Sensor Applications

A Novel Molecularly Imprinted Polymer Based Carbon Nanotube-Coated Microwave Sensor for Selective Detection of Methanol Gas

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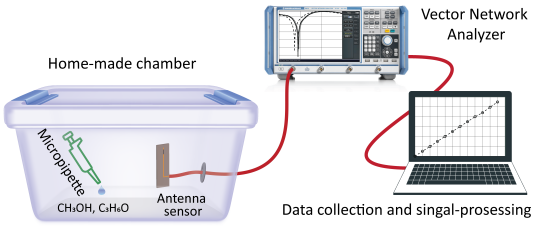
Abstract—In this letter, a novel molecularly imprinted polymer (MIP)-based carbon nanotube (CNT)-coated microwave sensor is developed for the selective sensing of methanol gas. First, a 2.45 GHz broadband monopole antenna with a 400 MHz 10-dB bandwidth is designed. A 5-mm Interdigitated Electrode (IDE) structure is then added to the antenna for high-precision sensing. The IDEs are coated with highly sensitive and conductive CNT with a MIP layer that is selective and specific for methanol gas. Measured sensor results confirm 5.3 to 58.6 parts-per-thousand (ppt) methanol detection with a sensitivity of approximately 1.0 MHz per 5 ppt. The developed sensor showed high selectivity for methanol when tested against acetone. The repeatability of the sensor was ensured by conducting several experiments on different days over a span of 15 days, all with the same concentration and ambient conditions. Furthermore, the antenna is not tuned out of its transmission bandwidth during gas sensing, indicating potential for integration into sensor nodes.



Index Terms—Antenna sensor, methanol gas sensor, molecularly imprinted polymer (MIP), carbon-nanotubes (CNT).

I. INTRODUCTION

Methanol, is a vital chemical raw-material with wide range of applications in pharmaceuticals, fuel, paint, automotive, and many other consumer products [1]. However, it is highly toxic, causing serious health problems. The permissible exposure limit for methanol is 200 parts-per-million (ppm) over 8-hour period [2]. Excessive exposure may cause bronchoconstriction [3], nervous system disorders [4], blood disorders [5], and irreversible damage to the retina [6]. Research further shows that 90% of methanol poisonings are due to insufficient awareness [4]. To promote awareness, selective detection of methanol gas is essential for the industries concerned. Over the past few decades, several sensors based on electrochemical, electroconductive, chemiresistive, and optical techniques have been developed to meet this need [7], [8], [9], [10], [11]. However, the operating conditions and requirements of these sensors increase the development and maintenance costs [12], severely limiting their mass deployment in sensor networks. [13]. Therefore, demand persists for the development of selective methanol gas sensors that are low-cost, reliable and operable at room temperature (RT) [14].

Recently, microwave sensing techniques have attracted great interest due to their simplicity, low-power consumption, cost-effectiveness, and room temperature operation [15], [16], [17], [18]. Microwave antenna sensors can be fabricated by depositing a thin film of sensing material onto the patch antenna. When exposed to the target gas, the sensor detects gas analytes by sensing the changes in the sensing material and measuring their concentrations accordingly [19]. In addition, antenna-type sensors can perform both communication and sensing functions, simultaneously, making them compatible with the integration of wireless sensor networks (WSNs) [20], [18].

Fig. 1. Simple diagram of the molecular imprinting principle. Crosslinking of polymer surrounding an analyte result in a cavity with affinity for that analyte.

Recently, carbon-based nanomaterials have become promising options for real-time gas sensing at RT, as they offer excellent sensitivity and specificity for molecular identification [21]. In particular, carbon nanotubes (CNTs) offer a large surface area for sensing [22], thus providing high sensitivity, fast response, stable performance, and thermal stability [22], [23]. Although sensor materials can be developed to further improve sensor sensitivity, response time, and recovery time, detection with high selectivity is still a challenge.

Molecularly Imprinted Polymers (MIPs) have been adopted in many sensor applications due to their selectivity property for specific target analytes [24], [25], [26], [27], [28], [29]. The selectivity of MIPs emerges during the template-assisted polymerization process, resulting in a cavity complementary to the analyte. A simple diagram explaining MIP synthesis and the principle of molecular imprinting is shown in Fig. 1. First, template molecules of the target analytes

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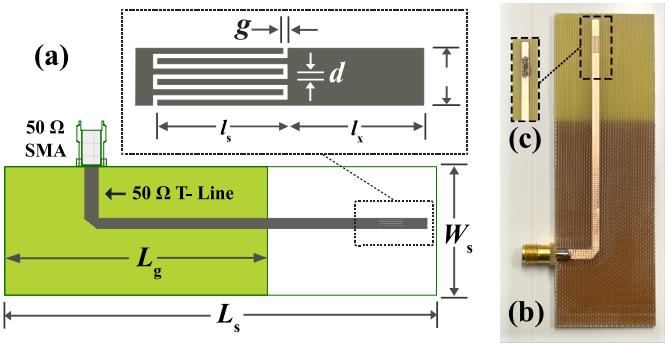

Fig. 2. (a) The configuration of the proposed antenna sensor with IDE structure (b) Realized antenna on FR-4 substrate, and (c) IDE-sensor loaded with MIP-CNT.

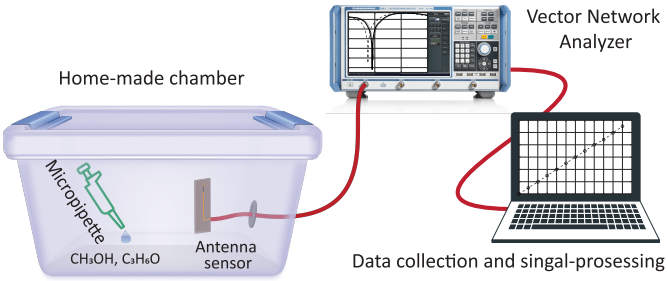

Fig. 3. The measurement setup for the antenna sensor.

are used to creat specific cavities in the material. After removal of the template, the resulting polymer matrix retains imprinted sites complementary to the target, creating rebinding cavities in the material specific for that analyte [30]. The sensitivity of MIP-based sensors can be further improved by incorporating carbon-based nanomaterials [31]. While MIPs have previously been used in gas sensing applications, little research has been devoted to their applications in microwave-based gas sensors. Previous examples of research in MIP-based microwave gas sensors has employed graphene and graphite as the transduction layer and measured $|S_{11}|$ variation for the selective detection of methyl salicylate [32], and methanol vapor [33].

In this letter, we propose a novel MIP-CNT-coated microwave antenna sensor for the selective detection of methanol gas. The sensor exhibits a sensitivity of ~1.0 MHz/5 parts-per-thousand (ppt), and operates at RT. To the best of our knowledge, this is the first CNT-MIP-based microwave sensor using frequency-based detection technique for methanol gas sensing. The selectivity of the developed MIP was additionally tested against acetone gas for 5.3, 10.7, and 16.0 ppt. The sensor demonstrated consistent performance when tested over various days within a 15-day period, thereby confirming its repeatability. Moreover, the shifts in resonance frequency during gas detection do not affect the antenna's transmission bandwidth, indicating its potential integration into WSNs.

II. EXPERIMENTAL DETAILS

A. Sensor-Integrated Antenna Design

Fig. 2(a) shows the geometry of the antenna-sensor developed in this work. The antenna-sensor with the IDE structure is fabricated on an FR-4 substrate (see Fig. 2(b)) has the following characteristics: relative dielectric constant (ε_r) = 4.7, loss-tangent (tanδ) = 0.02, substrate thickness (h) = 1.55 mm, and copper thickness (t) = 0.035 mm. The substrate dimensions include a length of (L_s) 93.4 mm, width (W_s) of 29.2 mm, and a ground plane length of (L_g) of 61.60 mm. The antenna is connected via a 50-Ω SMA connector to the VNA. An IDE structure, consisting of six interdigital fingers with an additional patch (IDE-patch), is integrated with the antenna's for precision detection. The antenna-sensor and IDE structure were designed, simulated, and optimized using Ansys HFSS simulation software. The integral structure provides a larger surface area that enhances the transduced signal through chemical interaction with the analyte being detected, thereby increasing sensitivity. By increasing the number of electrode elements in the IDE structure, sensitivity can be further enhanced. The dimensions of each IDE unit are as follows: w = 2.10 mm, g = 0.2 mm, d = 0.2 mm, l_s = 4.80 mm, and l_x = 5.0 mm). A thin film of CNT-MIP was deposited on the IDE structure, covering the electrodes as shown in Fig. 2(c), and the associated electrical changes were measured using a meter. These were then used to further optimize the geometric parameters to improve the sensing sensitivity. However, readjustments to the length and width of the antenna were necessary to achieve resonance at 2.45 GHz.

B. Synthesis of Molecularly Imprinted Polymer

Multi-wall carbon nanotubes (9.5 nm diameter, 1.5 μm length, Nanocyl NC7000^{TM}) were dispersed at 1 mg ml^{-1} in 1-methyl-2-pyrrolidinone (99%, Sigma-Aldrich) by sonication at 45°C. Poly(vinyl alcohol) (50 mg, Mw 9,000-10,000, 80% hydrolyzed, Sigma-Aldrich) was dissolved in distilled water (10 ml, obtained using a Stuart Merit W4000 water still) by sonication at 45°C for 30 min. Methanol (24.2 μl, ≥ 99.9%, Sigma-Aldrich) was added to the solution and sonication was continued at 45°C for a further 2 min. The solution was then gently stirred at approximately 45°C for 100 min before addition of glutaraldehyde (50 μl, 50 wt.% aq, Sigma-Aldrich). Following a further 200 min, 7.7 ml of the 1 mg ml^{-1} carbon nanotube suspension was added to the reaction, and the suspension was stirred under the same conditions for 17 h. Under constant stirring, the solvent was then evaporated to give a thick paste. 500 μl of 1-methyl-2-pyrrolidinone was added to redisperse the material in preparation for deposition. The final suspension was drop-cast onto the IDE structure (see Fig. 2(c)) in 3 × 0.5 μl volumes. Approximating the same film thickness, 3.7 μl of the CNT-MIP material was cast over the working electrode, counter electrode and bridging dielectric material of a gold screen-printed electrode (ItalSens 3 mm diameter working electrode, PalmSens).

C. Experimental Setup

Initially, electrical measurements were conducted using a CNT-MIP coated electrode attached to a potentiostat (PalmSens4) to understand its electrical behavior and methanol sensing capabilities. Chronoamperometry was performed at a constant potential of 1.0 V, recording current for approximately 2 hours after a 30 min equilibration period in a 10.5 L chamber (EM-Tec Save-Storr 10). Different gaseous environments were created by evaporating different volumes of liquid methanol within the chamber and calculating the final concentration from the ideal gas law. The experiments were conducted in standard laboratory air at room temperature and approximately 10% relative humidity.

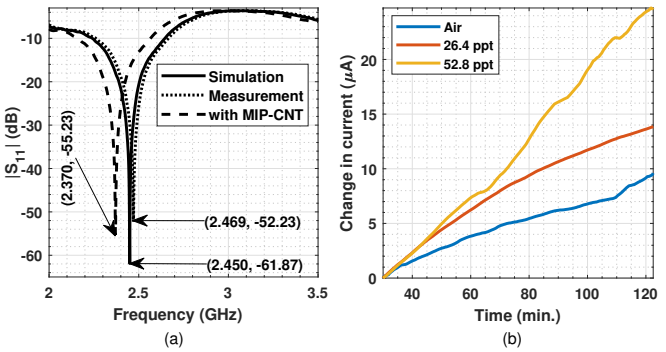

Fig. 4. (a) Antenna return-loss: simulated and measured before and after MIP-CNT coating. (b) Chronamperometry response of MIP-CNT coated electrode to methanol gas.

The antenna-sensor measurements were conducted within a custom-built measurement box with a capacity of 5.2 liters and dimensions of 32 × 21 × 12 centimeters, as shown in Fig. 3. All measurements related to $|S_{11}|$ and frequency were conducted using an R&S ZNB8 Vector Network Analyzer (VNA). In our experiments, the VNA was configured to operate at a power level of -10 dBm, with a frequency sweep ranging from 1 to 4 GHz, and a frequency spacing of 100 kHz. The sensor-antenna was placed inside the gas chamber, connected to the VNA, and the initial (baseline) frequency was recorded. Then, methanol was sequentially introduced into the chamber in liquid forms ranging from 50 to 550 μL (in increments of 50 μL). Following the evaporation of methanol, the resulting concentrations within the sealed containers were calculated to be 5.3, 10.7, 16.0, 21.3, 26.7, 32.0, 37.3, 42.6, 48.6, 53.3 and 58.6 ppt, respectively. A stable shift in the resonance frequency for each concentration is confirmed for a minimum duration of 90 minutes. The frequency shifts are determined relative to the baseline frequency. Sensor responses for all concentrations were remotely recorded with MATLAB.

III. RESULTS AND DISCUSSIONS

A. Sensor Performances

After CNT-MIP coating, the conductivity and susceptibility (between the antenna and IDE-patch) increased by 16.27 mS and 1.56 mS, respectively, while the measured impedance was 60.5 - j6.15 Ω. As a result, the conductivity between the interdigital electrodes increases, thereby increasing the current flow between the antenna and the IDE-patch and extending the antenna's effective length. This shifts the resonance frequency of the antenna to 2.469 GHz (see Fig. 4(a)). The shifts in resonance frequency during gas sensing are determined with respect to this frequency. In addition, chemiresistive measurements were conducted to gain a better understanding of the sensing characteristics of the CNT-MIP layer and verify its sensitivity to methanol gas. As shown in Fig. 4 (b), the rate of current change observed with a CNT-MIP coated electrode was proportional to the methanol vapor concentration. This indicates that the observed frequency shift is due to conductivity changes in the sensing layer in response to methanol vapor adsorption.

Although the antenna was simulated with a design frequency of 2.45 GHz, it reaches its maximum (51.99 dB) at 2.469 GHz, as shown in Fig. 4(a). This deviation (19 MHz) in the resonance frequency is due to the fabrication tolerance of the milling machine.

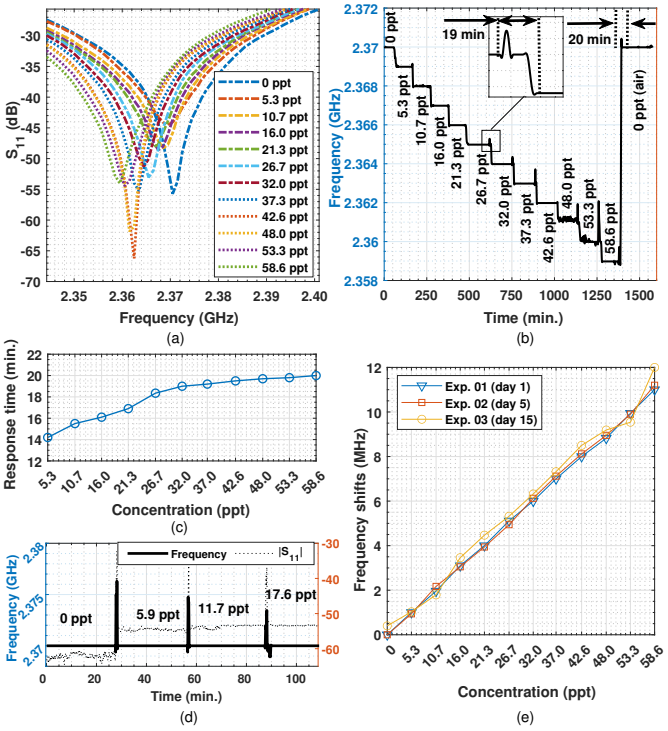

Fig. 5. Sensor's measured: a) $|S_{11}|$, b) instantaneous frequency, c) total response time, d) The selectivity test: sensor's response against ~0-18 ppt of acetone gas, and e) frequency shifts for ~0-58.6 ppt of methanol gas conducted on different days over a 15-day period.

The measured 10-dB bandwidth is 410 MHz (from 2.160 GHz to 2.570 GHz). This huge bandwidth enables frequency-based gas detection without compromising the bandwidth required for wireless applications, eliminating the need for complex tuning circuits. This allows gas detection to be a secondary function of the antenna without compromising its primary function, i.e., communication. Next, the sensor responses to varying concentrations of methanol gas were investigated at RT. When exposed to 5.3 ppt methanol gas, the sensor showed a clear and stable frequency shift of ~1.0 MHz. However, the amount of frequency shift can be controlled by optimising the IDE design (see Section II-A). The process was repeated for subsequent concentrations. The return loss, instantaneous frequency, total response time, selectivity test, and frequency shifts for each concentration were recorded, as shown in Fig. 5(a)-(e).

Although the sensor responds immediately to gas exposure as shown in Fig. 5(b), it takes ~14-20 minutes (see Fig. 5(c)) for the liquid methanol of 50 to 550 μL to evaporate and produce a stable frequency shift. The recovery time is ~20 minutes, which represents the time for the sensor to return to its baseline frequency in air, as shown in Fig. 5(b).

We tested the selectivity of the proposed sensor against acetone at 5.9, 11.7, and 17.6 ppt. Upon exposure to acetone, a 10 dB change in $|S_{11}|$ was observed; however, the sensor showed no measurable frequency shifts (see Fig. 5(d)). Unlike in Fig. 5(e), where linear shifts were observed upon exposure to methanol.

One important factor for a sensor is its repeatability, which demonstrates its ability to produce identical performances over time. To verify this, we conducted multiple experiments on the sensor at various intervals. The sensor exhibited consistent performance when

tested with the same concentrations of methanol on different days over a 15-day period (refer to Fig. 5(e)).

IV. CONCLUSIONS

In this letter, we report a novel, low-cost MIP-CNT composite gas sensor coupled to a 2.45 GHz wideband monopole antenna. A highly sensitive and selective layer of MIP-CNT composite was deposited onto an IDE structure, forming the sensing element for the selective detection of methanol gas at the ppt level. The sensor detected methanol gas concentrations ranging from 5.3 to 58.6 ppt with a sensitivity of ~1 MHz/5 ppt while maintaining the operational bandwidth of the antenna, indicating its potential for integration into WSNs. The sensor's repeatability was confirmed through multiple experiments conducted over 15 days. The developed sensor also demonstrated high selectivity and affinity for methanol gas when tested against ~0-18 ppt of acetone gas.

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