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A Miniaturized Amperometric Hydrogen Sulfide Sensor Applicable for Bad Breath Monitoring

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Abstract: Bad breath or halitosis affects a majority of the population from time to time, causing personal discomfort and social embarrassment. Here, we report on a miniaturized, microelectromechanical systems (MEMS)-based, amperometric hydrogen sulfide (H_2S) sensor that potentially allows bad breath quantification through a small handheld device. The sensor is designed to detect H_2S gas in the order of parts-per-billion (ppb) and has a measured sensitivity of 0.65 nA/ppb with a response time of 21 s. The sensor was found to be selective to NO and NH_3 gases, which are normally present in the oral breath of adults. The ppb-level detection capability of the integrated sensor, combined with its relatively fast response and high sensitivity to H_2S , makes the sensor potentially applicable for oral breath monitoring.

Keywords: hydrogen sulfide; amperometric; MEMS; gas sensor; bad breath; halitosis

1. Introduction

Bad breath or oral malodor, affects a majority of the population on a regular basis. The presence of plaque, tongue coating [1], gum diseases [2], exposed necrotic tooth pulp, and healing wounds [3] are known to be the cause of oral malodor. Microorganisms present in oral cavities react with organic compounds, releasing sulfur-containing by-products that lead to bad breath. Specifically, sulfur-containing by-products, such as hydrogen sulfide (H_2S), methyl mercaptan (CH_3S), and dimethyl sulfide ($(\text{CH}_3)_2\text{S}$), are associated with bad breath, which is also termed as halitosis [4].

Until recently, oral malodor was diagnosed by physicians in a purely subjective manner (smelling). However, recent developments in sensor technology have provided measuring instruments with sensitive detection of bad breath. The most successful commercial measuring instrument is the Halimeter™ [5], a standard clinical bench-top instrument used to measure volatile sulfur compounds (VSCs), particularly H_2S gas concentration. In this instrument, the user blows into a tube attached to the instrument and a concentration value is presented on a display. Halitosis in an adult is classified as “normal” if the concentration is within the range of 80–160 parts-per-billion (ppb), “weak” if the concentration is within the range of 160–250 ppb, and “strong” if the concentration is greater than 250 ppb [6,7]. The disadvantage of the Halimeter instrument is that it is a bench-top apparatus (3.6 kg) that requires warm-up times and yearly maintenance [8] and is thus an instrument that is primarily designed for patient examination or population studies. However, to more directly address and counteract personal discomfort, ad-hoc mobile monitoring of bad breath would be highly desired. To achieve such monitoring, the sensor element is essential, which requires a small form factor for integration, a fast response time, and ppb-level sensitivity.

Among the various types of H_2S sensors developed, amperometric sensors are particularly advantageous as it allows the fabrication of miniaturized and high sensitivity sensors with fast response time. Schiavon and Zotti achieved detection limits of 45 ppb using discrete porous silver

electrodes supported on separate ion-exchange membranes [9]. However, nonintegrated discrete components result in relatively large-size sensors, which is undesirable when developing a handheld instrument. Recently, Yang et al. showed a fast response Nafion-based amperometric sensor that could detect H_2S in the range of 0.1–200 ppm [10]. However, a complex fabrication method of the sensing electrode and lower sensitivity limits the sensor from being used in the ppb range, which is required for bad breath detection.

In the present work, a miniaturized and integrated electrochemical H_2S sensor with fast response time and a ppb-level sensitivity that is applicable for Halitosis measurement is demonstrated. A simple fabrication method involving high aspect ratio etching and atomic layer deposition of platinum provides the basic structure for preparation of the sensing electrode. The sensor was characterized for its cross sensitivity to nitric oxide (NO), which is normally present in the oral cavity and nasal cavity. Nasal cavity NO contributes to the high concentration in the oral cavity and can affect the NO concentration in the oral cavity. A typical concentration of NO in the nasal cavity is in the range of 0–900 ppb [11], while it is in the range of 20–100 ppb in the oral cavity. In addition, the sensor was characterized with ammonia (NH_3) gas, which is present in the oral cavity in the range of 0–450 ppb [12].

2. Sensor Design and Measurement Method

The sensor design is based on the principle of amperometric detection of H_2S gas. The working, reference, and counter electrodes, together with the electrolyte, constitute the basic elements of the sensor. Particularly in the present design, the working electrode consists of a nanostructured NafionTM (Chemours, Wilmington, DE, USA) coating that in turn is leveraged through a microporous high aspect ratio structure. The interaction between this large-area working electrode, the gas, and the electrolyte (5% H_2SO_4) under electrical bias leads to the oxidation of H_2S gas at the surface of the electrode, causing a current flow between the working and the counter electrodes. The working electrode current is then measured using a potentiostat, maintaining a constant voltage of +1.1 V with respect to the reference electrode. Figure 1a shows the schematic cross section of the sensor design, and Figure 1b shows the photograph of a bare die of the sensor with a dimension of 10 mm \times 10 mm \times 1 mm. The design, fabrication, and assembly of the sensor have been described in our previous work [13].

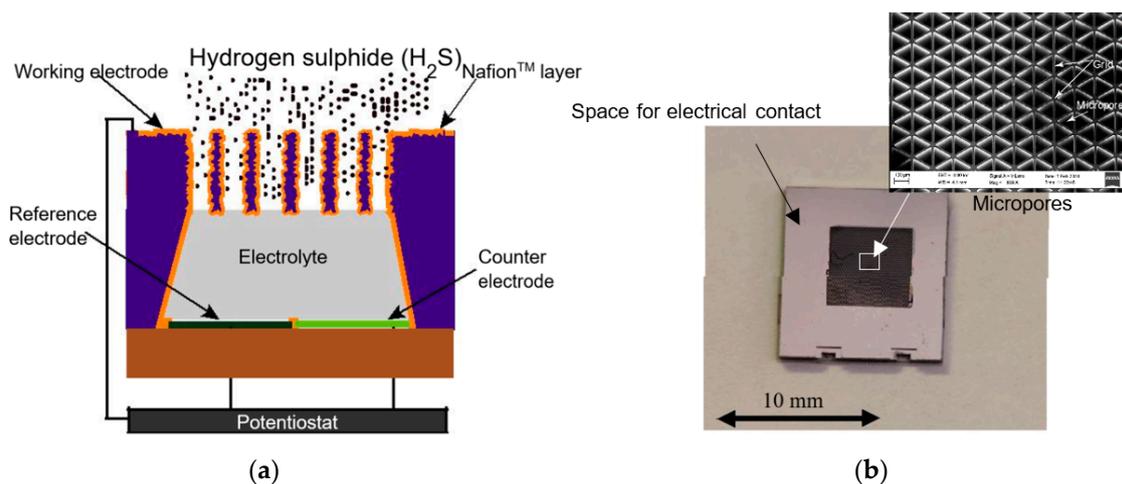


Figure 1. (a) Schematic cross section of the sensor design indicating the high aspect ratio micropores with a nanostructured porous NafionTM layer. (b) Photograph of the amperometric sensor with the porous structure in the middle (dark area). Inset: SEM image shows the microporous grid structure of the working electrode. The working electrode of the sensor is fabricated by deep reactive ion etching and platinum atomic layer deposition of a silicon on insulator (SOI) wafer, and the counter and reference electrodes are fabricated on a glass wafer, which is then assembled together by anodic bonding [13]. The sensor has a footprint area of 10 \times 10 mm² and a thickness of approximately 1 mm.

In order to test the sensor for different gases and gas concentrations, a measurement set-up was built as illustrated in Figure 2. In this set-up, a 10 ppm H₂S in N₂ gas (AGA gas AB, Lidingö, Sweden) was mixed with a pure N₂ gas (99.95% pure, AGA gas AB, Lidingö, Sweden) to obtain the desired concentration. A scrubber (Dräger, type 1140, Lidingö, Sweden) was used to remove potential residues in the N₂ gas. To measure the selectivity of the sensor to interfering gases, 200 ppb NO in N₂ gas (AGA gas AB, Lidingö, Sweden) and 45 ppm of NH₃ in N₂ gas (AGA gas AB, Lidingö, Sweden) were used. In order to humidify the gas mixture, a custom-made humidifier consisting of a syringe with moistened paper was used. A mechanical sealing module was further used to reduce evaporation of the electrolyte. Further details on the measurement set-up used for sensor characterization can be found in our previous work [13].

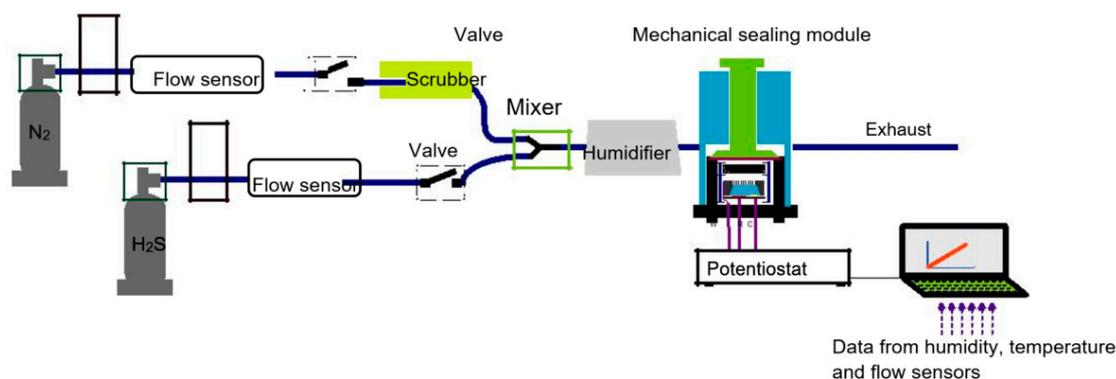


Figure 2. Schematic illustration of the measurement set-up used for characterization of the H₂S amperometric sensor. Data from the flow sensors, the temperature sensor, and the humidity sensor were accessed using a LabVIEW™ (National Instruments, Austin, TX, USA) program.

3. Results and Discussion

The sensor was tested for its H₂S gas sensitivity, selectivity to NO and NH₃, and response time. A gas flow of 550 mL/min and 50% relative humidity (RH) was maintained for all measurements.

3.1. Sensitivity

In order to determine the sensitivity of the sensor, the H₂S concentration was varied in five steps of 75, 150, 250, 500, and 820 ppb. Three such variations were carried out using the measurement set-up. The output current from each concentration was determined by calculating the difference between the working electrode current at t_{90} (cf. Figure 5) and the working electrode current at zero H₂S concentration. The output currents and the linear fitting for five different H₂S gas concentrations are plotted in Figure 3. Based on the linear fit, the maximum sensitivity of the sensor was calculated to be 0.65 nA/ppb. The sensor detects H₂S gas in the lower limit of 75 ppb and a higher limit of 820 ppb and is within the range required for monitoring the oral breath. The lower limit concentration of 75 ppb was measured without being affected by the noise in the system.

The sensitivity graph of commercial H₂S sensors as compared to the designed integrated sensor is shown in Figure 4. In order to maintain a fair comparison, the area of the working electrode is normalized to the sensitivity, i.e., 0.65 nA/ppb is obtained for a footprint area of 25 mm² arriving at a normalized sensitivity of 2700 nA/ppm/cm². The integrated H₂S sensor has a measured area normalized sensitivity that is approximately 2.5 times more than the sensitivities of commercial sensors. This shows a potential for the integrated sensor to be fabricated with a smaller footprint area with a reduced sensitivity in order to realize a smaller sensor, leading to a miniaturized handheld instrument.

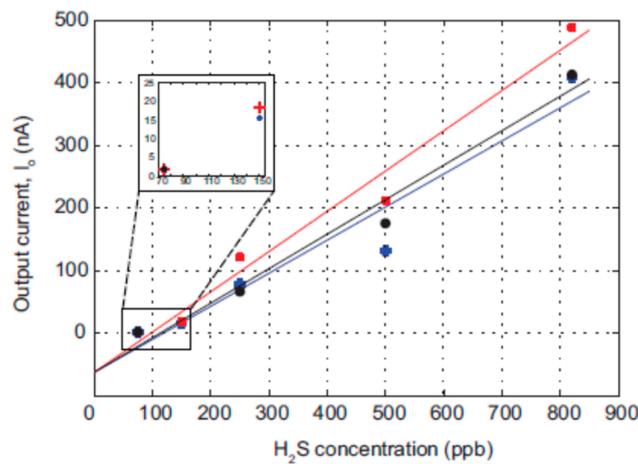


Figure 3. Output current I_o as a function of H_2S concentration. A linear fit to each concentration variation gives the slope, which is then related to the sensitivity of the sensor.

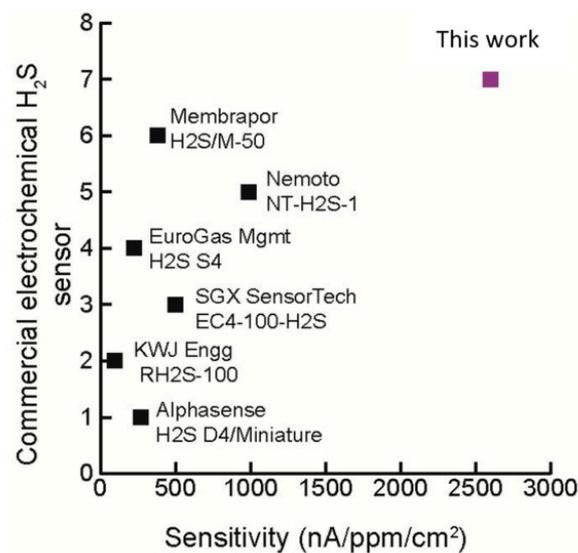


Figure 4. Comparison of area-normalized H_2S sensitivity ranges for several commercial amperometric sensors. The sensitivity of the integrated sensor is approximately 2.5 times higher than the sensitivity of commercial sensors.

3.2. Selectivity to NO and NH_3

To obtain the selectivity to NO gas, the output current was measured at 200 ppb NO gas concentration, and the NO sensitivity was calculated to be approximately 0.04 nA/ppb, which is in agreement with our earlier fabricated prototype [13,14]. The selectivity can be defined as the ratio of H_2S sensitivity to NO sensitivity and is calculated to be approximately 16. NO concentration of approximately 900 ppb is commonly found in the nasal cavity that can affect the oral breath [11]. However, a concentration of 900 ppb of NO results in an equivalent H_2S concentration of 55 ppb, which is within a normal halitosis range. Therefore, the NO contamination from the nasal cavity has negligible effect on the H_2S concentration from the oral breath. The selectivity of the sensor to NO could be further increased by reducing the nasal NO contamination from the oral cavity either by breath maneuver or by clamping the nostrils while measuring H_2S concentration from the oral cavity. Other sources of NO release, such as lungs and oral cavity, can be neglected due to a low NO concentration (20–100 ppb), which is likely to have a minimal interference with H_2S detection.

The output current of the sensor to 45 ppm NH_3 gas concentration was found to be below the detection limit. Therefore, the sensor will not be sensitive to NH_3 gas present in the oral cavity.

3.3. Response Time

The response time of the sensor to a 250 ppb H₂S concentration was estimated by measuring the rise time (t_{90}) of the sensor, i.e., the time required to reach 90% of the maximum output current. The response time of the sensor was measured to be 21 s, as shown in Figure 5. A thorough investigation of the method of oral breath sampling to capture the H₂S gas concentration at a constant rate that could be correlated to the sensor response time has not yet been reported. However, Tangerman et al. collected a sample of oral breath by breathing into a syringe for 5–10 s. The sample was then used for H₂S concentration detection [15]. The recommended procedure for Halimeter instrument includes an initial three-minute period during which the patient breathes through the nose with lips sealed. A pipe attached to the instrument is then inserted into the partially opened mouth, and a pump withdraws gas from the oral cavity for concentration measurement [16,17]. It is conceivable that an oral breathing in the range of 20–30 s could be considered for H₂S concentration measurement.

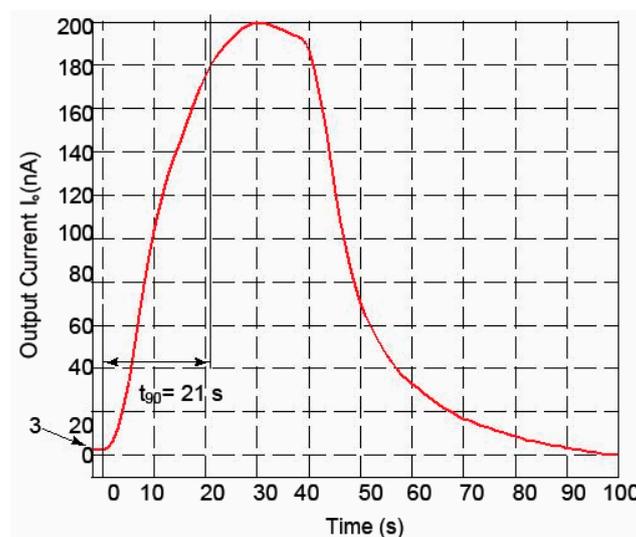


Figure 5. Output current response to 250 ppb step of H₂S gas concentration. A response time (t_{90}), i.e., the time required to reach 90% of the maximum output current, of 21 s was measured for the sensor.

In order to assess the response time of the integrated sensor, a comparison graph with commercial H₂S sensors is shown in Figure 6. The response time (t_{90}) of 21 s is comparatively better than most of the currently available commercial sensors. In order to have a real-time measurement, the response time can be further decreased by optimization of the sensor design.

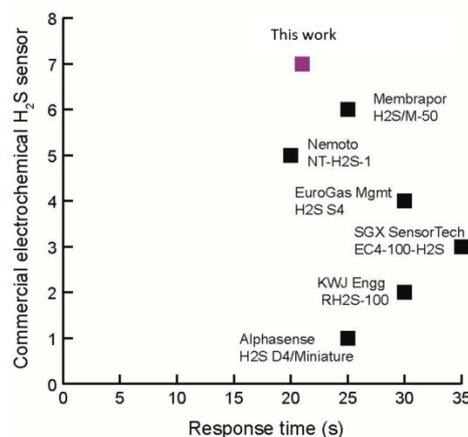


Figure 6. Response times of several commercial amperometric H₂S sensors. The graph shows that the integrated sensor has a better response time compared to commercial sensors.

3.4. Working Electrode Current Drift

The response of the sensor to five different concentrations is shown in Figure 7. The graph shows a background current drift of 0.675 nA/min, which is equivalent to approximately 1 ppb/min of H₂S concentration drift. Therefore, for a response time of 21 s, the drift component is approximately 0.3 ppb, which is negligibly small. Hence, an accurate measurement of H₂S concentration can be deduced from the output current.

3.5. Halitosis Measurement Range

Figure 7 shows the working electrode current for five different steps of H₂S gas concentration. The sensor can measure the H₂S concentration in the region of normal, weak, and strong halitosis that is required for monitoring the oral health. Consequently, the sensor can be applied to detect the entire dynamic range of H₂S concentration present in the oral breath. In addition, the sensor could be useful in dental clinics for follow-up measurement of the halitosis content before and after oral dental treatment.

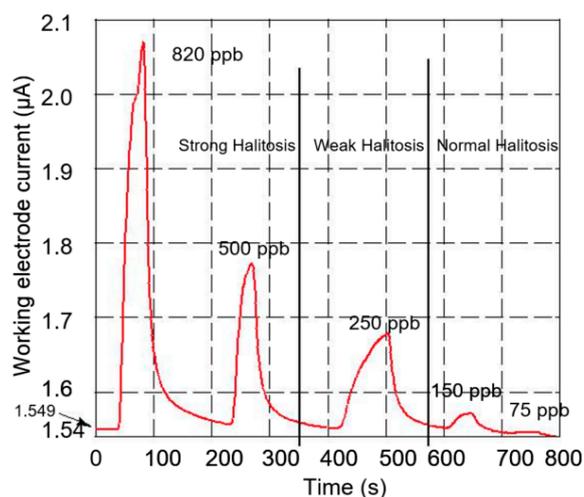


Figure 7. Working electrode current for five different H₂S concentrations. The sensor is able to detect the entire dynamic range of H₂S concentration that could be correlated to the concentration present in the oral breath. The background current of the sensor could be due to the interference from humidity or due to high conductivity of the electrolyte.

4. Conclusions

In this paper, an integrated amperometric sensor has been evaluated for the detection of hydrogen sulfide (H₂S) concentration present in the oral breath. The sensitivity of the sensor is measured to be 0.65 nA/ppb with a response time of approximately 21 s, which is comparatively better than commercially available sensors. The sensor can be applied to measure bad breath where the concentration of H₂S gas indicates a malodor in the breath. The entire range of H₂S gas concentration present in the oral breath can be diagnosed by the sensor. For more complete measurements, detection of methyl mercaptan (CH₃S) and dimethyl sulfide (CH₃)₂S concentration in combination with H₂S concentration will give a more comprehensive representation of oral health. Overall, a prototype has been realized to measure H₂S gas concentration that is relevant for bad breath monitoring.

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Conflicts of Interest: The authors are inventors on a granted patent and multiple patent applications describing a miniaturized amperometric gas sensor.

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