Poly(vinylidene fluoride-hexafluoropropylene) composite sensors for volatile organic compounds detection in breath

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Abstract

This paper presents three poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) composite-based sensors for detecting volatile organic compounds (VOCs) in the presence of water vapor applicable in breath based sensing. Three sensors with varying sensitivities to acetone, water, ethanol, isoprene, and 2-ethylhexyl acetate (2-EHA), representing VOCs found in breath, have been developed. A sensor fabricated by spray coating PVDF-HFP/C65 composite (*Sensor-1*) exhibited a 52.6% increase in resistance when exposed to acetone, while the change was less than 0.34% for water. The resistance changes for ethanol, isoprene, and 2-EHA, were 5.6%, 3%, and 0.11%, respectively. The second sensor (*Sensor-2*), with a two-layer design of PVDF-HFP and PVDF-HFP/C65, was fabricated by a spin coating method, which exhibited improved response times. The response times of *Sensor-2* compared to *Sensor-1* decreased by 52% for acetone, 92% for water, 30% for ethanol, and 61% for isoprene. In the third sensor (*Sensor-3*), the addition of carbon nanotube (CNT) in the composite (PVDF-HFP/C65/CNT) caused a decrease in resistance when exposed to water. This is in contrast to *Sensors 1 & 2* where resistance increased for all

VOCs, and provides a higher selectivity for the system. The results from the three sensors were analyzed using principal component analysis (PCA) and it was demonstrated that the combined responses of these sensors provide a high selectivity. The sensor fabrication, testing methods, and results are presented and discussed.

Keywords: Breath VOC sensor; PVDF-HFP/C65/CNT composite; High acetone selectivity; Low water sensitivity, PCA analysis

1. Introduction

Timely detection of health conditions can provide potentially life-saving information to patients [1–3]. Human breath has been shown to contain VOC biomarkers that can be used to identify numerous diseases. These VOCs allow for many applications of noninvasive detection of diseases and other biological metrics [4,5]. Acetone levels in breath are a significant indicator of the presence of diabetes, a disease that threatens the lives of millions of people in the US and around the world [6–9]. Moreover, links have been reported between breath isoprene level and oxidative stress, blood cholesterol level, and increased breath and heart rate [10–13]. Ethanol has been shown to have potential medical applications for diabetes detection [14–16]. Esters similar to 2-ethylhexyl acetate are common in breath and have been linked to multiple diseases, including lung cancer [16]. These and other VOCs can be used to non-invasively detect and monitor human health conditions. For example, diabetes patients experience rapid changes in their blood glucose levels throughout the day and may experience potentially life threatening conditions. However, reliable non-invasive methods for monitoring blood glucose levels currently do not exist. A sensor array that can monitor symptoms of diabetes by analyzing breath VOCs, most importantly: acetone, can offer lifesaving information for such patients.

Two of the major challenges in developing breath VOC sensors are as follows: (1) a need to be highly sensitive because the concentrations of VOC biomarkers in exhaled breath are extremely low and (2) a need to be highly selective in detecting the target VOCs due to the presence of hundreds of gaseous components in breath, including water vapor [17–20]. The human sense of smell works well in the presence of water as the olfactory receptors are not sensitive to water [18]. However, sensors developed to detect VOCs often exhibit a high response to water, which interferes with the detection of the target agents. This has been a major challenge in developing electronic

noses for breath VOC detection applications [17]. These requirements have encouraged researchers to consider a wide range of materials including: CNT, graphene, carbon black, gold nanoparticles, metal oxides, and various polymers [8,9,21–28]. Metal oxide-based sensors have shown promising results in detecting very low concentrations of acetone, but these sensors generally operate at an elevated temperature, which raises complexity and cost [28,29]. However, poor stability hinders the practical application of metal oxide based nanosensors. Gold nanoparticle-based sensors have also shown promise in the detection of low-concentration breath VOCs [24,30]. However, high sensitivity to water is problematic with these sensors. Conducting polymers have been shown to detect acetone at room temperature [8,31], yet these sensors often suffer from high sensitivity to moisture and performance degradation over time [32,33]. Carbon-based materials, including CNT, carbon black, and graphene have also been investigated intensely for breath VOC sensing applications [26,34,35]. Pristine CNTs do not efficiently adsorb VOCs, but functionalization improves their performance for sensor applications [36–38]. Functionalization of CNTs with carboxylic groups and defect sites on CNTs created through acid sonication have shown improved adsorption of organic compounds and detection of low concentration VOCs. Interestingly, these processes also increase the response to water [38,39]. Polymer-coated CNTs and polymer carbon black composites have also been utilized in detecting breath VOCs [23,40–43]. CNT, carbon black and polymer composites have been used to achieve high sensitivity and response time [23,43–48]. In CNT polymer composites, the swelling or contraction of polymers changes the separation between the conducting CNT material, which alters the resistance [41]. These CNT polymer composite-based sensors have been shown to have both high sensitivity and selectivity [23,41,45]. However, these sensors suffer from poor selectivity due to their high response to water molecules [17]. For example, CNT/poly(ethyleneterephthalate) (PET) sensor has been reported to exhibit a 2.7 times higher responsiveness to water than to acetone [46]. Carbon black (C65) composites with low-density polyethylene (LDPE) and poly(ethylene-block-ethylene oxide) (PE-b-PEO), polyethylene glycol (PEG), and poly methyl methacrylate (PMMA) have been used to detect acetone, however, their acetone selectivity in the presence water is still poor [23,45–47]. Adsorption of water molecules have also been known to accelerate sensor degradation [45–47]. Composites of PVDF-HFP, previously reported in battery and piezoelectric device applications [50–54], exhibit better material stability and more hydrophobic properties compared to PVDF, PMMA, or PEG [55–58]. PVDF-HFP is also known to swell when exposed to acetone [43,59]. However, PVDF-HFP itself is a poor electrical conductor, therefore requires infusion of conducting particles to form chemiresistive sensors. Combining the properties of

PVDF-HFP, C65, and CNT enables realization of a sensor that detects acetone and other VOCs such as ethanol and isoprene and rejects water.

This paper presents PVDF-HFP, super C65, and CNT based chemiresistor sensors with low water sensitivity for detection of VOCs in breath. It is shown that the presented sensors detect target breath VOCs with high selectivity against water. Material characterizations and sensor design and fabrications are presented in Sections 2 and 3. Experimental results are presented and discussed in Section 4. PCA of the sensor responses for a high selectivity is presented and discussed in Section 5.

2. Materials and Methods

2.1. Materials

Single wall CNT (HiPco) was purchased from Nanointegris, PVDF-HFP and 1-Methyl-2-pyrrolidinone (NMP) were purchased from Sigma Aldrich. Super C65 (carbon black) was obtained from Timical. The composites of PVDF-HFP/C65/CNT were formed in NMP [60]. The product was then stirred resulting in a slurry paste. The use of a slurry paste inhibits agglomeration of CNT and C65. The slurry was either used as-is for spin coating, or further diluted for spray coating. CNT's tendency to aggregate was also observed with PVDF-HFP/CNT dissolved in NMP. The addition of super C65 within the composite inhibits CNT agglomeration and increases the uniformity of the dispersion. A field emission scanning electron microscope (SEM) image of the PVDF-HFP/C65/CNT composite (20:1:10 by wt.) drop-casted over a gold coated substrate is shown in Fig. 1. It is observed that the film is uniform across the surface, with a porous hexagonal cluster structure.

FTIR analysis of PVDF-HFP, PVDF-HFP/C65, PVDF-HFP/C65/CNT are presented in Fig. 2. The results show that the crystal structure of PVDF-HFP is significantly altered in the presence of C65 and C65/CNT, indicating the formation of composite structures. PVDF-HFP exhibits peaks at 1724, 1726 and 1728 cm^{-1} (stretching of the carbonyl groups [61]), 1636 cm^{-1} ($>\text{C}=\text{O}$, $>\text{C}=\text{C}<$ bonding [62]), 1402 cm^{-1} (vibrations of plasticizer [63]), 1290 cm^{-1} ($-\text{C}-\text{F}-$ stretching vibrations [63]), 1203 cm^{-1} (asymmetrical stretching vibrations of the CF_2 group [64]), 1148 cm^{-1} (symmetrical stretching mode of CF [64]), 1062 cm^{-1} ($-\text{CF}_2-$ stretching vibration [63]), 879 cm^{-1} (CF_2 symmetric stretching [62,63]) and 839 cm^{-1} (CH_2 rocking [62,63]). The vibrations at 839 and 880 cm^{-1} are more distinct in PVDF-HFP/C65 composite than PVDF-HFP. This indicates a more amorphous structure for the

composite since these two bands are associated with the amorphous structure of PVDF-HFP [65,66]. The frequencies at 1344, 1170 (C=O), 1002, 983 (alpha phase crystal structure), 817 and 761 cm^{-1} (alpha phase crystal structure) disappear in the PVDF-HFP/C65 composite and the peaks at 1062 and 516 cm^{-1} shift to 1072 and 508 cm^{-1} , respectively. These phenomena indicate the presence of a polymer-plasticizer interaction. Insertion of CNT into the composite further modifies the structure. The new, but small, absorptions at 510 and 481 cm^{-1} (beta phase crystal structure) also demonstrate changes in the crystalline structure and polarity of the composite. The changes in polar properties of the composite change its sensing characteristics to different VOCs.

2.2. Fabrication

Interdigitated electrodes (IDE) of gold over silicon oxide were fabricated using a standard photolithography process. The spacing between the two electrodes was measured to be 25 μm . Spray coating and spin coating fabrication methods were used to cast films over the electrodes. For spray coating, diluted solutions of the materials were sprayed onto the IDE. The spray process was continued until a desired resistance for the film was achieved. For spin coating, a slurry solution of the materials was used. A small amount of the slurry was casted onto the IDE, which was mounted on a spin-coater. It was then spun at a high speed to achieve a desired film thickness. Next the film was dried in a vacuum oven. Three types of sensors were fabricated as described below.

Sensor-1: PVDF-HFP/C65

Sensor-1 consists of a spray coated layer of PVDF-HFP/C65 film over the IDE. A PVDF-HFP and C65 composite dispersed in NMP was prepared and spray coating was conducted as described in the Fabrication section above. In the spray coating process, the film was inspected under an optical microscope and the resistance was measured after each deposition. It was observed that the C65 forms a patchy network at the beginning and, after each additional layer, slowly changes to a continuous network supported by PVDF-HFP. An optical image of the edge of a PVDF-HFP film over IDE is shown in Fig. 3. The film thickness was measured using cross-sectional SEM imaging to be 1 μm . The resistance of the completed device was 864 Ω . This resistance can be viewed as the effective resistance of a parallel configuration of resistance due to the C65 network and resistance due to the PVDF-HFP outside of the network. However, as the resistance due to the PVDF-HFP outside of the network is much higher than the resistance of the C65 network, the overall resistance of the sensor is attributed to the resistance of the network. When exposed

to the target VOC, the swelling of PVDF-HFP weakens the C65 network, thus increasing the resistance measured across the electrodes.

Sensor-2: PVDF-HFP and PVDF-HFP/C65

This sensor design is composed of two layers, a PVDF-HFP layer and a PVDF-HFP/C65 layer. A thin layer of PVDF-HFP is deposited over the IDE via spin coating. This film covers both the gold electrodes and the gap in between, and forms the first layer. Then the PVDF-HFP/C65 composite deposited over the first layer forms the second layer. SEM image of a PVDF-HFP/C65 film is shown in Fig. 4(b). The top PVDF-HFP/C65 layer is porous and it is less than 1 μm thick (~ 760 nm as measured through SEM of the cross-section). Thus, the VOCs diffuse through the top layer and contact the bottom layer. The resistance of the sensor after vacuum drying was measured 3.04 k Ω . A representative schematic of the sensor is shown in Fig. 4(a). An equivalent circuit for the sensor can be considered as the resistances across PVDF-HFP layer (R_G) and resistance of PVDF-HFP/C65 R_{CP} (also indicated in Fig.4 (a)), placed in series. While the two layers were deposited separately, the second layer material may penetrate through the first layer forming vertical connections. This results in a less than expected overall resistance for the sensor. As these two layers respond differently with each of the VOCs, the selectivity of the sensor is enhanced. By adjusting thickness and other properties of these layers, selectivity to the presented and other VOCs can be further tuned. Interaction of the target gas with PVDF-HFP increases the volume of the polymer. Swelling of PVDF-HFP thin layer (bottom layer), increases the separation between the gold electrode and the conductive composite (top layer). This results in an increase in resistance R_G . Swelling of PVDF-HFP in the composite also increases the resistance of R_{CP} . The overall response of the sensor represents the sum of these two responses.

Sensor-3: PVDF-HFP/C65/CNT

In this sensor, the composite of PVDF-HFP/C65/CNT was prepared as described above, in the Materials section, and spin coated over an IDE. The film was then dried in a vacuum oven. SEM image of the surface of the film is shown Fig. 4 (c). It was observed that the CNT and C65 form a continuous network supported by the PVDF-HFP matrix. The film thickness was measured using cross-sectional SEM imaging to be 580 nm. The lateral resistance path of the film is the sum of resistances due to CNT/C65 clusters (R_C) in the PVDF-HFP matrix and the matrix itself (R_M). When exposed to a VOC, the swelling of PVDF-HFP increases the resistance of the network (R_M), which is caused by increased separation between the nanoparticles. On the other hand, the resistance of CNT, and

thus in turn R_C , decrease when exposed to the VOCs [36,67,68]. Each of the two sensing probes has a different role in the sensing mechanism of different VOCs. For example, with acetone, swelling of PVDF-HFP is more dominant; however, water does not stimulate PVDF-HFP as much as it increases the conductance of CNT/C65 clusters. This results in a phenomenon where the resistance across the two electrodes decreases when exposed to water and increases when exposed to acetone, ethanol and isoprene.

2.3. Test Set-Up

The experimental setup used is illustrated in Fig. 5. Nitrogen (99.99% pure) was used due to its wide use and acceptance as a carrier gas for sensor testing. Nitrogen, at a fixed flow rate, was bubbled through liquid acetone in a flask. This nitrogen/acetone gas was diluted with pure nitrogen using a mixing flask. The concentration of acetone in the test chamber was varied by controlling the flow of nitrogen (using mass flow controllers, MFC1 and MFC2) through the acetone and pure nitrogen. The concentration of acetone for given experimental conditions and the flow rate was determined through gas chromatography/mass spectroscopy (GC/MS). The mixture of acetone and nitrogen coming out of the flask was passed through a vial cooled by dry ice. The acetone trapped inside the vial was evaporated onto a solid phase micro-extraction fiber and transferred to GC/MS for analysis. The samples under scrutiny were placed inside the test chamber and the desired measurements were taken. The sensor resistance was measured using a Keithley 2700 Multimeter/Data Acquisition System and digital multimeters. The same process was utilized for testing water, ethanol, and isoprene; except isoprene was kept at 2.5 °C while all other liquid VOCs were kept at room temperature $22.5 \pm (0.5 \text{ } ^\circ\text{C})$.

3. Results and Discussion

QCM Analysis

Responses of the materials to various VOCs were studied using a quartz crystal microbalance (QCM). Dilute solutions of materials were prepared and drop-casted on top of a 9 MHz (resonant frequency) QCM. The resonant frequency of the QCM changes with the change in the mass of the material on the crystal. The relationship between the change in QCM resonant frequency (Δf) and the change in mass (Δm) on the crystal is given by eq. 1.

$$\Delta f = \frac{-2f_0^2}{A\sqrt{\mu\rho}} \Delta m \quad (1)$$

Where f_o is resonant frequency, A is the area of the gold disk on the crystal, and μ and ρ represent the shear modulus and density of the crystal, respectively; these parameters are all constants [8, 69]. Thus, (1) shows the change in measured frequency is proportional to the change in mass on the crystal. When the QCM coated material is exposed to the VOCs, the adsorption of molecules onto the sensing material increases the mass, thus decreasing the oscillation frequency as measured by the frequency counter.

Carboxylic-functionalized single wall CNTs (CNT-COOH) have been widely used to detect acetone [37,39]. Thus, in the first step, CNT-COOH were coated over QCM and tested for acetone. It was observed that exposure to acetone registers a 397 Hz change in frequency. However, the same sensor exhibited an 877 Hz change in frequency when exposed to moisture. This is exorbitant at 2.2 times higher than the acetone response. In a similar experiment with PVDF-HFP/C65/CNT composite, it exhibited a 1635 Hz change with acetone and a 106 Hz change with water, a 15.4 times higher response to acetone than water. This represents a significant improvement in acetone selectivity over water compared to existing sensors, which is a critical aspect for breath sensor applications. These QCM results give us insight into how well the target gases are adsorbed onto the sensing materials. Next, the electrical response of the different sensors to the presented VOCs was investigated.

Sensor-1: PVDF-HFP/C65

A PVDF-HFP/C65 composite sensor fabricated on gold IDE (*Sensor-1*) was tested with acetone, water, ethanol, isoprene, and 2-EHA VOCs using the setup shown in Fig. 5. The resistance of the IDE after deposition of PVDF-HFP/C65 was measured to be 864 Ω . The sensor was exposed to a VOC and nitrogen, each for 20 minutes. The flow of gas in the chamber was fixed at 200 standard cubic centimeters per minute (SCCM) at 22°C. Water, ethanol, isoprene, and 2-EHA were also introduced into the chamber using the above described parameters, except that isoprene was kept at 2.5°C. GC/MS measurements showed the concentration of acetone, ethanol, isoprene and 2-EHA was 44500 ppm, 10000 ppm, 50500 ppm and 248 ppm. The concentration of water (measured by a humidity sensor) was 6000 ppm. The measured resistances for the VOCs for three consecutive cycles are shown in Fig. 6. For further clarity, the plots without acetone are shown in the inset. As the VOCs are introduced into the chamber the molecules are adsorbed onto the sensor, increasing the effective resistance of the sensor. This is caused by two competing factors as described in the methods section. The swelling of PVDF-HFP matrix increases the overall resistance of the film, while the resistance of a C65 cluster decreases when the VOCs are adsorbed. The sensor exhibited a 52.6% increase in resistance when exposed to acetone, while the change was less than 0.34% for water.

The resistance change for acetone is 150 times larger than that of water. Resistance changes for ethanol, isoprene, and ethyl acetate were 5.6%, 3%, and 0.11%, respectively. It is observed that the interactions of the VOCs and sensor were reversible over the three cycles. The response and recovery times (time to reach 90% of the saturation value) for the VOCs are presented in Fig. 7. The standard deviations (σ) of the three cycles are also indicated in the figure. The sensor response to isoprene is faster (90 s) compared to that of ethanol and acetone (430 s and 450 s).

Sensor-2: PVDF-HFP and PVDF-HFP/C65

Sensor-2 consists of overlaid layers of PVDF-HFP and PVDF-HFP/C65. The resistance of the resulting sensor was measured 3.04 k Ω . The sensor was tested with VOCs using the measurement set-up as described for *Sensor-1*. The resistances measured for acetone, water, ethanol, isoprene, and 2-EHA for three consecutive cycles are shown in Fig. 8. For further clarity, the plots without acetone are shown in the inset. The changes in resistance were 26.23% for acetone, 0.32% for water, 2.6% for ethanol, 2.29% for isoprene, and 0.32% for 2-EHA. The two-layer design exhibits improved responses to VOCs than other considered sensor designs. The response and recovery times (presented in Fig. 9) are improved compare to *Sensor-1*. The sensor response time to acetone is 200 s (compared to 420 s for *Sensor-1*), 20 s to water (compared to 200 s for *Sensor-1*), 300 s to ethanol (compared to 430 s for *Sensor-1*) and 35 s to isoprene (compared to 90 s for *Sensor-1*). Additionally, a wide range of polymers can be selected to form the first layer of the sensor design (*Sensor-2*), which provides a tool to further customize the sensor. This feature can be used to generate an array of sensors and improve the selectivity of the system.

In another experiment *Sensor-2* was tested with a varying concentration of acetone, from 42 ppm to 4440 ppm. As shown in Fig. 12 (a), the resistance of the sensor increases as the concentration of acetone is increased stepwise. A plot of change in resistance versus the concentration of acetone is shown Fig. 10 (b). A linear relation between the resistance change and gas concentration was observed. The sensor response for a lower concentration of acetone is shown in the inset of Fig. 10 (a). The resistance changes by 1 Ω when exposed to 42 ppm acetone. For these lower concentration of acetone, the measured resistance was observed to fluctuate due to competing effect between swelling of PVDF-HFP (increase in resistance) and increased conductivity C65 (decrease in resistance). However, the overall resistance of the sensor increases when exposed to acetone. As the swelling (of PVDF-HFP) becomes

more dominant with increasing concentration of acetone, this effect was not observed at higher concentration measurements.

Sensor-3: PVDF-HFP/C65/CNT

Sensor-3 consists of a PVDF-HFP/C65/CNT composite spin coated on a gold IDE. The resistance of the resulting sensor was measured 1.876 k Ω . This sensor was tested with acetone, water, ethanol, isoprene, and 2-EHA using the testing procedure described for *Sensor-1* and *sensor-2*. The sensor was exposed to a VOC for 20 minutes followed by exposure to nitrogen for next 20 minutes. Fig. 11 shows the measured resistances for the various VOCs. This sensor exhibited a 17.9% increase in resistance when exposed to acetone, while it decreased by 2.4% with water, and increased by 3% with ethanol, 1.5% with isoprene, and 0.3% with 2-EHA. This sensor exhibited high contrast between other VOCs and water, as the resistance decreases with water unlike *sensor-1* & *-2*. The response and recovery times are presented in Fig. 12. Response times to acetone and ethanol improved compared to *Sensor-1*, however the recovery times were higher. This is attributed to the increased affinity of the VOC molecules to the composite material, which reduces the response time and increases the recovery time. For acetone (Fig. 12), it was observed that 20 minutes of exposure was not sufficient to clear out all the adsorbed acetone, thus the resistance did not return to the initial value. However, this duration was sufficient for the other VOCs, perhaps due to the fact that the absorption was much less for these VOCs compared to acetone.

Degradation Study

To study the degradation of the composite materials, a sensor of PVDF-HFP/C65/CNT was fabricated and tested with the VOCs over 42 days. During these experiments the sensor was kept in an ambient air environment and exposed to the VOCs and water at various times for over 40 hours of exposure. Over the observed period, the sensor's initial resistance changed by less than 3%. This is attributable to the hydrophobic property of PVDF-HFP which reduces the moisture absorption from the environment. PVDF-HFP is known to offer good stability and resistance against harsh environments [70]. Similarly, results for the *Sensor-2* tested with acetone on the day of fabrication (Day-1) and after two weeks (Day-16) are shown in Fig. 13. The responses to acetone were similar in both measurements and no significant degradation was observed. Within this period, the sensor was also tested with various VOCs, with over 10 hours of exposure. Additionally, no change in initial resistance was observed from Day-1 to Day-16 (3.04 k Ω).

4. Principal Component Analysis

The results from the three sensors presented and discussed above were subjected to PCA to demonstrate the selectivity of the combined sensors to the considered VOCs [71,72]. Table-1 shows resistance changes ($\Delta R = R_{\text{Saturation}} - R_{\text{Initial}}$) for the three sensors when exposed to the VOCs. The percentage changes in resistances ($\Delta R/R_{\text{Initial}}\%$) for the three sensors are also shown in the parentheses in the table. The change in resistance values shown in Table-1 were used in PCA, which resulted in the three distinctive principal components (PC_1 , PC_2 and PC_3). The aim of PCA is to map data into perpendicular dimensions and provide maximum variance. The first principal component (PC_1) is a linear combination of the normalized resistance changes in the three sensors (ΔR_1 , ΔR_2 , and ΔR_3 , for *Sensor-1*, *Sensor-2*, and *Sensor-3*, respectively) in such a way that the variance of PC_1 is maximized. This is mathematically presented below in eq. 2 [72].

$$PC_1 = a_{11}\Delta R_1 + a_{12}\Delta R_2 + a_{13}\Delta R_3, \text{ where } a_{11}^2 + a_{12}^2 + a_{13}^2 = 1 \quad (2)$$

The weights (a_{11} , a_{12} and a_{13}) that result in the variance maximization is found by the eigenvector $V = [a_{11} \ a_{12} \ a_{13}]^T$ of the covariance matrix of normalized sensor resistance changes associated to the largest eigenvalue (λ_{max}) [72]. The second principal component, PC_2 , is in the direction perpendicular to PC_1 and results in the second largest variance. This would be calculated by multiplying the second largest eigenvector to the normalized sensor resistance changes. The third principal component, PC_3 , is perpendicular to both PC_1 and PC_2 and results in the third largest variance. From these components the most distinctive component was selected as the feature in the plot shown in Fig.14. As can be seen in the figure, the VOCs separate from one another. The small variance between the features in the same class shows the repeatability of the sensor response. The variance within each class is much less than the mean between the classes. This assures the selective separation of the VOCs from one another. The distance between the features related to acetone and water is the highest. This indicates the high selectivity of the system to acetone from water. The result shows that extracting one feature from each sensor was sufficient to selectively identify the target VOCs.

5. Conclusions

Two major challenges in the development of a practical sensor array that detects VOCs in breath are sensor degradation and a high response to water vapor. The three presented sensors have the following characteristics: sensitivity to VOCs, selectivity in the presence of water vapor, and low degradation. The response to water was significantly lower than the response to acetone, an important parameter as human breath contains more than 80% humidity. This low sensitivity to water was achieved by a combination of material selection and sensor design. The hydrophobic properties of PVDF-HFP coupled with those of C65 and CNT have resulted in the development of sensors which both identify specific VOCs present in breath and reject water vapor. Utilization of multiple sensors that exhibit different responses to the target VOCs led to a highly selective system. The spray coated sensor (*Sensor-1*) offers a more sensitive response to acetone while the spin coated sensors (*Sensor-2* and *Sensor-3*) offer a faster response to the VOCs. For *Sensor-3*, unlike *Sensor-1* and *Sensor-2*, the resistance decreased when exposed to water vapor. The sensor responses were further analyzed using PCA, and demonstrated a high selectivity towards the tested VOCs. In the present work, the tests with the VOCs were conducted in dry atmosphere and at VOC concentrations higher than found in human breath. Thus, further improvements are needed to non-invasively detect diseases from human breath. Improving the sensor, including exploring additional composite materials such as graphene, and testing of the system with simulated breath containing air and water vapor are planned for the future and the outcomes of the planned works will be reported in future publications.

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Fig.1. SEM image of PVDF-HFP/C65/CNT casted over a gold coated substrate.

(1) -CH_3 asymmetric bending 1486 cm^{-1} , (2) 1402 cm^{-1} β phase, (3) C-O stretching 1402 cm^{-1} (α phase), (4) CF stretching 1290 cm^{-1} , (5) 1230 cm^{-1} γ phase, (6) CF stretching, (7) CF_2 stretching 879 cm^{-1} (α phase), (8) CH_2 rocking 839 cm^{-1} (β phase)

Fig.2. FTIR analysis of PVDF-HFP, PVDF-HFP/C65 and PVDF-HFP/C65/CNT composites.

Fig.3. Optical image of C65/PVDF-HFP composite spray coated over the gold IDE.

Fig.4. (a) Schematic of *Sensor-2* showing PVDF-HFP/C65 layer over a thin PVDF-HFP layer. SEM image of spin coated (b) PVDF-HFP/C65 and (c) PVDF-HFP/C65/CNT composites.

Fig.5. Schematic of sensor testing setup.

(a)

Fig.6. (a) Change in resistance of *Sensor-1* in response to acetone, water, ethanol, isoprene, and 2-ethylhexyl acetate. (b) Plot of change in resistance versus acetone concentrations. The measurements were conducted at $22.5 (\pm 0.5) ^\circ\text{C}$.

Fig.7. Response and recovery times for *Sensor-1* when exposed to the four VOCs.

Fig.8. Change in resistance of *Sensor-2* in response to acetone, water, ethanol, isoprene, and 2-EHA. The measurements were conducted at $22.5 (\pm 0.5) ^\circ\text{C}$.

Fig.9. Response and recovery times for *Sensor-2* when exposed to the four VOCs.

Fig.10. Change in resistance of *Sensor-2* in response to various concentration of acetone. The initial resistance of the sensor was 3040 Ω and the measurements were conducted at 22.5 ($\pm$ 0.5) $^{\circ}\text{C}$.

Fig.11. (a) Change in resistance of *Sensor-3* in response to acetone, water, ethanol, isoprene, and 2-EHA. (b) Plot of change in resistance versus acetone concentrations. The measurements were conducted at $22.5 (\pm 0.5) ^\circ\text{C}$.

Fig.12. Response and recovery times for *Sensor-3* when exposed to the four VOCs.

Fig.13. Comparison of responses of *Sensor-2* to acetone on Day-1 and Day-16.

Fig.14. PCA plot for extracted features (percentage of resistance change) in each sensor.

Table-1 Resistance change of the sensors exposed to the VOCs, ΔR (%).

	<i>Sensor-1</i>	<i>Sensor-2</i>	<i>Sensor-3</i>
Water	3 Ω (0.34%)	10 Ω (0.32%)	-46 Ω (-2.45%)
Acetone	455 Ω (52.66%)	800 Ω (26.23%)	344 Ω (18.33%)
Ethanol	48 Ω (5.56%)	80 Ω (2.62%)	28 Ω (1.49%)
Isoprene	26 Ω (3.0%)	70 Ω (2.3%)	58 Ω (3.09%)
2-EHA	1 Ω (0.16%)	10 Ω (0.33%)	3 Ω (0.16%)

Title: Poly(vinylidene fluoride-hexafluoropropylene) composite sensors for volatile organic compounds detection in breath

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