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WIRELESS, BATTERY FREE WEARABLE ELECTRONIC NOSE

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ABSTRACT

Volatile organic compounds (VOCs) are excreted through the skin or exhaled breath. They are end products of human metabolism, metabolism of gut microflora, and ingested or inhaled substances. VOCs can be noninvasively sampled and could be a useful marker for disease. However, medical diagnostics rarely considers the VOCs that are expelled from the body. Here, we introduce a miniature, low-cost, and battery-free electronic nose (e-nose) sensor for passively identifying chemical patterns that are excreted from the human skin or exhaled breath. The platform is composed of an array of conductive polymer filaments created with a two-layer system of multi-walled carbon nanotubes and four different, solution processable polymers. The "breathprint" signature–consisting of the resistance of each filament–can be read from the sensor using a near-field communication-enabled device, such as a smartphone. The e-nose sensor contains a system on a chip with near-field communication (NFC) functionality and a radio frequency antenna to harvest power. The sensor was tested against six common VOCs that are released from the human body.

Keywords: electronic nose, wearable electronics, battery-free, gas sensor

1. INTRODUCTION

Portable e-nose sensors, such as the Cyranose 320, can be used to analyze the VOCs in exhaled breath, which are rich in physiological information [1,2]. The technique is noninvasive, painless, inexpensive, and could improve diagnosis and monitoring. The mixture of VOCs excreted from the human body include both ingested or absorbed substances as well as end products of human metabolism, and products of intestinal microflora. The composition of VOCs excreted are associated with health and disease. Several studies have provided evidence in support of using a portable e-nose sensor as a diagnostic tool for diseases with a high degree of specificity and sensitivity [3,4]. Other methods for detecting VOCs include conductive polymers, metal-oxide semiconductors, and surface acoustic wave sensors. Conductive polymer composites passively and reversibly interact with VOCs without requiring power and have been shown to be effective in classifying previously identified VOCs [2,5,6].

Here, we introduce a wearable e-nose sensor that can be worn anywhere on the body to measure the VOCs excreted through the skin (**Figure 1**). The e-nose sensor can also be integrated with a mask to measure the VOCs excreted through exhaled breath. The sensor mimics the olfactory system of the human body by using an array of different sensors that will react differently to VOCs that are present. This array of sensors was made to fit on a compact sensor that is flexible and battery free.

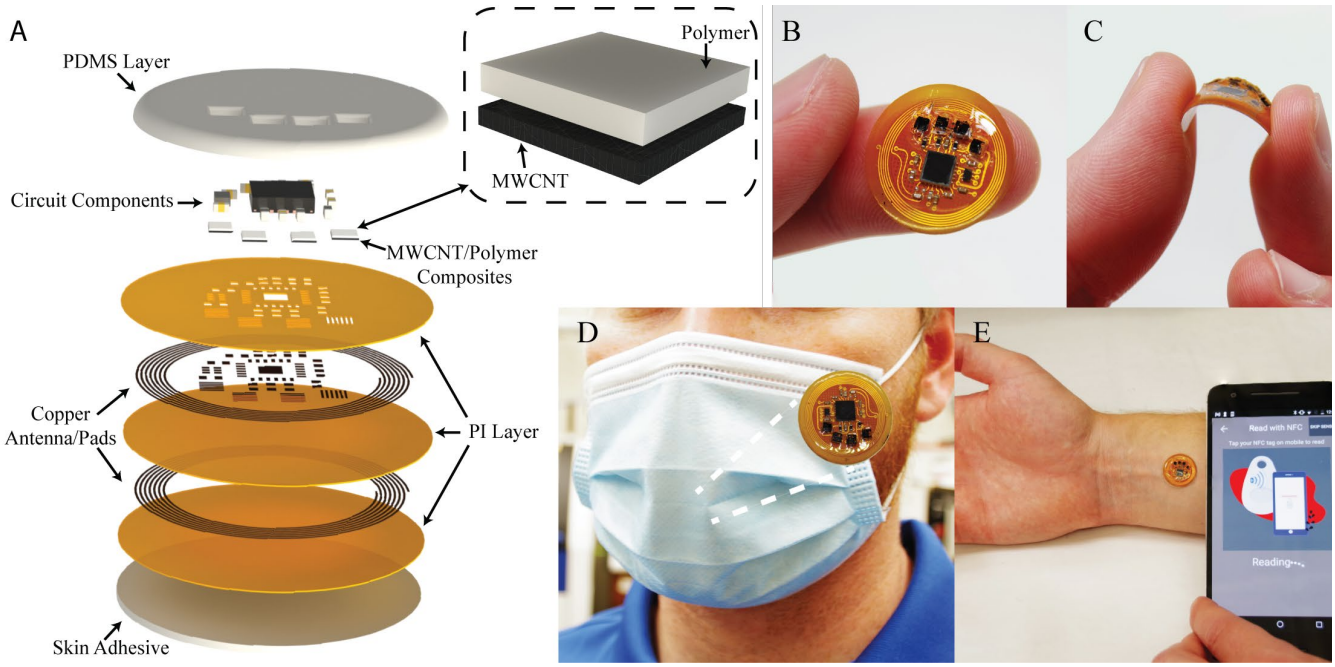

FIGURE 1: A) EXPLODED VIEW ILLUSTRATION OF THE E-NOSE SENSOR CONSTRUCTION. B) PHOTOGRAPHS OF THE FLEXIBLE E-NOSE SENSOR LOCATED ON THE INDEX FINGER AND C) BENT BETWEEN THE THUMB AND INDEX FINGER. D) PHOTOGRAPHS OF THE E-NOSE SENSOR THAT CAN BE INTEGRATED WITH A MASK TO MEASURE THE VOCS EXCRETED BY THE HUMAN BODY OR E) ATTACHED THE SKIN TO MEASURE VOCS EXCRETED THROUGH THE SKIN. THE BREATHPRINT SIGNATURE CAN BE READ FROM THE SENSOR USING AN NFC-ENABLED DEVICE (E.G. SMARTPHONE).

Importantly, the conductive polymer composites passively and reversibly interact with VOCs, allowing the sensor to sample the local environment without requiring power. The "breathprint" signature–the resistance of the array of sensors–can be read from the sensor using an NFC-enabled device, such as a smartphone. The e-nose sensor includes a system on a chip with NFC functionality, analog-to-digital converter, and a radio frequency antenna to harvest power. This miniaturized, wearable, and battery-free e-nose sensor provides an efficient, cost-effective, and rapid screening tool to identify previously identified breathprint signatures that are associated with health or disease.

2. MATERIALS AND METHODS

A wearable e-nose sensor was designed that is small, lightweight, battery-free, and wireless. This device was built with the goal to provide a simple, inexpensive (less than $20), and non-invasive way to measure VOC mixtures that are excreted from the human body. The unpowered sensor can passively and reversibly interact with VOC mixtures that are released by the body through sweat glands or the exhaled breath, which can indicate the patient's health status [1]. The small wearable device enables noninvasive and continuous monitoring and provides a path towards rapidly identifying changes in patient's health status.

2.1 Circuit Design

The wearable e-nose device shown in **Figure 2** was centered around a system on a chip with NFC functionality (RF430FRL152H, Texas Instruments) that included a low-power microcontroller, nonvolatile memory, and 14-bit analog-to-digital converter (ADC). A 13.56-MHz antenna was included to provide a two-way wireless interface to transmit data as well as harvest power from an NFC-enabled device. The overall size of the antenna was minimized by placing a planar coil inductor on both the top and bottom layer of the flexible printed circuit board (PCB). The flexible PCB was 0.15mm thick with a copper weight of 0.5oz. Data was gathered from the e-nose sensor using an NFC-enabled smartphone (Nexus 6P) with custom Android application (Figure 1E).

Interdigitated electrodes were integrated into the flexible PCB design for each of the conductive polymer sensors. Four different polymer composites were used while the microcontroller had three ADC channels. An analog switch (FSA4157L6X, Onsemi) was used to increase the number of ADC channels to include four e-nose filaments on the device.

The entire device was coated in a transparent poly(dimethylsiloxane) (PDMS; Sylgard 184, Dow Corning with oligomer-to-curing agent ratio of 10:1) that was cured at 80 °C for one hour. During casting, 2 x 2 mm wells were created over the interdigitated electrodes by temporarily bonding pieces of acrylic, coated in silane, to the flexible PCB. After curing, the acrylic pieces could be easily removed. The wells helped contain the solution during drop casting of the multi-walled carbon nanotube (MWCNT) ink and polymer solutions to create the array of conductive polymer sensors. The PDMS encapsulation also provided a soft and flexible waterproof seal.

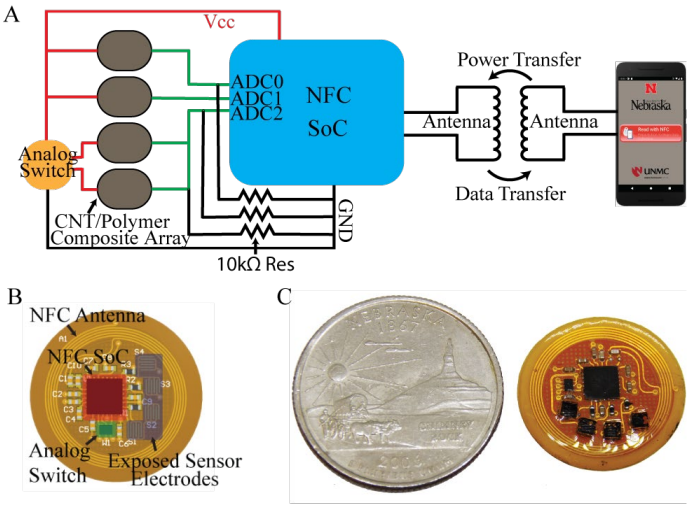

FIGURE 2: A) SCHEMATIC OF THE E-NOSE SENSOR, INCLUDING NFC SYSTEM ON CHIP, CONDUCTIVE POLYMER FILAMENTS, AND RF ANTENNA FOR POWER AND DATA TRANSFER. B) RENDERING OF THE E-NOSE SENSOR. C) PHOTOGRAPH OF THE E-NOSE SENSOR NEXT TO A U.S. QUARTER.

2.2 E-Nose Sensor Design

The e-nose sensor is composed of an array of four chemoresistive gas sensors that are created using carboxyl acid functionalized short multi-wall carbon nanotubes (MWCNT-COOH) and four different solution processable polymers. A carbon nanotube ink was made by mixing an aqueous suspension of 0.2% MWCNT-COOH (0.2 – 0.5 μm in length, < 8 nm in diameter, and 95 % wt. purity; Cheap Tube Inc) and 0.5% sodium dodecyl sulfate (SDS). This mixture was sonicated for 30 minutes to disperse and detangle the MWCNTs and then mixed on a magnetic stirrer for 30 minutes to produce an evenly dispersed suspension. This process was repeated two more times to ensure a uniform suspension. The mixture was then placed in a centrifuge at 6,000 rpm for 10 minutes to pull any remaining large particles out of the suspension. The top portion of the suspension was then drop coated onto the interdigitated electrodes of the flexible PCB using a micropipette. The coated PCB was placed into a vacuum oven at 80 °C under vacuum for one hour to remove the water from the deposited ink. The connectivity was then tested to ensure the resistance was within the desired range of 1-20 kΩ.

A polymer layer was then cast onto the conductive MWCNT mat. Four polymers were selected based on previous studies, including (i) Polyvinyl chloride (PVC), (ii) cumene terminated polystyrene-co-maleic anhydride (cumene-PSMA), (iii) poly(styrene-co-maleic acid) partial isobutyl/methyl mixed ester (PSE), and (iv) polyvinylpyrrolidone (PVP). The polymers were first dissolved at a concentration of 0.5% PVC, cumene-PSMA, PSE, and PVP in a solvent of tetrahydrofuran, acetone, acetone, and water, respectively. These four mixtures were placed on a magnetic stirrer for 30 minutes before drop coating 5 μL of the solution onto the conductive MWCNT mat. The PCB was placed in a vacuum oven at 80 °C under vacuum for one hour. Another 5 μL of the polymer solution was drop coated on top of the previous layer and placed back into the oven at 80 °C under vacuum for 6 hours to eliminate any remaining solvent. The resistivity of the sensor was measured again to ensure the resistance remained in the desired range.

The two-layer MWCNT/polymer composite design was shown to yield more consistent and repeatable results during the production of the e-nose sensor. In addition, depositing the MWCNT ink first allowed for tuning of the resistance through depositing more MWCNT ink if the resistance was too low.

3. RESULTS AND DISCUSSION

3.1 E-Nose Sensor Training and Characterization

The e-nose sensor was trained by exposing the sensor to six known chemicals that have been previously identified, using gas chromatography-mass spectrometry, as VOCs that are commonly excreted from the body [4,5]. Pyridine, tetrahydrofuran, ethanol, methanol, acetic acid, and ammonium hydroxide were the VOCs tested in this study. The testing environment consisted of placing an assembled and coated electronic nose in an 8.4 L acrylic desiccator with a small fan, and a heating element on a glass slide. For testing, the resistance of each e-nose sensor was measured continuously using a multifunction data acquisition system (PCIe-6323, National Instruments). The data were collected and analyzed using a custom MATLAB script.

Training data were collected by first purging the desiccator with nitrogen gas to create a stable and repeatable environment. The VOCs were then introduced into the desiccator at different concentrations by depositing the VOC onto a glass slide with a heating element using a micropipette. The heating element on the bottom side of the glass slide was used to rapidly vaporize the VOC and a fan was used to evenly disperse the VOC throughout the desiccator. After 6 minutes, a vacuum was applied to the desiccator for 3 minutes and then purged with nitrogen gas to completely evacuate the chamber and expel the VOC. The e-nose sensor response to methanol as a function of time is shown in **Figure 3**. The process was observed to be reversible as exposure

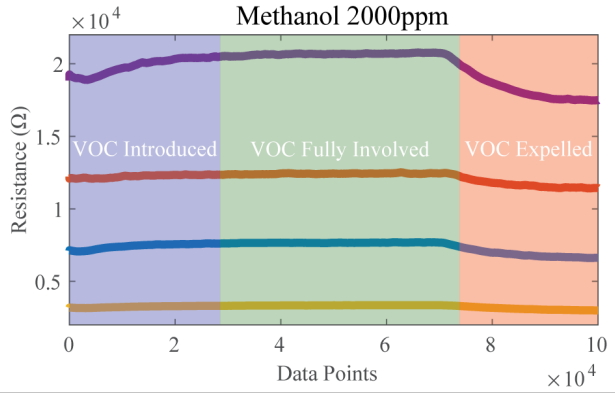

FIGURE 3: E-NOSE SENSOR RESPONSE WHEN EXPOSED TO METHANOL AT A CONCENTRATION OF 2,000 PPM. THE E-NOSE SENSOR PASSIVELY AND REVERSIBLY INTERACTS WITH THE VOC.

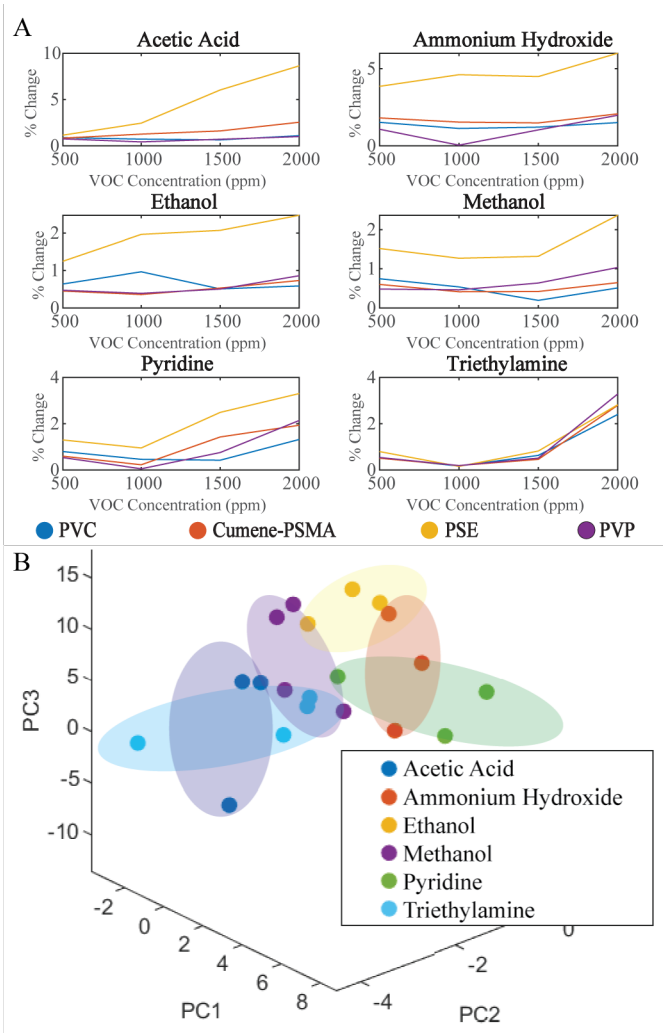

FIGURE 4: A) RESPONSE IN PERCENT CHANGE OF THE FOUR SENSORS AS A FUNCTION OF VOC CONCENTRAION 500, 1000, 1500, AND 2000 PPM. B) PCA PLOT OF THE DATA SHOWN IN A. ELLIPSES ARE DRAWN AROUND THE DATAPOINTS TO VISUALLY GUIDE THE READER.

to a VOC generally increases the resistance of each of the chemoresistive gas sensors. After 6 minutes, the chamber was purged, and the resistance of the array is observed to return to the initial resistance value.

The e-nose sensor response to the six VOCs was measured at four different concentrations, 500, 1000, 1500, and 2000 parts per million (**Figure 4a**). The response of the e-nose sensor against the six known VOCs resulted in expected trends, where the sensor response generally increased as the concentration of the VOC was increased. Some of the e-nose sensors were observed to decrease before increasing at higher concentrations. The non-monotonic relationship could be due to negligible interactions with the conductive polymer sensors or the small percent change in the signal that was observed at the low VOC concentrations.

These data were then analyzed using principal component analysis (PCA) to reduce the dimensionality of the breathprint signature data (**Figure 4b**). Ellipses are drawn around the datapoints to visually guide the reader. The PCA resulted in significant overlap but provides a clearer distinction between the response patterns that were viewed during the raw data collection shown in **Figure 4b**. The ability to passively react to VOCs without power, wirelessly transmit the data, and then analyze the breathprint signature of the VOC demonstrates great promise in the capabilities of this wearable e-nose sensor and provides a path towards monitoring the changes in breathprint signature as patients transition from health to disease states.

4. CONCLUSION

We have introduced a miniaturized, flexible, and battery-free wearable e-nose sensor that can be used to detect previously identified VOCs. Importantly, the e-nose sensor can passively and reversibly interact with VOCs without requiring power. The breathprint signature can be read from the sensor using an NFC-enabled device. Such a sensor system provides a path towards a rapid, inexpensive, and noninvasive screening system to detect breathprint signatures that are associated with health or disease. Future work includes using the wearable e-nose sensor in an observational clinical study.

ACKNOWLEDGEMENTS

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