Molecularly Imprinted Polymer Based Antenna Sensor for Methanol Vapour Sensing

Kabir Hossain, Todd Cowen, and Michael Cheffena

***Abstract*—We report a state-of-the-art molecularly imprinted polymer (MIP) based antenna sensor to detect methanol vapour at room temperature. A conductive MIP-graphite composite was synthesised with specificity to methanol and deposited on a 3.6 GHz resonant patch antenna by drop coating. The copper-layered antenna with affinity composite worked in tandem to produce a sensitive and selective room temperature antenna sensor. Continuous sensing was accomplished by monitoring the reflected power, S_{11}, of the antenna in a chamber with methanol vapour. The sensor functions under ambient conditions, providing a strong S_{11} response of approximately 554 $\mu mol\ dm^{-3}\ dB^{-1}$. Thus, the proposed sensor has great potential in gas sensing applications, paving the way for antenna-based pollution monitoring.**

***Index Terms*—Antenna, antenna sensor, microwave sensor, molecularly imprinted polymer, MIP, MIP-based antenna sensor, methanol, gas sensor.**

I. Introduction

DUE to the prevalence of air pollution in both indoor or outdoor spaces, gas sensing and sensor development have become essential in monitoring the poisoning of toxic gases in the surrounding environment [1]–[3]. Methanol is one of the toxic gases that can cause irreparable harm to tissues when it is ingested, inhaled, or absorbed through the skin. Methanol contamination can cause death in the absence of urgent treatment. In addition, methanol is frequently employed in laboratories and chemical plants as a solvent, which creates a high risk of exposure to dangerous concentrations of methanol vapour [4], [5].

In recent years, microwave sensors have become popular due to their real-time sensing capabilities and their ability to work without an additional energy source, contrasting with other sensors (e.g., electrochemical sensors, chemo resistive sensors). Microwave/antenna sensors function using electromagnetic (EM) wave propagation within a specific frequency [6]–[8]. Advancements in sensors have generated interest for numerous applications including their usage in public safety [7], home automation [9], environmental protection [10], and industrial and agricultural monitoring [11]. Nanomaterials (such as MXene and graphene including their derivatives and nanohybrids) are often used in the development of sensors, however, enhancements to the sensor performance as well as the material design and fabrication processes are of paramount importance to attain optimum sensitivity, selectivity, and reliability [12]. These nanomaterials have been integrated into microwave resonator-based sensors, within which they have improved the selectivity for a particular analyte [13]–[15]. Microwave sensors incorporating nanomaterials have also developed for gas-sensing applications [16], [17]. Singh *et al.* [16] reported a carbon nanotube-coated fibre split ring resonator (SRR) microwave sensor for methanol detection. Bailly *et al.* discovered in [17] that properly depositing nanomaterials on the microstrip interdigital capacitor produces an ammonia gas sensor. Instead of utilising a resonator for microwave sensor development, a microstrip patch antenna could be designed to work as a sensor. An additional benefit of this technology is the capacity to transmit/receive signals at the same time, and therefore has the potential to be integrated into a sensor network [18], [19]. However, selectivity can be a limitation when working with nanomaterial-based gas sensors. Improvements in the selectivity for the targeted analyte typically require the surface of the nanomaterials to be doped, defected or functionalised [13], [20]. These processes however are labour-intensive and selectivity issues often remain, leading researchers to adopt molecularly imprinted polymers (MIPs) to improve gas sensor selectivity [21]–[23].

Molecularly imprinted polymers convey selectivity by displaying an affinity for a specific target, giving the potential to be adopted for sensor development [24]–[27]. The specificity of MIPs for a given analyte results from appropriate synthesis in the presence of the target molecule. Removal of the molecule following synthesis leaves an imprint which selectively rebinds the analyte. MIPs are typically applied in liquid samples, with recent emphasis on aqueous conditions, but can also be used in the identification of gaseous analytes (e.g., ethanol, methanol, acetone) [22], [28], [29]. However, they must be coupled to a suitable transducer device to generate a readable response [29]. Although antenna sensors are one of the popular options when it comes to real-time sensing capabilities, limited research has been done on MIP-based antenna sensor development. Adams *et al.* [19] reported a highly selective MIP-based antenna sensor to detect methyl salicylate. However, the chosen Volatile Organic Compound (VOC) was a relatively large molecule that is functionalised in a manner similar to common drug targets of aqueous MIP sensors [30], [31]. To develop these foundations, we chose methanol as a model in this study—which is more volatile (lower inherent affinity) and less chemically distinct—to develop the antenna sensor [4]. The developed MIP was deposited on a 3.60 GHz patch antenna by drop coating.

In this paper, we report a MIP-based antenna sensor for methanol, which is the first of its kind to the best of our knowledge. The sensor relies on radio frequency signals, and it is workable at room temperature with continuous detection by

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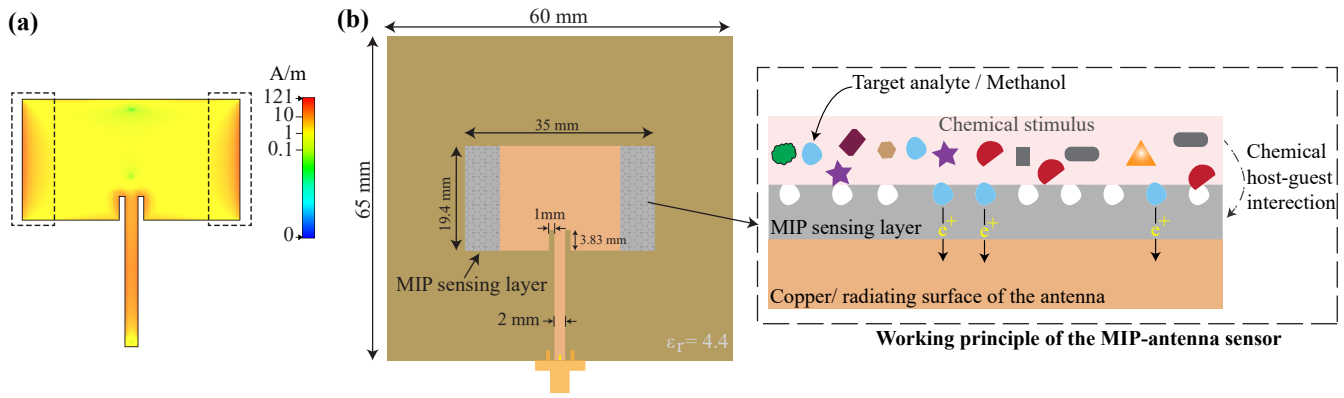

Fig. 1. (a) Surface current distribution of the antenna with highlighted strong region. (b) An illustrative description of the proposed MIP-antenna sensor, which contains a MIP sensing layer on top of the antenna's radiating surface. It also shows possible working principle of the MIP-antenna sensor: the MIP sensing layer traps the target analyte, resulting in electron transfer to its immediate transducer layer (i.e., antenna surface) upon analyte binding. The current is therefore augmented on the radiating surface, which ultimately changes the observed antenna impedance.

monitoring the reflected signal power from the antenna port. Molecularly imprinted polymer-based antenna gas sensors are therefore shown to be an effective basis for selective and sensitive air pollutant monitoring.

II. Methodology

A. Sensor Preparation

The sensor preparation process was completed in three steps: (1) antenna prototype development, (2) preparation of the MIP-composite, and (3) depositing the MIP-composite on the antenna surface.

In step 1, a low cost 1.6 mm thick FR4 substate with a copper thickness of 35 μm was chosen to develop the antenna prototype development.

In step 2, a highly selective MIP-graphite composite for methanol vapour analyte were developed. Poly vinyl alcohol (15 mg) was first dispersed in distilled water (37.5 ml) by flask submersion in a heated ultrasonic processor water bath. Sonication was performed for 20 minutes at 40 °C to maximise polymer dispersion. Graphite (76 mg in 7.5 ml distilled water) was simultaneously sonicated then stirred in parallel with the polymer. Methanol (4.73 μl, added as 100 μl of 47.5 μl ml^{-1} aqueous solution) was then added to the polymer dispersion, and sonication was continued for a further 2 minutes. The flask was then transferred to a heater water bath (40 °C) and stirred gently, followed by dropwise addition of glutaraldehyde (15 μl of 50 wt.% aqueous solution) after 60 minutes. After a further 120 minutes, 6.82 ml of the concentrated suspension of graphite was slowly added to the flask, followed by further stirring for approximately 20 hours. The contents of the flask were then transferred to an evaporation dish and stirring continued until all solvent and template had evaporated. The composite was then resuspended in distilled water at a concentration of approximately 30 mg ml^{-1} by stirring under ambient conditions for approximately 15 minutes.

In the third step, the MIP-graphite composite sensing layer was deposited on the patch antenna surface with strong surface current regions (shown in Fig. 1(a)). First, the antenna surface was cleaned with an ultrasonic cleaner for five minutes. After the antenna surface was properly dried 1 ml of MIP-graphite composite was drop-cast onto the each side of the antenna surface. The antenna sensor prototype was then heated at 50 °C, resulting in the MIP sensing layer being bound to the antenna surface. Fig. 1(b) depicts the proposed MIP based antenna sensor which consists of a MIP sensing layer on top of the two sides of the antenna surface.

B. Sensing Mechanism

When the target analyte (methanol) binds with the MIP layer, a charge transfer process modifies the resistance of the MIP-composite. This in turn alters the antenna surface current distribution resulting in variation of the conductivity of the antenna surface. Fig. 1(b) contains a graphical presentation of the sensing mechanism of a MIP based antenna sensor. Analyte sensing can therefore be performed by monitoring the changes in the impedances (i.e., output-to-reflected signal ratios) between the antenna and the load termination.

C. Experimental Setup

Fig. 2 depicts the graphical representation of the experimental procedure and experimental setup in this study. We injected and sealed 2 ml of methanol via micropipette into an airtight chamber (10.5 ± 0.05 dm^3 EM-Tec Save-Storr 10 inert gas container). The methanol was then allowed to evaporate at room temperature over the following 2.5 hours. This leads to the concentration of methanol vapour 4.708 mmol dm^{-3}. The antenna reflected power, S_{11}, was measured in regular 5-minute intervals using a Vector Network Analyzer (VNA, ZVA 67, Rohde and Schwarz).

III. Result and Discussion

A. Antenna Performance

We designed a patch antenna to work at 3.50 GHz using Computer Simulation Technology (CST) Microwave Studio Suite (MWS) in a time-domain solver. We measured the antenna reflected power using a VNA. Fig. 3(a) shows the

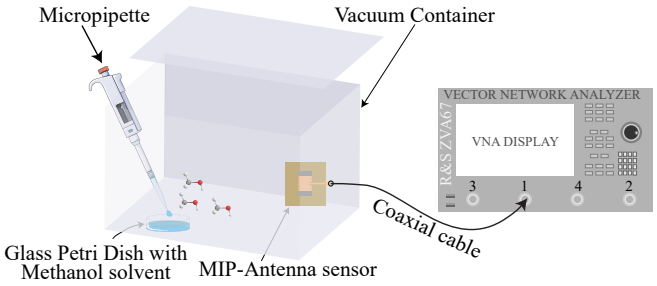

Fig. 2. Graphical illustration of the overall experimental setup.

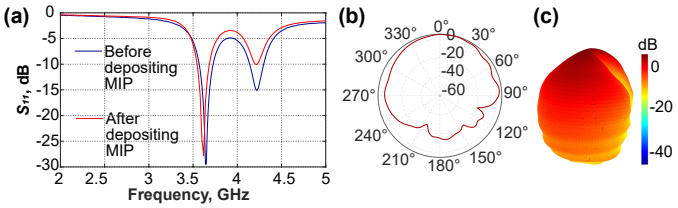

Fig. 3. Measured (a) reflected power of the antenna, (b) radiation pattern at *xz*-plane, and (c) 3D radiation pattern.

measured reflected power of the antenna before and after depositing the MIP. The resonant frequency of the bare antenna (without MIP deposition) is at 3.60 GHz and the resonant frequency is shifted to 3.595 GHz after depositing the MIP-composite on the surface of the antenna. This is a result of the MIP composite containing graphite, a relatively conductive material [32]. The MIP sensing layer on the antenna resonant surface not only changes the conductivity of the antenna, but also changes the direction of the surface current, which causes a slight shift in the resonant frequency.

The MIP fictionalised antenna's radiation pattern was measured to ensure the performance was not affected by the addition of the composite. Fig. 3(b) and Fig. 3(c) show a directional radiation pattern of the MIP-antenna sensor and its 3D radiation pattern, respectively. The measured radiation efficiency was 53.92% with a peak gain at 3.60 GHz of 4.85 dB.

B. Performance Evaluation of the Sensor

We analysed the performance of the MIP based antenna sensor over time and recorded its corresponding S_{11} measurements. The results in Fig. 4 indicate that our proposed sensor responded to a very low concentration of methanol vapour, evidenced by the change of approximately 3-dB in just 15 minutes. After 90 minutes the response levels (from approximately 30 dB to 29 dB) were stable as the methanol vapour reached its maximum concentration. The response is therefore approximately 554 $\mu mol\ dm^{-3}\ dB^{-1}$, suggesting a limit of detection in the parts-per-billion range with appropriate radiation shielding. Fig. 5 provides a visual representation of the data in the form of reflected power versus time, which suggests a time-dependent variation in gas concentration. Hence, based on the concentrations of the target molecules present, the impedance of the antenna was altered. According to the guideline of the US Occupational Safety and Health

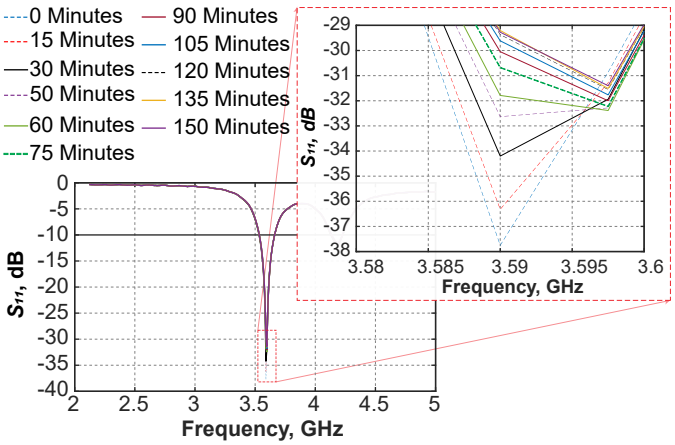

Fig. 4. The effect of methanol concentration in the vacuum container at different time intervals (from 0 to 150 minutes).

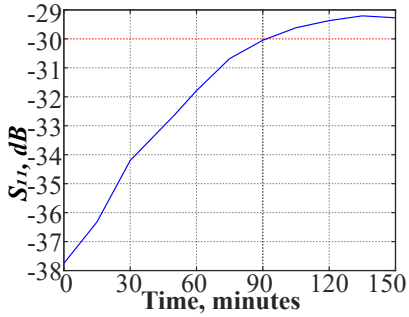

Fig. 5. MIP-antenna sensor's mean response in terms of antenna reflected power versus concentration changes of methanol vapour over 150 minutes at 3.59 GHz.

Administration, the permissible methanol exposure limit is around 200 ppm [33]. The detection limit of the proposed MIP-antenna sensor for methanol vapour is predicted to be far below this, based on these initial finding. The described device therefore has great potential in gas sensing applications due to its reliable functioning under ambient conditions.

The sensing layer could be improved by replacing the graphite in the MIP-graphite composite with more conductive material. Selectivity studies also need to be conducted but the composite has previously shown good selectivity for methanol over similar VOCs. This was beyond the scope of this article, but it could be an exciting basis for future work.

IV. Conclusion

We demonstrated a low-cost MIP-based antenna sensor for sensing methanol vapour. The MIP sensing layer provides good selectivity and sensitivity while functioning at room temperature in a laboratory setting. However, further investigations need to be conducted to test the sensor's selectivity against other VOCs, evaluate the limit of detection, and determine the optimal sensor recovery protocol. According to our preliminary research, the sensor may be sensitive to very low levels of methanol vapour, making it a potential tool for monitoring pollution in the future and opening the door to antenna-based gas sensing technologies.

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