomers of 2-butanol. 1-butanol is a natural product found in some organisms in
52 nature, however it is primarily obtained by fermentation [31]. 1-butanol has been presented as an exhaled air
53 biomarker for lung cancer [32]. 1-butanol is the gas that presents the highest concentration in the exhaled
54 breath of patients with lung cancer in all the stages of the disease. As a consequence, 1-butanol can be used
55 as lung cancer biomarker. Therefore, the development of simple and accurate 1-butanol detection tools in
56 exhaled breath have excellent potential for applications in lung cancer detection and diagnosis [32].

57 Furthermore, World Health Organization (WHO) has fixed 20 ppm of 1-butanol as the threshold risk level
58 for professional and work environment [33], according to the risk level to human health. Moreover, other
59 studies have reported that concentrations in air exceeding 50 ppm can produce ocular irritation, disgusting
60 odor, slight headache and dizziness, nose and throat irritation and dermatitis in fingers and hands [34]. Thus,
61 1-butanol detection is of great importance in terms of safety and healthcare.

62 So far, different approaches for 1-butanol detection have been explored using a variety of materials and
63 technologies comprising but not limited to the following:

- 64 ➤ AuNPs-modified $\text{Fe}_2\text{O}_3/\text{ZnFe}_2\text{O}_4$ heterostructures, which can detect 1-butanol concentrations in the ppb
65 range, while operating at temperatures from 100 °C to 340 °C [35].
- 66 ➤ ZnOMWCNT nanocomposites, which take advantage of the chemisorption electron conduction
67 phenomena. These devices accomplish 1-butanol detection limits from 50 ppm to 500 ppm at room
68 temperature [36].
- 69 ➤ QCM coated with co-polymer P(HEMA-co-MA), achieving 1-butanol detection down to 72 ppm also at
70 room temperature [37].
- 71 ➤ The integration of a thin film of ZnO and an inter-digitated electrode fabricated on a flexible Teflon
72 substrate for tested sensitivity between 50 ppm and 100 ppm at 27 °C [38].
- 73 ➤ In the field of optical sensors, an “optical nose” based on Au@MOFs nanoparticles arrays through
74 surface/enhanced Raman scattering [39] achieved to detect a 1-butanol concentration of 1000 ppm.

75 Table 1 shows a summary of the mentioned of 1-butanol sensors found in the literature.

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78

79

80 Table 1: Summary of 1-Butanol sensors performance.

Sensor technology	Detection limit [ppm]	Operating temperature [°C]	Response / Recovery times [s]	Reference
Electro-chemical	0.05	100 – 340	6 / 16	[35]
Electro-chemical	50	Room temperature	60 / 80	[36]
Electro-chemical	72	Room temperature	Not informed	[37]
Electro-chemical	50	27 °C	62 / 70	[38]
Optical	1000	Room temperature	Not informed	[39]

81

82 To avoid ignition risk, it is preferable to operate these sensors at low temperatures. Nevertheless, it is still
 83 challenging to reach 1-butanol detection limits below 50 ppm at room temperature. Consequently, the aim of
 84 this work consists of the design and characterization of a highly sensitive GO-based LMR-planar device for
 85 1-butanol gas detection operating at room temperature for its use in different applications in industry and
 86 healthcare.

87 The paper is organized as follows. First, the procedure for the assembly and characterization of the devices
 88 is described. Then, studied the sensor fabrication process as a function of the number of GO/PEI bilayers
 89 fabricated is studied. Finally, the sensitivity of the obtained devices to 1-butanol is tested together with the
 90 cross sensitivity to other gaseous species and temperature.

91 **2. Materials and Methods**

92 *2.1. Sensor fabrication*

93 The sensing coating was fabricated by means of Layer-by-Layer (LbL) deposition of GO/PEI bilayers onto
 94 a planar CaF₂ substrate, which was priorly coated with a thin film of sputtered SnO₂ (see zoom in Figure 1).

95 This sputtered layer acted as LMR generator. The thickness of the SnO₂ was controlled to operate at
 96 wavelengths close to or greater than 2 μm. Having the resonance in the MIR region responds to the direct
 97 proportionality relationship between the LMR sensitivity and the square of the wavelength where it occurs
 98 [13, 40] according to equation (1). The transmission of light in the MIR region of the spectrum was possible
 99 due to the use of fluorinated materials, such as CaF₂, as substrate and ZrF₄ as fiber patch cords (Figure 1).

$$100 \quad S = \frac{\lambda^2}{2\pi d_2} \frac{\left(\frac{n_2^2}{n_3 \sqrt{n_1^2 - n_3^2}} + \frac{2n_2^2 \sqrt{n_1^2 - n_3^2}}{n_3^2} \right) n_3^4}{n_2^4 (n_2^2 - n_1^2) + n_3^4 (n_2^2 - n_1^2)} \quad (1)$$

101 Fluorinated Calcium (CaF₂) glass cover slides 10 x 10 x 0.5 mm purchased from UQG Optics were used as
 102 substrates. The transmittance of CaF₂ is 90 % up to a wavelength equal to 7 μm when the substrate size is 10
 103 mm, and its refractive index is 1.42 at 2.3 μm [41].

104 SnO₂ thin films were fabricated onto the CaF₂ substrates by means of DC-sputtering using a Benchtop High-
 105 Vacuum Magnetron Sputtering System purchased from MOORFIELD. The substrate was placed into the
 106 sputtering chamber, 10 cm under the SnO₂ target. Deposition conditions were 1.2 x 10⁻² mBar vacuum
 107 pressure, 120 mA DC current, 20 °C coolant temperature and 90 min deposition time with rotational speed
 108 of 2 s⁻¹. GO/PEI bilayers were deposited onto the SnO₂ covered substrates by means of LbL electrostatic self-
 109 assembly, following the procedure explained elsewhere [24].

110 Before the LbL deposition process, the substrates were cleaned with deionized (DI) water and soap and
 111 subsequently submerged into a 1 M KOH solution for 30 minutes. Afterwards, they were cleaned with DI
 112 water and dried in air. This process was performed to promote a negative charge in the substrate surface. For
 113 the LbL fabrication process, a 0.5 mg/mL GO (from Graphenea, S.A., San Sebastian, Spain) dispersion and
 114 2 mg/mL PEI (from Sigma-Aldrich) solution were employed. Both samples were prepared in DI water. PEI
 115 solution was stirred overnight and the GO dispersion was sonicated for two hours prior to deposition to
 116 prevent aggregation [24]. The LbL deposition started with the immersion of the substrate into the PEI solution
 117 for 5 minutes. Then, it was rinsed in DI water for 1 minute to remove the excess of material and dried in air
 118 for 1 min. Afterwards, the substrate was immersed into the GO dispersion for 5 minutes followed by the rinse

119 and drying processes described before, obtaining the first bilayer of GO/PEI. At the end of each bilayer, the
120 substrate was kept for 5 minutes in an oven at 180 °C to achieve a stable position of the resonance at the
121 studied spectrum region.

122 *2.2. Experimental setup*

123 The optical experimental set-up used to perform the gas measurements is shown in Figure 1. The setup
124 consisted of a stabilized light source (Thorlabs SLS 201L) that coupled light into the edge of the substrate by
125 means of a ZrF₄ optical fiber (Thorlabs MZ41L1, with a working range up to 4.5 μm). The Arcoptix FTNIR
126 spectrometer (Arcoptix Switzerland, with maximum wavelength range of 2.6 μm) collected the light at the
127 output edge of the substrate using another ZrF₄ optical fiber (Thorlabs MZ41L) with a resolution of 4.8 nm
128 at the wavelength of interest (2.2μm). It is worth mentioning that the estimation of the resonance wavelength
129 is not performed directly on the values measured by the spectrometer. However, the parabola method is used
130 to obtain the LMR central wavelength, which allows precise monitoring of the performance of the sensor. As
131 it was previously mentioned, the substrate material, CaF₂, has a transmittance of 90% up to 7 μm. Thus, the
132 working wavelength range in this case was imposed by the spectrometer, which permitted to observe
133 resonances in the range from 0.9 μm to 2.6 μm.

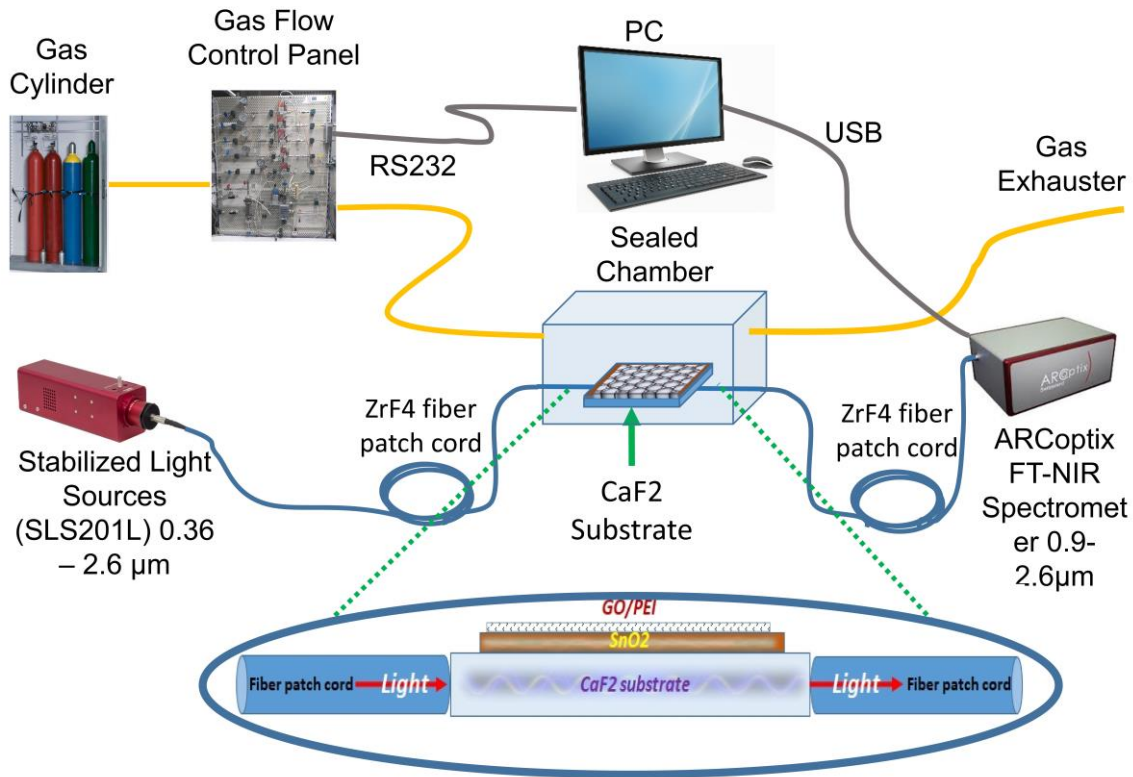


Figure 1: Experimental set-up and sensor structure.

2.3. Gas concentration measurements

Gas measurements were done using a gas flow controller (from Bronkhorst, NL-7261 AK Ruurlo, Netherlands) that permitted to maintain a continuous flow. N_2 gas was used as carrier and mixed with 1-butanol and water vapor using a controlled evaporation mixer (CEM - from Bronkhorst, NL-7261 AK Ruurlo, Netherlands). Since the 1-butanol mass flow was given in mg/h and the nitrogen gas flow in mL/min, it was required a transformation to express the concentration in ppm [42]. Unit transformation was done considering the molar mass of 1-butanol (74,121 g/mole) and the molar volume of gases (22.4 L/mole) in the formula shown in equation (2):

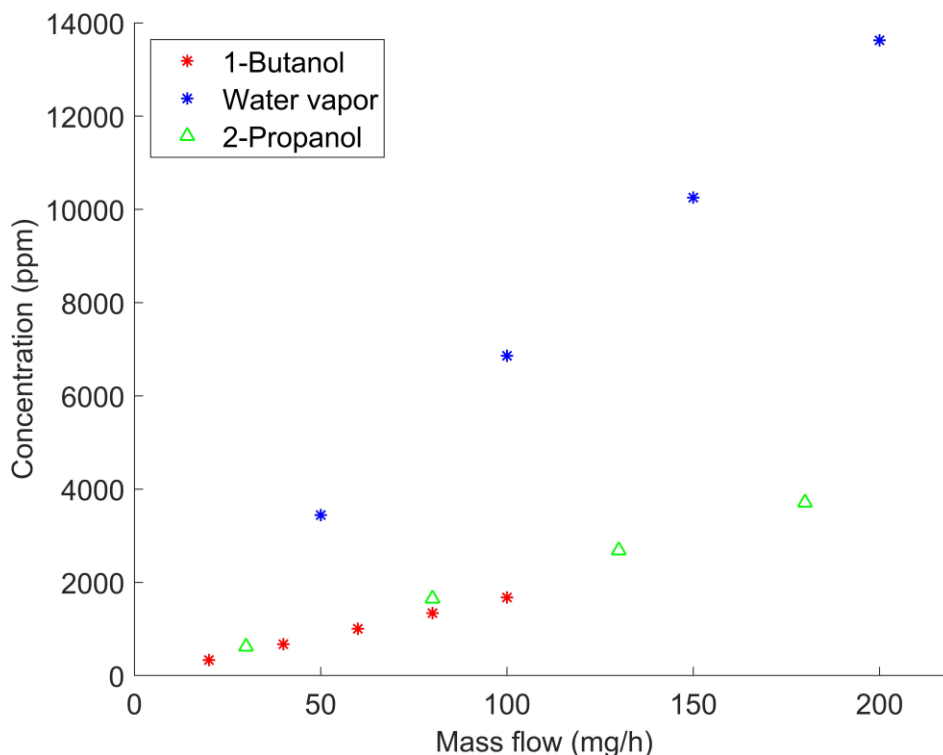
$$Bppm = \frac{Fb}{Fb + Fn} * 10^6 \quad (2)$$

145 Where F_b is the molar flow of 1-butanol, F_n is the molar flow of nitrogen and B_{ppm} is the resulting
146 concentration of 1-butanol expressed in ppm.

147 According to equation (2), the concentration of 1-butanol is shown as a function of the mass flow in Figure
148 2. N_2 gas flow used during the measurements was kept constant at 300 mL/min to preserve the measuring
149 conditions and the 1-butanol mass flow was kept in the range of 20 to 100 mg/h. A mass flow lower limit of
150 20 mg/h represented in Figure 2 is associated to the minimum stable concentration permitted by the mass
151 flow controller. Previous limitations permitted to achieve concentrations of 1-butanol in the range of 335 to
152 1676 ppm. The sensitivity of the obtained devices is determined by the quotient of the LMR wavelength shift
153 (nm) and the gas concentration (ppm).

154 In the same manner, Figure 2 also shows the concentrations of water vapor and 2-propanol gas, at different
155 mass flow rates for a given N_2 flow of 300 mL/min. The studied concentration range for water vapor and 2-
156 propanol were 3442 - 13627 ppm and 620 - 3713 ppm respectively.

157 All the measurements were performed at a fixed temperature of 20 °C, controlled by the *CEM*, except the
158 one described in section 3.3 *Temperature cross-sensitivity*. Temperature cross sensitivity study was
159 performed at a constant water vapor concentration of 1723 ppm for three different temperatures (20, 100 and
160 180 °C).



161

162

Figure 2: ppm concentrations of 1-butanol, water vapor and 2-propanol in the sealed chamber as function of the mass flow for 300 mL/min N₂ flow.

163

164

The response and recovery times are referred to the time required for a sensor to reach 90% and 10% respectively of the final response from a stable condition. All the measurements for the different gaseous species were taken for the lowest concentration measured in that experiment.

165

166

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The CEM response and recovery times for water vapor and other pressurized liquids were 180 and 93 seconds, respectively. In the case of gas controller, the response and recovery times were 3 and 1 seconds, respectively.

168

169

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The cross sensitivity of sensor A (with GO/PEI bilayers) was also tested with other gases at different concentrations, such as NH₃ (1890 ppm), C₂H₂ (400 ppm) and CO₂ (10⁶ ppm, pure).

171

172

Subsequently, the fabricated device was characterized. Cross sensitivity tests at different temperatures were performed, as well as the response of the sensor towards 1-butanol, water vapor and 2-propanol. The impact of the number of bilayers of the GO/PEI coating on the resonance sensitivity was also studied and, accordingly, the suitability of GO for 1-butanol detection demonstrated.

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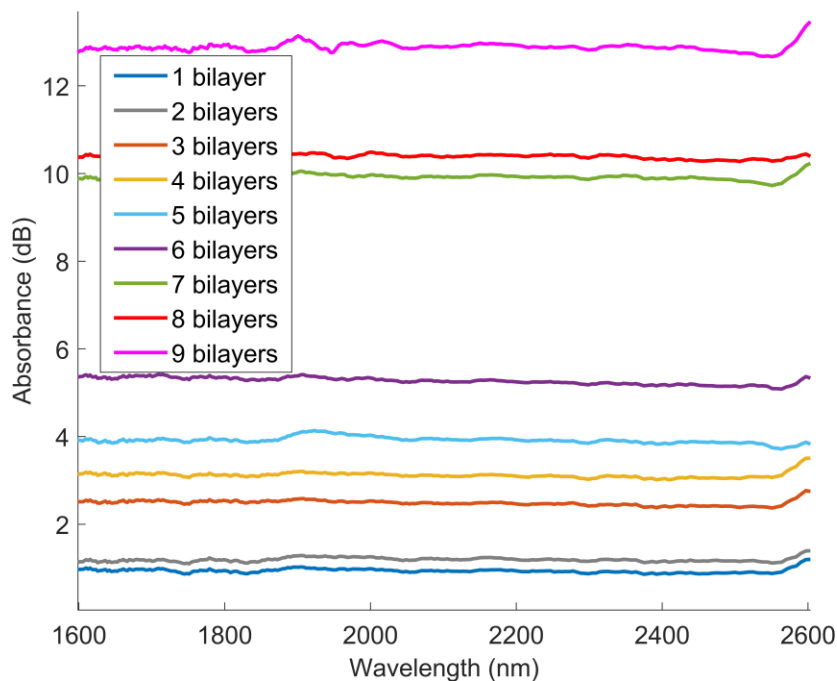
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176 3. Results and Discussion

177 3.1 Fabrication of the GO/PEI sensitive coating

178 GO/PEI nanostructured coatings have been presented in previous works as suitable materials for the
179 generation of LMRs [24, 26]. Figure 3 shows the absorption spectrum as a function of the GO/PEI bilayers
180 fabricated onto the CaF₂ substrate. As it can be noted, this approach is not feasible in this case. A direct
181 deposition of GO/PEI bilayers onto the surface of the CaF₂ substrates reveals an increase in absorption in the
182 entire band of the spectrum and no LMR is observed in that region. Therefore, an intermediate LMR
183 generating thin-film, SnO₂, was used prior to the fabrication of the GO/PEI bilayer structure.

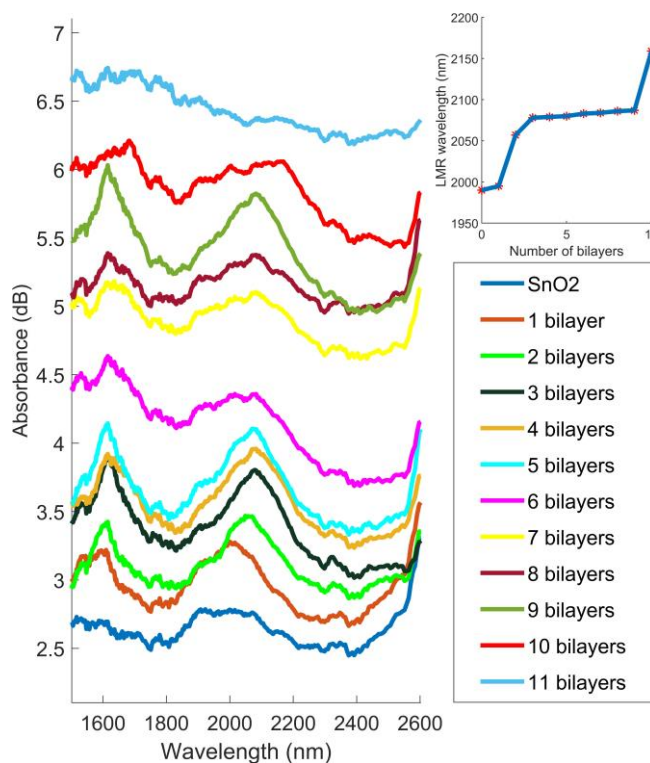


184
185 Figure 3: Absorbance spectrum as a function of the GO/PEI bilayers fabricated onto the CaF₂ substrate.

186 Thus, GO/PEI bilayers were fabricated onto a sputtered SnO₂ thin film, which acted as LMR generator [6].
187 This resonance was generated at a wavelength of 1976 nm with a thin film of 280 nm.

188 GO/PEI bilayers are expected to provide the device a gas sensitivity enhancement due to the oxygen
189 functional groups in the chemical structure of the GO at the outer surface [43].

190 The study of the fabrication of the GO/PEI coatings onto the SnO₂ layer as a function of the number of
191 bilayers is shown in Figure 4. It is observed that the LMR central wavelength changes notably in bilayers 1,
192 2 and 3 and very slightly from 4-9, vanishing completely in 11, which establishes a limit of 10 bilayers for
193 the utilization of this LMR-based device for sensing purposes. Additionally, the resonance retains the
194 sensitivity to the RI changes despite the increase in the number of GO/PEI bilayers. These shifts were tested
195 from air (RI=1) to water (RI=1.333). For all bilayers it was 318 nm/RIU. Therefore, the final decision was
196 made to carry out the investigation with a structure of 10 bilayers of GO/PEI because it represents a balance
197 between the figure of merit of the LMR resonance and the highest possible number of bilayers, while the
198 amount of GO in the coating, and thus oxygen functional groups, is also maximized. It means that the
199 resonance will be still visible at the absorbance spectrum while the GO sensitive coating will be as sensitive
200 as possible.



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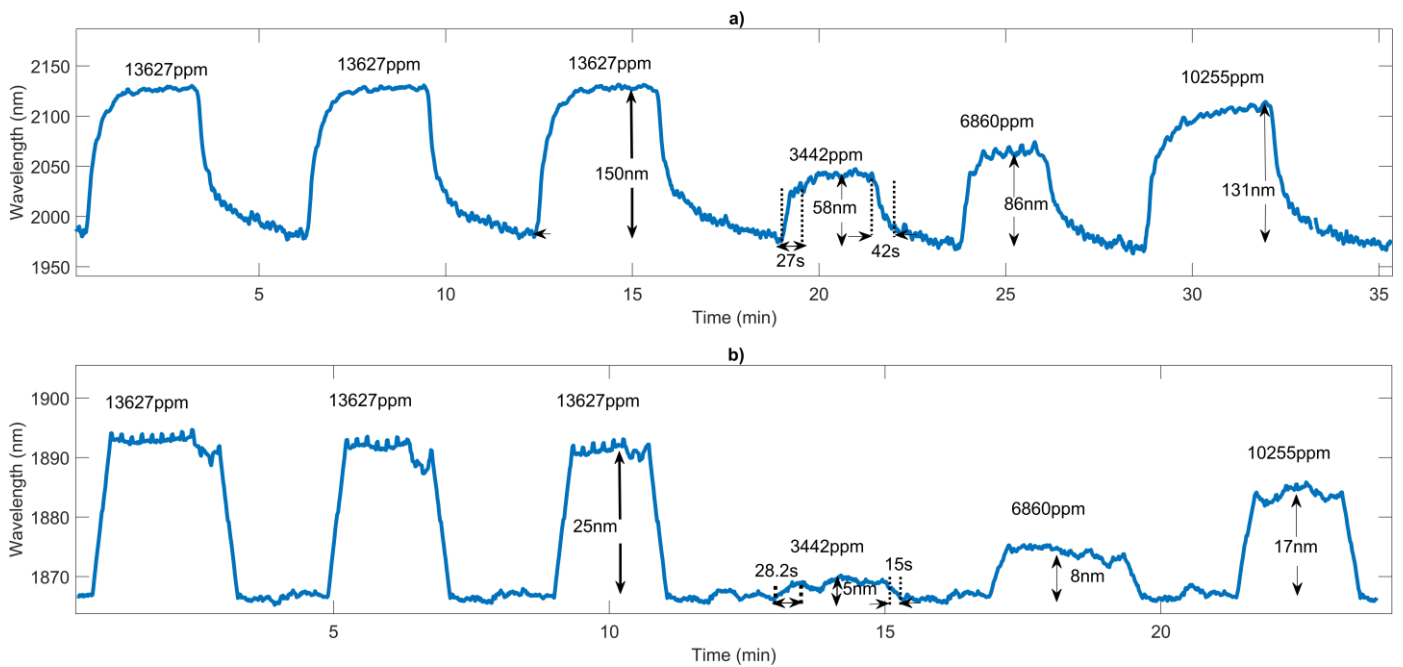
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Figure 4: Resonance evolution as function of the number of GO/PEI bilayers.

204 3.2 Gas measurements

205 In order to study and compare the performance of the devices for gas sensing purposes, a GO/PEI device
 206 with 10 bilayers (Sensor A) and the device without the GO/PEI multilayer structure, only with the SnO₂ thin
 207 film (Sensor B), were subjected to different concentrations of water vapor and 1-butanol. In the case of water
 208 vapor measurement, sensor A shows a sensitivity 5.5 times higher than sensor B (see Figure 5). Specifically,
 209 sensitivity of sensor B is 2 pm/ppm and that of sensor A is 11 pm/ppm. The small fluctuations observed for
 210 both devices are related to inaccuracies of the CEM. The sensitivity enhancement is mainly associated to the
 211 high potential of GO to adsorb and store water molecules owing to the oxygen-containing functional groups
 212 on its hydrophilic surface [44].

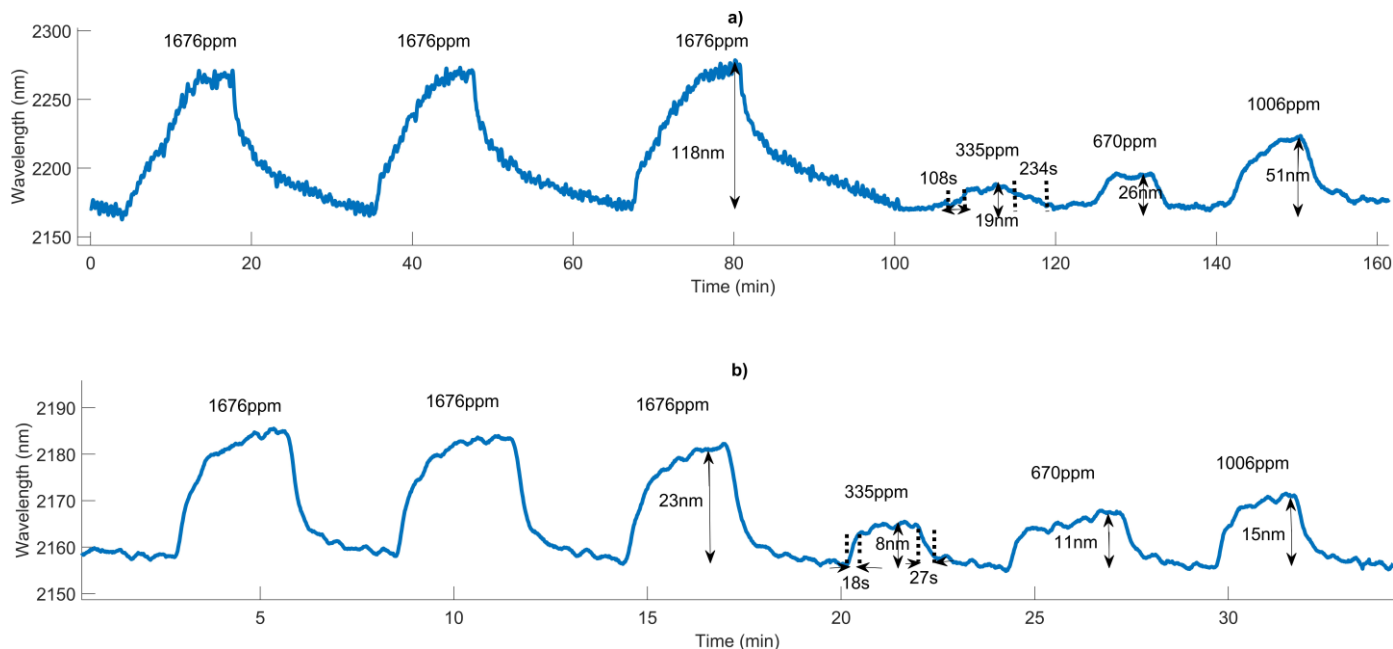
213 The response and recovery times of sensor A were 27 and 42 seconds respectively (measured for the lowest
 214 concentration). This recovery time is associated to strong interaction between the GO and the water molecules
 215 demonstrated in [44], which in turn is due to the exponential dependence of the number of O-H bonds in
 216 hydrated GO to the water content [45].



217
 218 Figure 5: LMR wavelength shift as a function of water vapor concentrations: a) sensor A (with 10 bilayers
 219 of GO/PEI) and b) sensor B (without GO/PEI).

220 In a same way, Figure 6 shows the response of both, sensor A and sensor B to 1-butanol gas. Sensor A
 221 shows a sensitivity of 70.4 pm/ppm, which denotes 5.13 times enhancement compared to sensor B for
 222 changes of 1-butanol concentrations in the range from 0 to 1676 ppm. In this interval, sensor B has a
 223 sensitivity of 13.7 pm/ppm.

224 Response and recovery times of sensor A to 1-butanol were 108 and 234 seconds respectively (measured
 225 for the lowest concentration).



226
 227 Figure 6: LMR wavelength shift as a function of 1-butanol concentrations: a) sensor A and b) sensor B.

228 Sensor A exhibits an excellent sensitivity to water vapor and 1-butanol detection in comparison to sensor
 229 B. Additionally, the response of sensor A was tested to 2-propanol, a gaseous compound of the same family
 230 of 1-butanol. The test was performed at the concentrations indicated in Figure 2 (from 620 ppm to 3723 ppm),
 231 and results are shown in Figure 7. Response and recovery times for 2-propanol were 36 and 102 seconds
 232 respectively (measured at the lowest concentration).

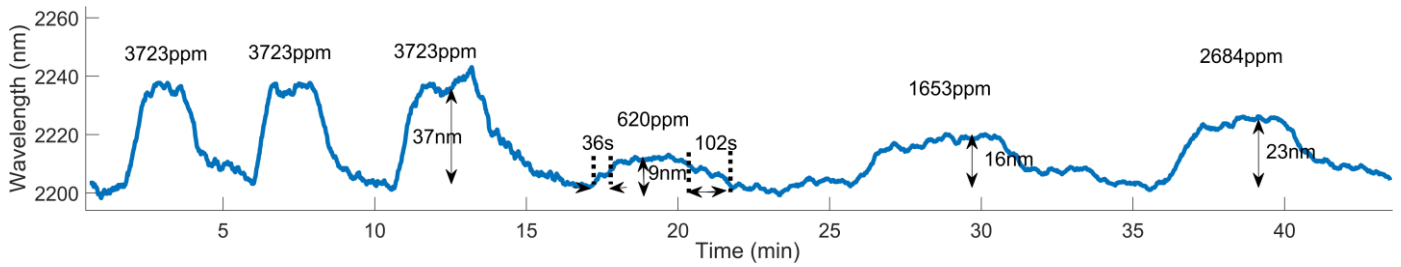
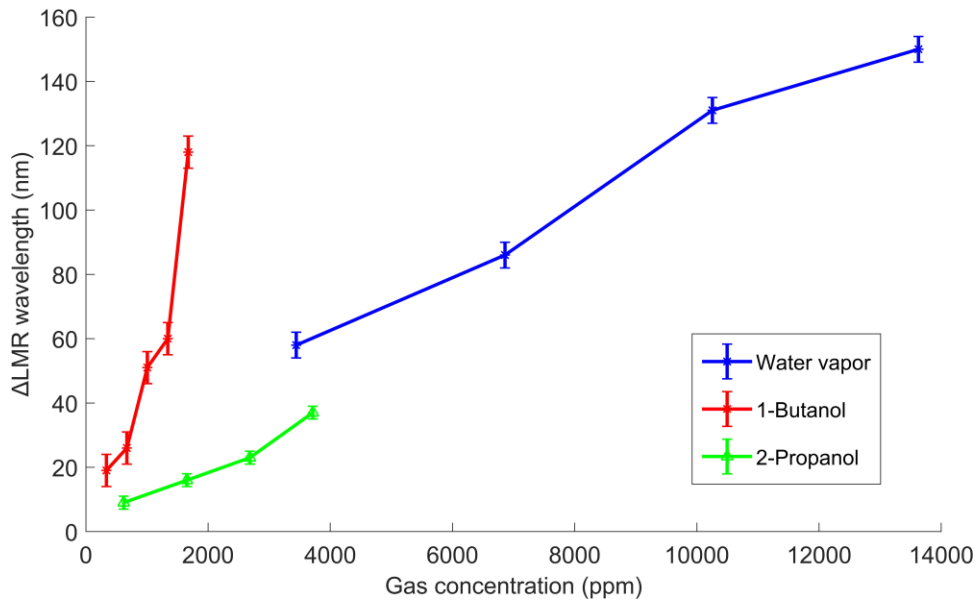


Figure 7: LMR wavelength shift of sensor A as a function of 2-propanol concentrations.

Additional experiments were performed with sensor A to test the cross sensitivity with other gases (NH_3 , C_2H_2 , and CO_2), showing negligible sensitivity (less than 1%) to NH_3 (1890 ppm), C_2H_2 (400 ppm) and CO_2 (10^6 ppm, pure).

Sensor A shown good repeatability in the response to water vapor, 1-butanol and 2-propanol. Figure 8 shows the LMR wavelength shift of sensor A as a function of the measured concentrations of the target gases and includes the standard deviations of the measurements associated to *CEM* inaccuracies.

In the case of water vapor, the LMR wavelength shift shows a linearity factor of $R^2=0.970$ with the increase of the gas concentration in the measured range, achieving a sensitivity of 11 pm/ppm. Gas sensitivity achieved for 2-propanol was 10 pm/ppm with a linearity factor $R^2=0.965$. Gas sensitivity for 1-butanol was 70.4 pm/ppm, with a linearity factor $R^2=0.876$, which reveals the non-linear response of the device to 1-butanol gas, particularly at higher concentrations, which also occurs with other LMR-based optical sensors [6, 46]. This behavior is directly associated with the non-linear adsorption capacity of GO at the external surface of the sensor for higher concentrations of 1-butanol. This was demonstrated in [44] with the exponential adsorption capacity of GO, which depends on the number of O-H bonds that exponentially increases with gas concentrations.



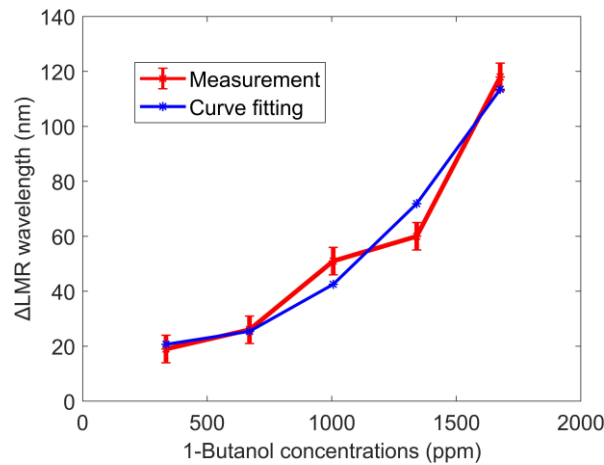
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251 Figure 8: LMR Wavelength shift of sensor A for different concentrations of water vapor, 1-butanol and 2-
 252 propanol.

253 Figure 9 shows a nonlinear adjustment of the behavior of sensor A for the studied concentrations of 1-
 254 butanol, by means of a polynomial fit defined by equation (2). The error bars represent the standard deviation
 255 produced by the *CEM* inaccuracies. The new R^2 for this polynomial fit is equal to 0.959.

256

$$p = 5.47 * 10^{-5} x^2 - 0.04081x + 28.22 \quad (2)$$



257

258 Figure 9: Nonlinear adjustment of sensor A response to 1-butanol.

259 Table 2 shows a performance index data of sensors A and B.

260

261

Table 2: Comparison of performance parameters of sensors A and B.

Sensor	Response time (s)		Recovery time (s)		Sensitivity (pm/ppm)	
	Water vapor	1-butanol	Water vapor	1-butanol	Water vapor	1-butanol
A	27	108	42	234	11	70.4
B	28	18	15	27	2	13.7

262

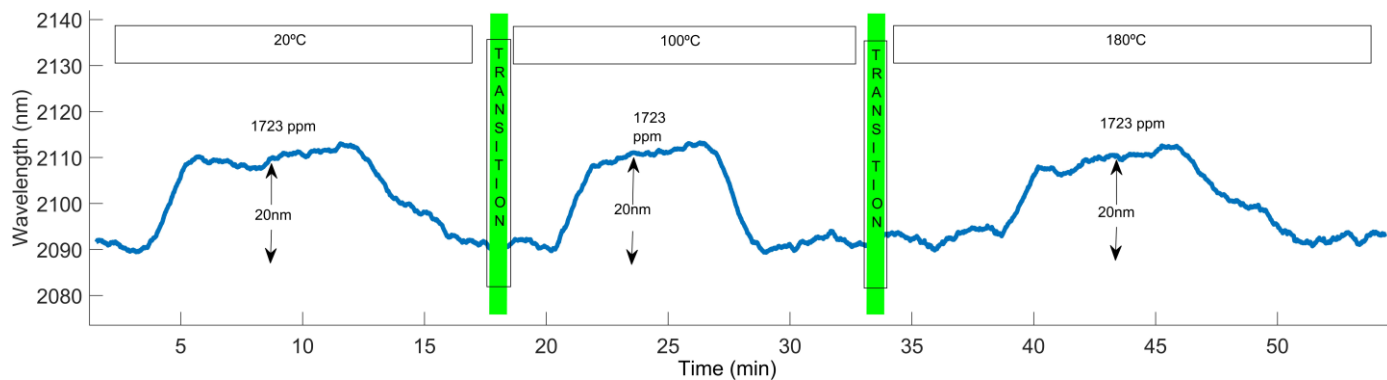
263 Larger response times can be observed for the highest concentrations of 1-butanol. This is associated with
 264 two fundamental causes. First, in general it is due to the local stress or strain that must be exerted by the
 265 nitrogen flow to expel the 1-butanol out of the sealed chamber system, which is explained by the dynamic
 266 viscosity of 1-butanol (2.947 mPa·s at 20 °C [47]), that is 2.6 times greater than that of the water (1.002 mPa·s
 267 at 20 °C [48]). Second, in the particular case of sensor A, it is due to the exponential dependence of O-H
 268 bonds in the hydrated GO structure [45]. Thus, the increase in hydrogen bonding leads to a greater delay in
 269 the recovery of the initial resonance wavelength when the 1-butanol is expelled out of the sealed chamber.

270 However, the only 1-butanol optical sensor found in literature [39] does not offer information about the
 271 response and recovery times of 1-butanol detection for comparative purposes. On the other hand,
 272 electrochemical sensors require for a concentration of 100 ppm of 1-butanol gas between 6 and 9 seconds of
 273 response and recovery time respectively at 200 °C [35]. These are significantly different operating conditions
 274 to those of sensor A, as it was tested at room conditions (20 °C) and it is not directly comparable.

275 3.3 Temperature cross-sensitivity

276 Cross-sensitivity to temperature fluctuations was also tested with sensor A subjected to temperature
 277 variations under the same cycles of humidity conditions. Here, the *CEM* was set to heat up to 20 °C, 100 °C
 278 and 180 °C for the first, second and third water vapor injection cycles respectively. This test was performed
 279 using N_2 as gas carrier with a flow of 300 mL/h. Both temperature transitions took 55 ± 2 sec to complete.
 280 Results (see Figure 10) reveal no LMR shift associated to temperature variations, demonstrating that the
 281 device provides robust water vapor measurements independent to temperature fluctuations in the range 20

282 °C-180 °C. Temperature tests could not be performed with 1-butanol to prevent CEM damage, since its
283 ignition temperature is 29 °C. However, it is likely that the device also presents consistent measurements for
284 this alcohol under slight temperature fluctuations.



285

286 Figure 10: Sensor A: test of temperature sensitivity during the measurement of water vapor for 20, 100
287 and 180°C.

287

288 4. Conclusions

289 GO/PEI nanostructured coatings were fabricated directly on the CaF₂ substrate and over a CaF₂ substrate
290 covered with a SnO₂ layer in order to enhance the sensitivity of LMR-based sensors for gas detection. To the
291 best of authors knowledge, in this work LMRs in the MIR region was obtained for the first time using CaF₂
292 planar waveguides as substrates and sputtered SnO₂ thin films.

293 Sensitivity enhancement of LMR based gas sensors fabricated on planar waveguides was achieved using
294 GO/PEI bilayers. Sensitivity enhancement for water vapor and 1-butanol gas, achieved a six-fold increase
295 and a fivefold increase respectively. Studied device revealed cross-sensitivity with gaseous compounds of
296 the family of 1-butanol, such as 2-propanol, but negligible response to other gaseous compounds, such as
297 NH₃, C₂H₂ and CO₂. Temperature cross sensitivity studies also exhibited that temperature fluctuations in the
298 range between 20-180 °C do not affect the performance of the sensor. Consequently, this study reveals the
299 possibility of fabricating robust LMR-based gas sensors on planar waveguides for a variety of applications.

300 According to the sensitivity to 1-butanol, the developed device could achieve 15 ppm of 1-butanol detection
301 with an optimized gas configuration setup, which make it faceable for environmental monitoring
302 applications.

303 ***Credit Authorship Contribution Statement***

304 The contributions of EEGM to the present results were the preparation of the materials, the fabrication of
305 the sensors and the performance of the measurement experiments. MH and SME developed the deposition
306 protocol. CRZ and IRM conceived the idea of the research and supervised the process. The first draft was
307 written by EEGM, and all authors commented on previous versions of the manuscript. All authors read and
308 approved the final manuscript.

309 ***Declaration of Competing Interest***

310 The authors declare that the research was conducted in the absence of any commercial or financial
311 relationships that could be construed as potential conflict of interest.

312 ***Data Availability***

313 All data generated during the research are available at the following link:

314 https://drive.google.com/drive/folders/1-l_Ae4IBNzQBB17RVepfYN3TeHNyfaKv?usp=sharing

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