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Enhancing CO₂ sensitivity of a polymer-based RF sensor through functionalisation

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Abstract—In this study, we present a dual Radio Frequency sensor coupled with a polymer sensitive material for Carbone dioxide gas detection. A commercially available polymer underwent functionalization to produce a derivative polymer with enhanced properties. The sensing performances of both polymers, when integrated with the RF transducer, were evaluated. The results demonstrate that functionalization led to an increased sensitivity to CO₂ while simultaneously reducing sensitivities to relative humidity (%RH) and temperature. The functionalized material exhibited good reversibility and repeatability, displaying a sensitivity of 17.3 MHz/ppm to CO₂ at 0% RH, in comparison to the commercial polymer with a sensitivity of 1.35 MHz/ppm. Nevertheless, it is important to note that the sensor's CO₂ sensitivity is compromised when exposed to %RH levels exceeding 0. Moreover, the sensor demonstrated a high specificity during tests involving alternative gaseous compounds such as CO, NO₂, and O₃.

Keywords—Radiofrequency sensor, polymer sensitive material, functionalization, carbon dioxide

I. INTRODUCTION

In recent years, there has been a significant surge in the development of polymer-based microwave gas sensors [1]. This growth can be largely attributed to their efficient energy utilization, cost-effectiveness, high operational frequencies, and, most importantly, the inherent flexibility of polymers, which allows for straightforward functionalization to enhance sensitivity and selectivity [2, 3]. For example, I. Pavel et al. [4] introduced a Radio Frequency (RF) ammonia gas sensor based on functionalised polymer materials (electrodeposited Polypyrrole-Nickel Phthalocyanine sodium dodecyl sulphate (PPy/NiPc-SDS), and Polypyrrole sodium dodecyl sulphate (PPy-SDS)). This sensor demonstrated a linear sensitivity of 3.2 mdB/ppm for PPy-SDS film-coated sensors and 0.98 mdB/ppm for PPy/NiPc-SDS film-coated sensors. Carbon dioxide (CO₂) is a fundamental gas produced through human respiration, the combustion of fossil fuels, and various industrial processes [5]. While essential for plant growth and certain industrial applications, elevated concentrations of CO₂ can have adverse effects on human health and contribute to climate change [6]. This paper presents the introduction of a dual RF sensor designed for the CO₂ gas detection. The sensor

incorporates both an available commercial polymer and a custom-synthesized derivative polymer. The performance of these materials in gas detection was comprehensively evaluated. Preliminary experiments were carried out to measure the sensor's activity to atmospheric variables, including humidity and temperature. Subsequently, the sensor underwent testing to assess its specificity and sensitivity to various gaseous compounds.

II. MATERIAL AND METHODS

A. Sensitive polymer synthesis

Commercial Hyperbranched Polyethyleneimine (Com HBPEI, Mw = 10 kDa) was purchased from Polysciences inc, Warrington Pennsylvania, USA and used for the synthesis of HBPEI-silane. All other reagents used in the synthesis were acquired from Sigma-Aldrich, St. Louis, Missouri, USA. All glassware was oven-dried prior to use, and, unless specifically mentioned, all starting materials and reagents were used as received without additional purification. NMR spectra were recorded at room temperature using a Bruker Advance Spectrometer (400 MHz) in CDCl₃. To begin, Com HBPEI (4.0 g, 0.93 mol, 1 eq., MW = 10 kDa) was dissolved in 15 mL of methanol. Subsequently, 1,2-epoxybutane (12.1 mL, 0.14 mol, 1.5 equiv. relative to the nitrogen content in PEI) was introduced into the polymer solution while stirring at room temperature for 10 minutes. An excess of epoxybutane was used to ensure the complete conversion of primary and secondary amines into tertiary amines. After 24 hours, the unreacted epoxybutane and methanol were evaporated under vacuum at 60°C using a rotary evaporator, followed by a vacuum oven. The synthesized HBPEI-BuOH (5 g) was dissolved in anhydrous chloroform under an inert atmosphere and stirred at room temperature for 10 minutes. Subsequently, an excess of trimethoxy(3,3,3-trifluoropropyl) silane was added, and the mixture was stirred for an additional 10 minutes. Boron trifluoride etherate was then added dropwise to the homogeneous solution, while any generated fumes were evacuated by passing argon through the system. The reaction mixture was stirred for 12 hours at room temperature, after which the solvent was evaporated to yield a viscous liquid. The crude product was vacuum-dried for 12 hours to remove any residual reagents, resulting in the formation of HBPEI-Silane.

B. RF sensor design

The dual microwave sensor designed for this study consists of five-fingered microstrip interdigitated resonators. These are fabricated with 200 μm wide and 20 μm thick copper lines, which are printed on a flexible Kapton substrate, 100 μm thick. One of the two resonators is coated with the sensitive polymer layer to function as a sensitive channel, while the other is left uncoated to serve as a reference channel. This differential configuration is designed to minimize any drifts and variations that are not caused by the interaction with the sensitive material. The interdigitated structure is specifically chosen to maximize the surface electric field density in contact with the sensitive material. This improves sensitivity to fluctuations in the material's dielectric properties, such as permittivity and dielectric loss tangent, upon interaction with the target gas. Changes in these dielectric properties, in turn, alter the effective permittivity of the microstrip, leading to a measurable shift in both the resonance frequency and the magnitude [7].

C. Sensor fabrication and characterisation

The microwave sensor, designed to operate at a resonance frequency of 3.28 GHz, was fabricated by Würth Electronics. A double-sided copper-clad Kapton laminate from DuPont™ Pyralux® AP, 100 μm thick, was used as the substrate [8]. This substrate exhibits high hydrophobicity (with a contact angle of $64.4 \pm 2.2^\circ$) and excellent thermal resistance. To inhibit oxidation, the copper-clad surface underwent an immersion coating process with electroless nickel and gold. Subsequently, the sensors were coated with a 1.2 μm layer of Com HBPEI and HBPEI-Silane using spin coating, covering an approximate area of $17 \times 22 \text{ mm}^2$, as shown in Fig 1 (a) and in Fig 1 (b).

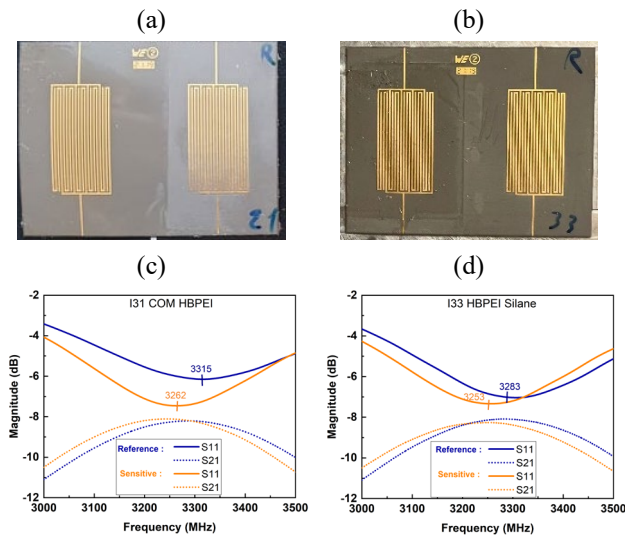


Fig. 1. Fabricated Com HBPEI-based sensor (a) and HBPEI-SILANE based sensor (b) with their corresponding S_{ij} parameters measured with a VNA (c) and (d).

Prior to deposition, the substrates underwent a pre-baking process for 4 hours at 120 $^\circ\text{C}$ in an air oven. The electrical characterization of the reference and sensitive channels of the fabricated sensor was performed using a vector network analyzer (VNA) for the Scattering parameters (S_{ij}) measurement under ambient conditions Fig 1 (c) and (d). The resonance frequency of the uncoated resonator was observed to be close to 3.3 GHz. For both devices, the coated

resonator exhibited a decrease in resonance frequency. This shift can be attributed to the increased effective permittivity of the microstrip resonators due to the deposition of the sensitive material. For applications related to humidity sensing, a hydrophilic polymer is recommended as the sensitive material. Conversely, for gas monitoring, a hydrophobic sensitive material is preferable due to the influence of relative humidity as a significant environmental variable. The hydrophilic or hydrophobic nature of these polymers was evaluated using a contact angle goniometer (Kruss, Germany). Com HBPEI registered a water contact angle of $11.6 \pm 0.4^\circ$, while HBPEI-Silane measured at $91 \pm 5.8^\circ$, indicating that HBPEI-Silane is considerably more hydrophobic than Com HBPEI. The surface roughness of the deposited material was assessed using Atomic Force Microscopy, as shown in Fig 2 (a) and (b). The surface roughness is quantified by calculating the root mean square roughness ($R_q = \sqrt{\frac{\sum_{i=1}^N (z_i - \bar{z})^2}{N}}$) and the average roughness ($R_a = \frac{1}{N} \sum_{i=1}^N |z_i - \bar{z}|$) from the height data. Here N is the total number of height data points on the surface, z_i represents the height value at each data point, and \bar{z} is the mean height value of the surface.

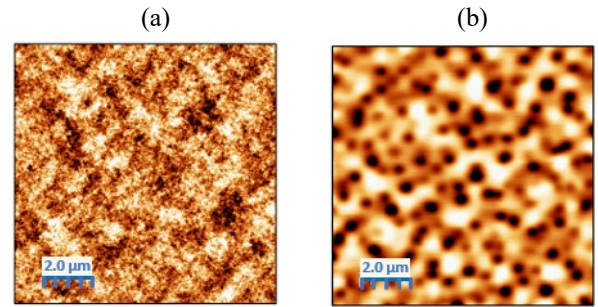


Fig. 2. AFM images of (a) Commercial HBPEI, and (b) HBPEI Silane.

The images (of size $10 \times 10 \mu\text{m}$) highlight a high degree of surface roughness for HBPEI-Silane. This polymer exhibited the highest roughness values ($R_q = 4420 \pm 1270 \text{ pm}$ and $R_a = 3540 \pm 1034 \text{ pm}$), which were approximately 15 times higher than those of Com HBPEI ($R_q = 298 \pm 8 \text{ pm}$ and $R_a = 237 \pm 8 \text{ pm}$). Surface roughness plays a pivotal role in gas sensing performance. Indeed, because the interaction between the target gas and the polymer occurs primarily at the surface, the topography significantly impacts the sensing characteristics. A rougher surface expands the available surface area for gas molecule interactions, thereby facilitating adsorption. This, in turn, results in more pronounced variations in dielectric properties, enhancing the sensor's sensitivity to gas. Moreover, rough surface may also slow down the diffusion of gas molecules to active-sites, potentially increasing the response and recovery times.

III. CHARACTERISATION UNDER LABORATORY CONDITION

A. Experimental setup

The experimental setup used at IM2NP laboratory for characterizing these gas sensors under laboratory conditions is depicted in Fig 3. This configuration includes a sample placed in a test cell containing four Sub-Miniature-A (SMA) connectors, a gas generator bench (Omicron technologies) with gas cylinders and mass flow controllers (MFC), a VNA controlled a computer to measure the sensor S_{ij} parameters,

a commercial temperature and humidity sensor (SHT85) and a flow meter placed before or after the test cell. The sensors were placed always in the same test cell, dry air was used as carrier gas at 300 mL/min. In addition, humidity was generated in the Omicron test bench by pressurized deionized liquid water and injected through a proportional valve to regulate RH from 0 to 90%.

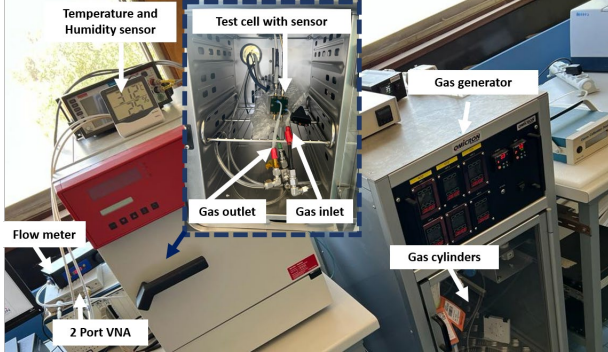


Fig. 3. Detrended HBPEI-Silane sensor frequency response to CO₂ at 0%RH and ambient temperature

B. Sensor response to common atmospheric interferences (humidity and temperature)

In gas sensing applications, the influence of water molecules on sensor performance can be substantial, particularly for outdoor measurements. To explore this effect, the sensing properties related to humidity for both Com HBPEI and HBPEI-Silane sensors were evaluated under controlled laboratory conditions, within a RH range of 0–90% as shown in Fig 4 (a) and (b).

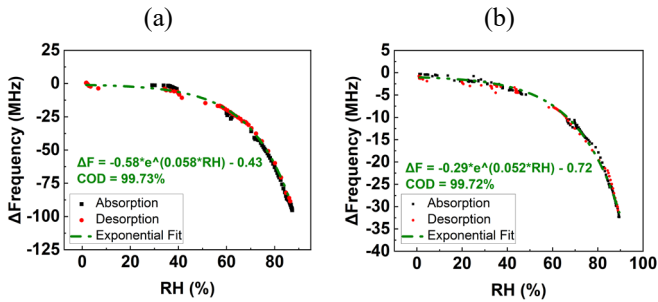


Fig. 4. (a) Test bench for experimental measurement under controlled atmosphere at IM2NP laboratory. Frequency differential response to RH of the (b) Com HBPEI based sensor and (c) HBPEI-Silane based sensor, exponential fits and their corresponding coefficients of determination (COD).

Both sensors exhibited an exponential response to changes in RH within this range. For the Com HBPEI sensor, the frequency shift (Δf) was modeled by $\Delta f \text{ (MHz)} = -0.58 \cdot e^{(0.058 \cdot RH)} - 0.43$ while for the HBPEI-Silane sensor $\Delta f \text{ (MHz)} = -0.29 \cdot e^{(0.052 \cdot RH)} - 0.72$. To assess linear sensitivity, the tangent to the curve was computed at specific RH values. For instance, the Com HBPEI sensor demonstrated sensitivities of -0.035 MHz/%RH and -1.09 MHz/%RH at 1% RH and 60% RH respectively. Conversely, the HBPEI-Silane sensor exhibited sensitivities of -0.015 MHz/%RH and -0.34 MHz/%RH at 1% RH and 60% RH respectively. Notably, functionalizing the Com PEI with silane groups reduced its sensitivity to RH to approximately 43% at 1% RH and 31% at 60% RH. The uncoated resonator shows a lower sensitivity of -0.045 MHz/%RH, and negligible response to RH in magnitude. Response and recovery times were determined by measuring

the time required for the sensors to reach 90% of the maximum change in response during RH absorption and desorption, respectively. At a constant temperature of 22 °C, the Com HBPEI sensor had response and recovery times of 22 s and 44 s, respectively, whereas the HBPEI-Silane sensor recorded times of 44 s for response and 88 s for recovery. The longer times for the HBPEI-Silane sensor can be primarily attributed to its hydrophobicity. Temperature is another critical parameter that influences the performance of gas sensors. The temperature sensitivity of both Com HBPEI and HBPEI-Silane sensors was evaluated within a range of 20–45 °C, while maintaining a constant RH of 60%, as illustrated in Fig 5.

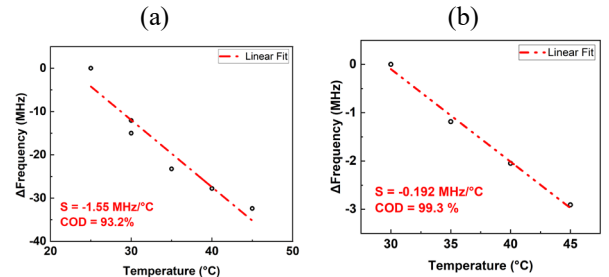


Fig. 5. Temperature calibration curves at 60%RH for the Com PEI sensor (a) and the HBPEI-Silane sensor (b)

Com HBPEI displayed a temperature sensitivity of -1.55 MHz/°C, whereas HBPEI-Silane exhibited a much lower sensitivity of -0.192 MHz/°C. These differences indicate that temperature fluctuations can significantly alter the dielectric properties of the polymers used. The uncoated resonator which is mainly sensitive to temperature (0.07 MHz/°C and 0.01 dB/°C) can be used to correct for temperature variation of the sensor [9].

C. Sensor response to CO₂

The sensors were tested under varying CO₂ gas concentrations ranging from 0 to 10,000 ppm, with different levels of humidity and ambient temperature conditions. Fig 6 shows the differential frequency response of the HBPEI-Silane sensor (represented by the green line), plotted versus the corresponding CO₂ concentration (depicted by the grey line) generated by the gas generator at 0%RH and ambient temperature. As CO₂ concentration increases, the resonance frequency decreases, reflecting an increase in effective permittivity, and vice versa. Notably, the sensor shows reversibility without requiring heating.

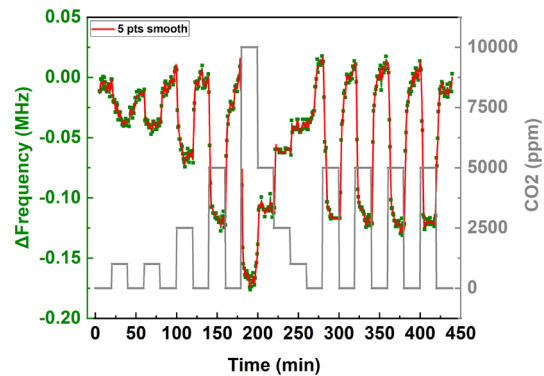


Fig. 6. Detrended HBPEI-Silane sensor frequency response to CO₂ at 0%RH and ambient temperature

The HBPEI-Silane showed a higher sensitivity of -17.3 Hz/ppm (0.17 MHz/%CO₂) as compared to the Com HBPEI

sensor which showed negligible sensitivity of -1.35 Hz/ppm ($-0.012 \text{ MHz}/\% \text{CO}_2$) to CO_2 as shown by Fig 7 (a) and (b) respectively with corresponding fitted lines and CODs. The standard deviation (SD) for the RF sensor frequency response is estimated to be 4 kHz . This corresponds to a limit of detection (LOD) of 760 ppm for the HBPEI-Silane sensor and $9,777 \text{ ppm}$ for the Com HBPEI sensor. The LOD is calculated as $\text{LOD} = 3.3 \cdot \sigma / S$ where σ is the standard deviation of the response and S is the sensitivity. The sensitivities to CO_2 and RH in the same $0 - 1\%$ range for both sensors are compared in Fig 8 (a).

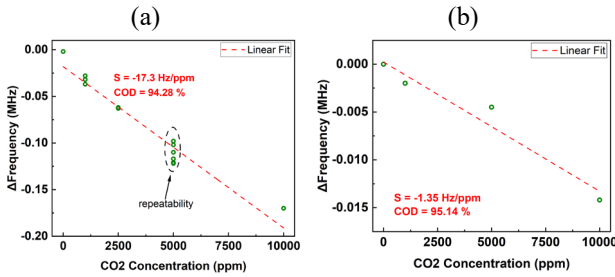


Fig. 7. Sensitivity to CO_2 at $0\% \text{RH}$ at room temperature (a) HBPEI-Silane sensor and (b) Com HBPEI sensor

This highlights the great interest of HBPEI-Silane in increasing sensitivity to CO_2 while decreasing sensitivity to relative humidity. This greater sensitivity to CO_2 may be attributed to a synergistic effect of the full tertiary amine functions (more reactive towards CO_2) and, probably to a lesser degree, of the film morphology (higher surface area). To further explore the impact of humidity on CO_2 sensitivity, both sensors were exposed to CO_2 at $60\% \text{RH}$. The results are displayed in Fig 8 (b), which shows the differential frequency response of the HBPEI-Silane sensor to varying CO_2 concentrations at $60\% \text{RH}$.

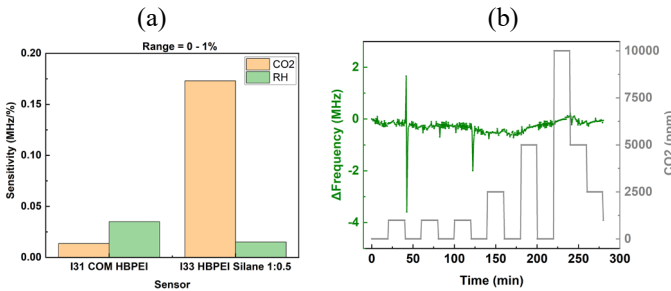


Fig. 8. (a) Comparison of the sensors sensitivity to CO_2 and RH in a range ($0-1\%$) and (b) differential frequency response to CO_2 at $60\% \text{RH}$.

At $60\% \text{RH}$, both the Com HBPEI and HBPEI-Silane sensors displayed no discernible response to CO_2 . This might be due to the saturation of all functional amino groups with water molecules. Given these factors, the integration of an air-drying system or layer is advisable to dehumidify the air before detection, ensuring more reliable air quality monitoring.

D. Specificity analysis

The sensors were characterized under a variety of atmospheric gases, including CO in the range of $0-1,000 \text{ ppm}$, NO_2 up to $5,000 \text{ ppb}$, and O_3 up to $1,000 \text{ ppb}$. These concentration ranges were selected based on typical environmental levels. Characterization for CO and NO_2 was performed at different RH levels (0% , 30% , and $60\% \text{RH}$), while for O_3 , testing was conducted at ambient RH due to

limitations of the ozone generator. Notably, both sensors exhibited negligible responses to these gases within the specified concentration ranges, underscoring their specificity towards CO_2 .

IV. CONCLUSION AND PERSPECTIVES

RF gas sensors employing two types of sensitive materials, commercially available HBPEI and custom-synthesized HBPEI-Silane, were studied. The impact of functionalizing commercial HBPEI to produce HBPEI-Silane on gas sensing properties was rigorously assessed under controlled laboratory conditions. The functionalization process effectively reduced the polymer's sensitivity to RH and temperature while significantly boosting its sensitivity to CO_2 . This enhancement may be also partly attributed to an increase in rugosity in the case of the functionalized polymer. The HBPEI-Silane sensor demonstrated repeatable and reversible responses without the need for heating and exhibited noteworthy sensitivity to CO_2 across a range of 0 to $10,000 \text{ ppm}$. Moreover, the sensor displayed a high degree of specificity to CO_2 . However, it should be noted that the sensor's performance is influenced by humidity, which could necessitate drying the ambient air for reliable outdoor air quality monitoring applications. Future work will explore various functionalization techniques to address these limitations.

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