AFRL-RH-WP-TR-2018-0021

ISOPROPYL ALCOHOL SENSOR DEVELOPMENT FOR AIR-QUALITY MONITORING

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MARCH 2018
Interim Report

AIR FORCE RESEARCH LABORATORY
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KIM.STEVE.SANGNYON.1299478919 Digitally signed by KIM.STEVE.SANGNYON.1299478919 Date: 2018.07.27 15:31:22 -04'00'

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
02 03 18	Interim Report	1 January 2017 – 1 December 2017

4. TITLE AND SUBTITLE
Isopropyl alcohol sensor development for Air-Quality Monitoring

5a. CONTRACT NUMBER
In-House

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Yen H. Ngo[*], Mike Brothers*, Jennifer A. Martin,[1] Claude Grigsby,[1] Rajesh R. Naik,[1] Kathy Fullerton,[1] and Steve S. Kim[1]

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER
H0SL

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
*UES, Inc., Beavercreek, OH, 45432

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
[1]Air Force Materiel Command
Air Force Research Laboratory
711th Human Performance Wing
Airman Systems Directorate
Human-Centered ISR Division
Human Signatures Branch
Wright-Patterson AFB, OH 45433

10. SPONSORING/MONITORING AGENCY ACRONYM(S)
711 HPW/RHXB

11. SPONSORING/MONITORING AGENCY REPORT NUMBER(S)
AFRL-RH-WP-TR-2018-0021

12. DISTRIBUTION/AVAILABILITY STATEMENT
Distribution A: Approved for public release. RH-18-118143 88ABW-2018-1040 3/2/2018

13. SUPPLEMENTARY NOTES
Report contains color. Journal Article: ACS Sensors (http://pubs.acs.org.wrs.idm.oclc.org/loi/ascefj)

14. ABSTRACT
The personal data from medical records; profiles of the patient's genes, metabolites, and microorganisms in and on the body; environmental and lifestyle data; patient-generated information; and personal device and sensor will play key roles in finding the right preventive, diagnostic, and treatment tools for the disease in conjunction with Big Data and cloud-based computing. Thus, developing a personal real-time chemical exposure sensor that enables the profiling/reporting of exposure data throughout 8-24hr time frame will greatly benefit the general population's health and performance. We chose isopropyl alcohol (IPA), a main component of de-icer spray for commercial/non-commercial flights, as a target that has to be selectively detected due to its potential to contaminate flight breathing air from occasional accumulation/evaporation in the airplane structure during or pre/post flights. Moreover, IPA has been shown to act as an anesthetic and central nervous system depressant, resulting in symptoms that can deter the cognitive ability of the individual. Thus it is imperative to be able to monitor IPA content and accumulative exposure level.

15. SUBJECT TERMS
chemical sensor, carbon nanotube, polymer, alcohol sensor, volatile organic compounds

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT:	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON (Monitor)
a. REPORT	b. ABSTRACT	c. THIS PAGE			Steve Kim
Unclassified	Unclassified	Unclassified	SAR	22	19b. TELEPHONE NUMBER *(Include Area Code)* N/A

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39-18

Isopropyl alcohol sensor development for Air-Quality Monitoring

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KEYWORDS chemical sensor, carbon nanotube, polymer, alcohol sensor, volatile organic compounds

INTRODUCTION

The degree of exposure to the volatile organic compounds, gases, and air-borne particles for a human subject can significantly vary from others due to his/her differences in work, recreational, and residential settings. The personal data from medical records; profiles of the patient's genes, metabolites, and microorganisms in and on the body; environmental and lifestyle data; patient-generated information; and personal device and sensor will play key roles in finding the right preventive, diagnostic, and treatment tools for the disease in conjunction with Big Data and cloud-based computing. Thus, developing a personal real-time chemical exposure sensor that enables the profiling/reporting of exposure data throughout 8-24hr time frame will greatly benefit the general population's health and performance. We chose isopropyl alcohol (IPA), a main component of de-icer spray for commercial/non-commercial flights, as a target that has to be selectively detected due to its potential to contaminate flight breathing air from occasional accumulation/evaporation in the airplane structure during or pre/post flights. Moreover, IPA has been shown to act as an anesthetic and central nervous system depressant, resulting in

symptoms that can deter the cognitive ability of the individual.[1] Thus it is imperative to be able to monitor IPA content and accumulative exposure level.

Commercial alcohol sensors do not fit the requirement for selective IPA sensing, in addition they 1) are bulky, 2) suffer from sensor drift, 3) are chemically unstable, 4) require optical/electrical components (cost/size), 5) and/or have a slow response time.[2] Thus it is necessary to develop a noiseless, low-powered and selective IPA sensing platform for wearable or attachable personal air-quality monitors.

The unique electrical, chemical, structural and mechanical properties of carbon nanotubes (CNTs) make them ideal candidates for chemical sensors.[3,4] The single atom-thin cylindrical semiconductor/semi-metal/metal CNTs change their resistance as a function of ion concentration, doping level, and solvent conditions with unmatching sensitivity compared to the most bare metal-oxide or inorganic semi-conductors, offering ultimate sensitivity as a nanoelectronic sensors.[5] CNTs often serve as p-type semi-conductors in ambience, and thus their resistance should change as a function of ionic content and/or electrochemical reactions. The chemical oxidation of alcohol is a way of converting alcohol absorption to electron/proton products that changes the CNT electronic density of states, enabling a measurable sensing signal. For SWCNT sensors in ambient air, the detection levels are in the order of ppm.[6] In short, hydroxyl functional groups are oxidized first to aldehydes and then sometimes to carboxylic acids in the presence of potassium dichromate, sulfuric acid, and silver nitrate catalyst.[7] In the case of IPA, which is a secondary alcohol, the reaction can only progress to the ketone, resulting in the generation of acetone, water, and chromium sulfate. The net result is a modification of the ion concentration, ion content, and solvent composition that can possibly be exploited for measurement.

Previously, Lee et al., demonstrated IPA absorption into the PVP coating matrix, followed by subsequent absorption into the base layer solvatochromic sensor. The solvatochromic 10,12-tricosadynoic acid (TCDA)/polydiacetylene (PDA) co-polymer is selective for alcohols, making this particular solvent gated solvatochromic sensor highly selective to IPA. However, above colorimetric assays have only been demonstrated for liquid phase IPA which require optics that are difficult for integration and may have long regeneration times or be irreversible. Therefore, we were motivated to

move into an electrochemical sensor based off of this methodology, where upon the concentration of gas phase IPA can thus be correlated directly to the resistivity of the carbon nanotubes embedded within the PVP matrix, resulting in a potentiometric signal. Using polymers as surface modifications to SWCNT improves sensing performance and behaves as a suitable molecular recognition element.[8]

In this work, we describe IPA sensor development process what consist of 3 components: 1) a polymer matrix that serves as an analyte capture matrix, 2) oxidizing agents that react with isopropanol, and 3) carbon nanotubes which change resistance as a function of ion content/concentration. Through this process, we analyzed and modified various components to improve the quality of the sensor. As a result, we created an electrochemical device that responds preferentially to IPA, where the increase in the resistance corresponds directly to the concentration of IPA.

More specifically, we explore 1) fabricating carbon nanotube based electronic sensor in a polymer matrix deposited via spin coating and/or dipping process, 2) enhancing the sensor selectivity to IPA by using Polyvinyl-pyrrolidone (PVP), a polymer which has been previously used as an IPA-selectivesolvatochromic sensor,[9] and 3) amplifying sensor response signal to IPA target by integrating a redox chemical agent. Therefore, proper control of the surface chemistry and fucntionalization are highly important for semiconducting CNT-based sensors.[10]

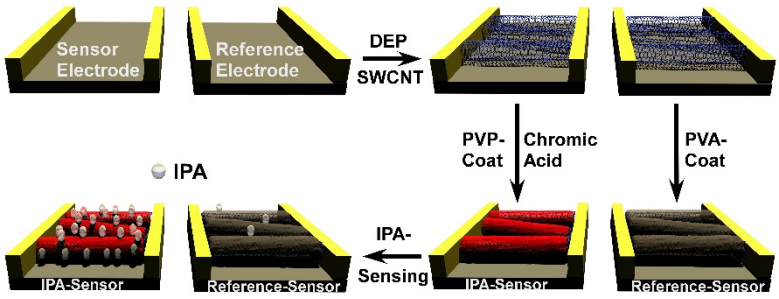

Figure 1: General CNT device platform for detecting IPA using PVP polymer matrix

EXPERIMENTAL METHODS

Interdigitated electrode (IDE) sensors

IDEs with 10µm gap, 20µm width on 28x5mm glass supported with 150nm Au layer were purchased from NanoSPR (Chicago, IL), and used as the base electronic structure. The devices were soldered onto the surfboard mounts with silver rosin and electrical contacts were made. Assembly of nanotubes was performed via dielectrophoresis following the process described below.

Dielectrophoresis of CNTs

The SWCNT (Southwest Nanotechnologies, Norman, OK) purchased were special grade 90% purity with 0.83nm mean diameter. SWCNTs were ultrasonicated into a water based suspending medium of PVP or PVP-colpolymer solution at 2 wt % concentration Prior to depositing the SWCNT, the solution was carefully left out to let large CNT bundles settle to the bottom before use. The sensor was then placed in a probe station and electrical contact was made through the Au electrodes. Using the top layer of the PVP-SWCNT suspension, 5µl was pipetted and the droplet was placed over the area of interest. Due to the nature of the process being solution based, the solution should be aligned across the gap between the pair of electrodes.[11] Process parameters such as frequency of the voltage applied, time exposure to the AC field, CNT size/length, and solution concentration were studied to determine the suitable parameters needed for deposition. AC electrophoresis retains CNT bundles in the electron gap thus enabling them to serve as good candidates for gas sensing elements[12] by using dielectrophoretic forces to propagate the CNT along the electric field lines onto the electrodes.[13] Optimal conditions were 60s deposition time at a frequency of 10MHz with a peak to peak voltage (V_{p-p}) of 6 V. After DEP step, the substrates were rinsed with distilled water and then dried with house air. Reproducibility of the CNT arrangements are determined by the electrode dimensions and deposition conditions.[14]

Generation and Deposition of Polymer Coating

Commercial grade polymer coatings such as polyvinylpyrrolidone (PVP), polyvinyl alcohol, poly(1-vinylpyrrolidone-co-styrene), poly(1-vinylpyrrolidone-co-vinyl-acetate), and poly(1-vinylpyrrolidone-co-2-dimethylaminoethyl-methacrylate) were all purchased from Sigma Aldrich (St. Louis, MO). Dip-coating was used to cast polymer film onto the SWCNT device. The dip coating comprise of hand dipping the sensor into the polymer solution for 10 minutes followed by drying inside a heated vacuum chamber (< 60ºC) for a five minutes.

Addition of Dopants to polymer matrices

After the polymer coating process, water based chromic acid solution was added to the mixture to enhance device sensitivity. This was prepared by making a solution containing (400mg) of Gastec (Airgas, Dayton Ohio) pellets containing potassium dichromate ($K_2Cr_2O_7$) in distilled water with 1M sulfuric acid (H_2SO_4). The devices were then placed in the solutions for 1 minute and then allowed to dry via air.

Sensor Testing

Post-characterization, in order to conduct preliminary static vapor experiments, the sensors were placed in custom built chamber (17.43L) that precisely controls chemical compound concentration, flow rate, and pressure for high concentration exposures. These sensors were mounted onto a breadboard inside of the chamber and electrically connected to a Keithley (4200SCS, Tektronix, Inc, OR) semiconductor analyzer instrument. The chamber contained a gas inlet/outlet along with a hole for sample injection. The sensors were placed inside of the chamber filled with ambient house air.

Devices were tested simultaneously with a commercial off the shelf piD-TECH plus photoionization detector (PID) (MOCON Inc., Brooklyn Park, MN). Sample gases are exposed to the UV light which ionizes the sample that is detected by the PID and displayed as a concentration value. Additionally, a blank reference sensor coated with Poly-vinyl alcohol (PVA) was used to calibrate for variability and background as a control. Acetone, IPA, and Isoprene were circulated and fed into the static chamber at differing concentrations ranging from 100ppm to 10000ppm. Voltage changes were measured in real time with constant current of 1μA applied to the device terminals and a user specified voltage compliance of 0.5V. In addition, baseline adjustments were completed for each collected data sets.

RESULTS AND DISCUSSIONS

SWCNT Channels Generated by Dielectrophoresis

The carbon nanotubes in our device are the main sensing modality, as carbon nanotubes are known to have changes in resistance as a function of surface charge density.[15] Therefore, coming up with a consistent methodology for generating SWCNT matrices between our IDEs is imperative for sensor performance. We used DEP because of the ability to tune deposition as a function of voltage and to create uniform bundles of SWCNTs between electrodes. Process parameters such as frequency of the voltage applied, time exposure to the AC field, SWCNT size/length, and solution concentration were studied to determine the suitable parameters needed for deposition on IDE devices. We found that an AC voltage of 6 V_{p-p} at 10MHz frequency, applied for 1 minute to the electrode pair in a probe station produced 1 ± 0.18 kΩ CNT resistor indicating repeatable nanotube assembly for further experiments.

Polymer Film Coating

Solvent semi-selective polymer films have been demonstrated in the liquid phase to act as a diffusion barrier for solvatochromic solvent sensors. Both the PAA and PVP coatings served as a solvent-selective gate, whereupon only solvents with the correct polarity would reach the colorimetric reagent as discussed in greater detail in the introduction.[9] In order to simplify the fabrication, as well as to likely enhance response times, we attempted to optimize the polymer composition by adding co-polymers and identify the ideal coating thickness to maximize the sensitivity and reproducibility of the sensors. We believed that not only film composition but also film thickness will impact sensor performance. Therefore, device sensitivity is greatly affected by film preparation techniques.[16] When exposed to a VOC, the vapor penetrates into the polymer layer and causes the film to expand which results in the increase of electrical resistance of the device.[17] For example, a film layer that is too thick may create too large of a diffusion barrier, reducing sensitivity. However, a film that is too thin and non-uniform may provide problems with reproducibility, and possibly selectivity/sensitivity if the entire CNT is not coated and/or coated evenly. Therefore, film homogeneity and film thickness needs to be controlled in order to produce conductive polymer films.[18] To test the impact of film thickness and composition, we deposited various films using

both dip coating and tested how the composition of the polymer, as well as the film thickness impacted deposition properties, and eventually sensor performance. For 0.25 wt % and 0.55 wt % poly(1-vinylpyrrolidone-co-vinyl-acetate) dip-coating resulted in film thickness of 35nm and 53nm respectively. Dip-coating with 0.08 wt % poly(1-vinylpyrrolidone-co-2-dimethylaminoethyl-methacrylate), resulted in film thickness of 15nm and 0.152 wt % with 20nm (Fig. 2). Due to the viscosity of poly(1-vinylpyrrolidone-co-styrene), the majority of the film thickness were 75nm or higher regardless of wt % concentration used. Of the polymers previously mentioned, PVP (40k MW) provided the thinnest uniform coating (15nm at 0.2wt % concentration). As expected, higher PVP concentrations resulted in higher film thickness. Based on these, using PVP in dip coating technique emerged as the method of choice for produced better film results and sensor response.

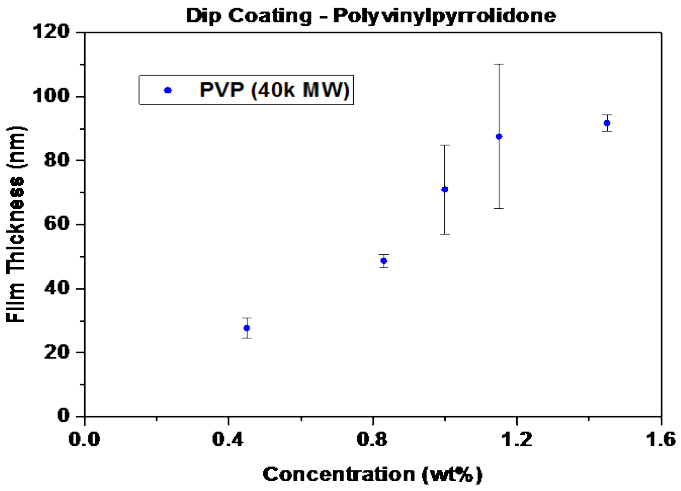

Figure 2: PVP dip coating film thickness as a function of wt % concentration of the polymer.

In order to verify that coating did not break the electrical connection or harm the SWCNTs, we tested the IDEs pre/post polymer coating. The aligned PVP-SWCNT combination displayed consistent device conductivity following coating using PVP (MW= 40,000) and subsequent chromic acid treatment process. (Fig. 3). This implies that the device operates as a general resistor mode, enabling its use in a sensor to detect changes in ion composition.

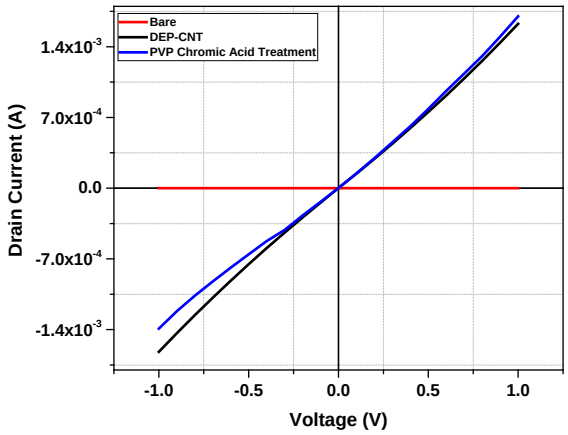

Figure 3: Drain current vs voltage for comparison of SWCNT device using CNT suspended in 2 wt % PVP (40k) polymer. PVP-SWCNT combination displayed consistent device conductivity following post chromic acid treatment.

Polymers with Chromic acid Dopant on Pre-Fabricated Chips

Selectivity based solely on polymer absorption of solvent is limited, since many solvents have similar dielectric constants and/or polarities, i.e. one polymer can absorb many solvents. We sought to introduce additional selectivity and sensitivity by using a dopant that can react with the isopropanol, creating a change in the ionic environment. Based on the literature and looking towards breathalyzer technologies,[7] we decided to dope with a dichromate mixture found in Gastec pellets, containing 1 M sulfuric acid. Oxidizing agents such as dichromate have been studied extensively and most commonly used.[19] The putative reaction is as follows:

$$3\ CH_3CH(OH)CH_3 + K_2Cr_2O_7 + 4\ H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3\ CH_3(CO)CH_3 + 7\ H_2O + 1\ K_2SO_4$$

It is presumed that the IPA molecule absorbed to the dichromate therefore treated PVP decreases the concentration of protons. The p-doped SWCNT increases its resistance upon exposure to the decrease of nearby protons as indicated by resistance increase of IPA sensor response.

Sensor Testing

After device fabrication, the IPA sensor as well as the commercial PID was placed in a static high concentration chamber for their parallel testing of VOC exposure at the various injections points of 100ppm, 1000ppm, and 10,000ppm for IPA, acetone, and isoprene. Sensors were equilibrated until the drift in applied voltage was less than 0.01 V/min. Thus the interaction between the active film coating and IPA analyte is depicted by the sensor signal change of the source-drain current.[20] Sensor response data was then collected in real time with 1sec intervals. The resistance change from the equilibrium point was recorded at 10 min following PVP protocol.

Poly(1-vinylpyrrolidone-co-2-dimethylaminoethyl-methacrylate),poly(1-vinylpyrrolidone-co-vinyl-acetate), and poly(1-vinylpyrrolidone-co-styrene) did not give noticeable response to the IPA vapors regardless of the concentration (SI1-SI4). Even with Poly(1-vinylpyrrolidone-co-2-dimethylaminoethyl-methacrylate) being the thinnest film (approximately 15nm), there is no signal response detected upon exposure to IPA. Both poly(1-vinylpyrrolidone-co-vinyl-acetate) and poly(1-vinylpyrrolidone-co-styrene) displayed identical no response behavior. It was determined that PVP was the better candidate vs its co-polymer counterparts in responding to IPA. Therefore, we proceeded with all further tests only using the optimized PVP coating.

In order to test the impact of dichromate agents, we compared the SWCNT IPA sensors in the presence and absence of the dopants. A commercial PID was used as a control in both experiments. A less than 5% change in resistivity was observed in the absence of dichromate agents even at 10,000 ppm IPA (Figure 4a). However, upon addition of potassium-dichromate dopants, a greater than 100% change in resistivity was observed at the highest concentrations of IPA (Figure 4b), supporting the chromic acid chemical reaction as the key mechanism for achieving high sensitivity SWCNT IPA sensor.

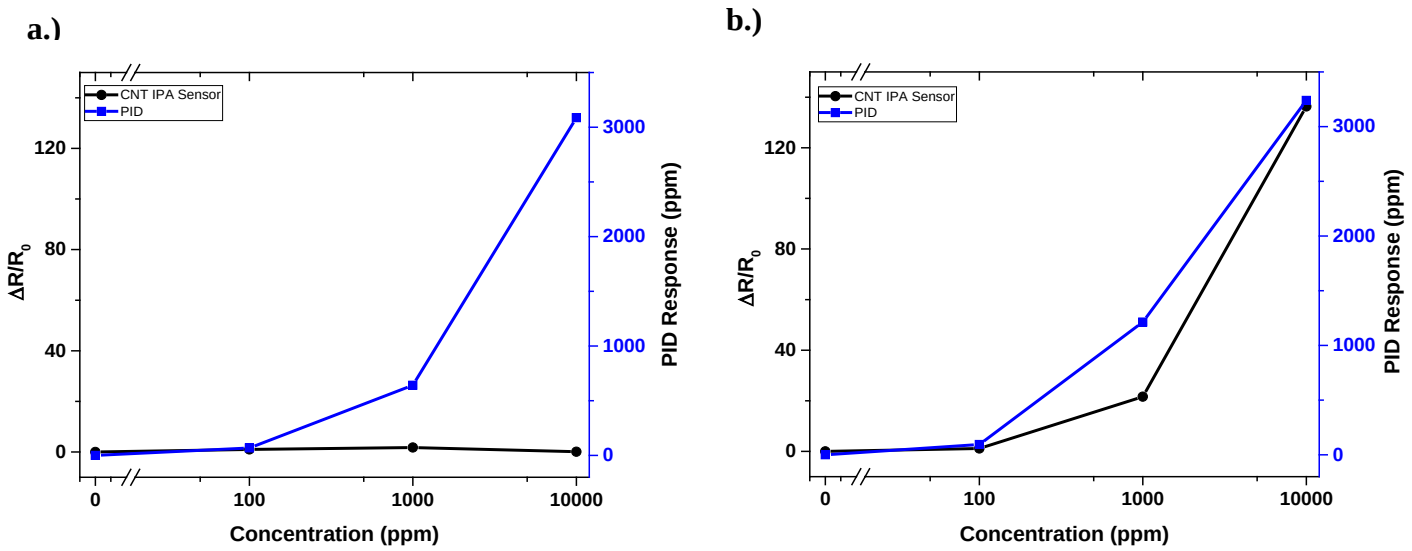

Figure 4: IPA sensor testing effect of a) in the absence b) in the presence of dichromate treated PVP-SWCNT sensor. The SWCNT IPA sensor displayed greater signal response change when the dichromate agents were added to the polymer film compared to no dichromate added sensor.

Comparison to the large area printed CNT electrode

Using the key parameters identified to generate an IPA sensor on a hard glass IDE substrate, we proceeded to test the protocol to PVP coated large area printed flexible SWCNT electrode (5cm x 15cm). A commercial PID was again used to contrast the performance in detecting the vapor IPA. Both sets of CNT devices underwent the same polymer and chromic acid treatment as mentioned before. The PID was used off the shelf according to instructions. Both of the sensors had larger response changes for IPA compared to the other VOCs (acetone and isoprene) (Fig. 5a and 5b), and outperformed the PID with regards to selectivity in all trials (Figure 5c). It is obvious that PIDs use only the absorption of UV light to generate ions that can be detected, which is inherently selective only towards aromatic or conjugated moieties that would absorb UV light. The DEP SWCNT IDE sensor outperformed the PVP coated large

area printed SWCNT sensor with regards to the sensitivity, providing over a 40X increase in the IPA response. (Fig. 5a and 5b).

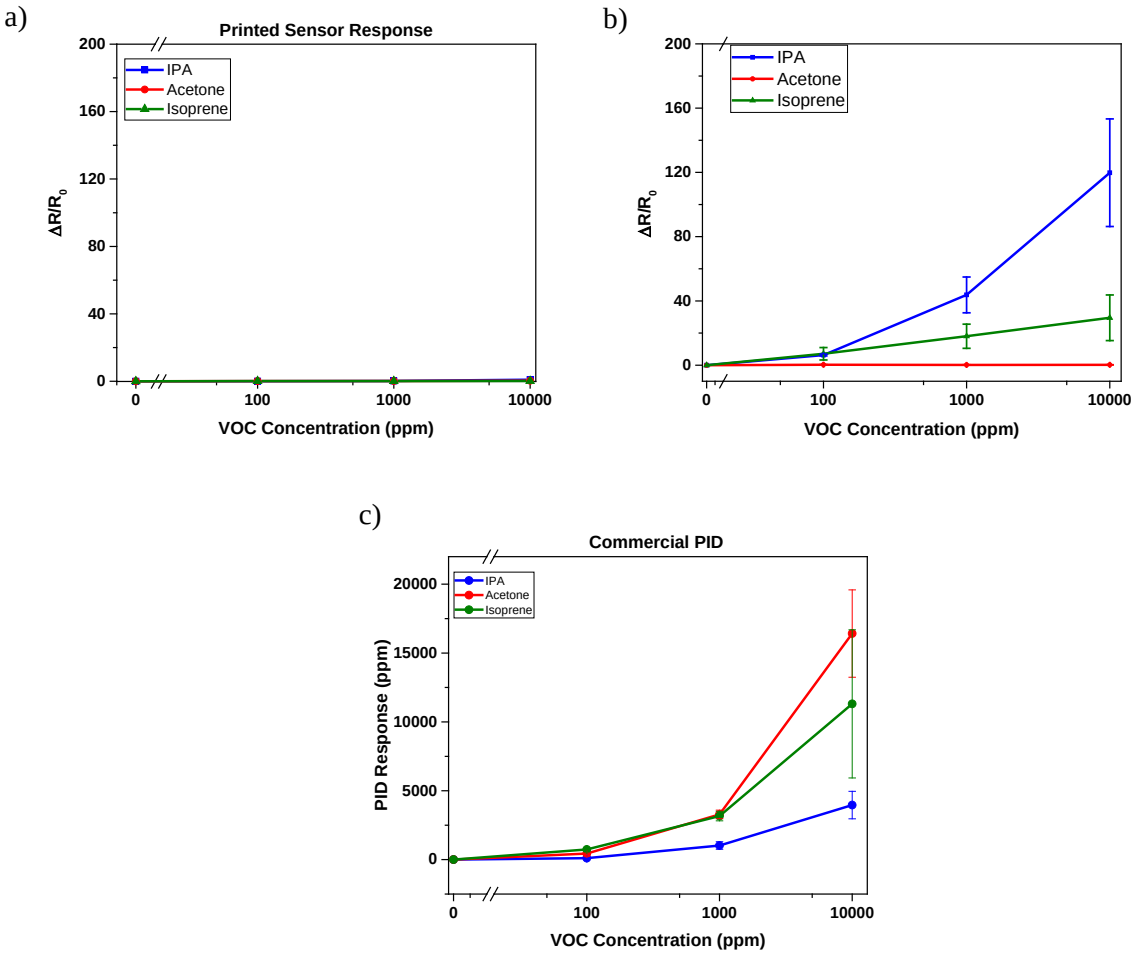

Figure 5: a) Printed SWCNT sensor response at various chemical concentration point injections b) DEP-IDE sensor response at different chemical concentrations. c) Commercial PID response displayed no specificity to IPA while showing highest signal change for other compounds.

CONCLUSION

Recent work demonstrating a colorimetric output upon solvent binding[9] provided a novel proof of principle assay; however colorimetric techniques are difficult for quantitation and/or real-time detection due to the need to integrate an optical sensor, and the difficulty in regeneration due to the irreversibility.

Electronic/Electrochemical techniques have the promise for real-time data since resistance can be measured continuously and translated by a program to provide real-time alerts of solvent contamination. Here, we examined how IPA selective, polymer composition and coating, SWCNT deposition and dichromate chemical additives impact the performance of the sensor.

In summary, the development of coupling polymeric solvatoselective capture elements for IPA into an electrochemical sensor has been demonstrated. We have successfully constructed a sensor based on the procedure determined that drastically improved sensor performance while distinguishing IPA from other VOCs. We have established the basic foundation to further develop a sensor that is specific to IPA detection. We have identified key metrics (film thickness, CNT deposition, presence of reactive dopants) that directly impact sensor performance. The results showed improved signal response demonstrating that the device is selective enough to detect IPA, exceeding the level of performance from a commercial PID. While much progress has been done to display selective response to high ppm level IPA, there are still challenges that need to be addressed being precise control of chromic acid concentration, increasing signal to noise ratio, miniaturization of sensor, multiplexing data acquisition, and more detailed chemical vapor chamber work. Future work needs to be done to optimize the chemistry and the device geometry in order to improve the limit of detection to the low ppm/ppb level. Future work will also look towards additional polymeric gating that should provide enhanced selectivity at the potential expense of time resolution and/or sensitivity. Finally, future work will also apply this approach to other gaseous compounds of interest using orthogonal chemistries for specific detection of VOCs or classes of VOCs. Regardless, this proof of principle demonstration opens up the pathway to sensitive and selective electrochemical sensors that can enable real-time monitoring in a variety of environments.

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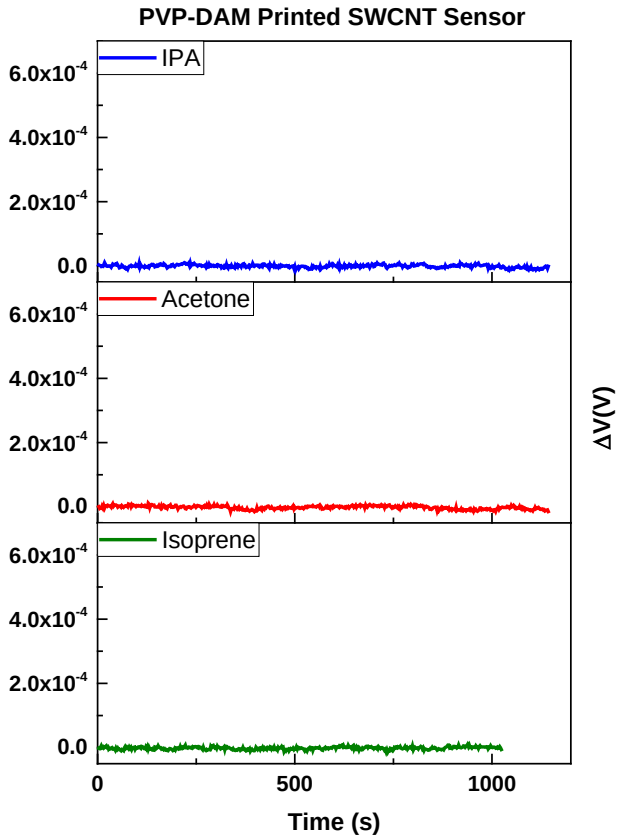
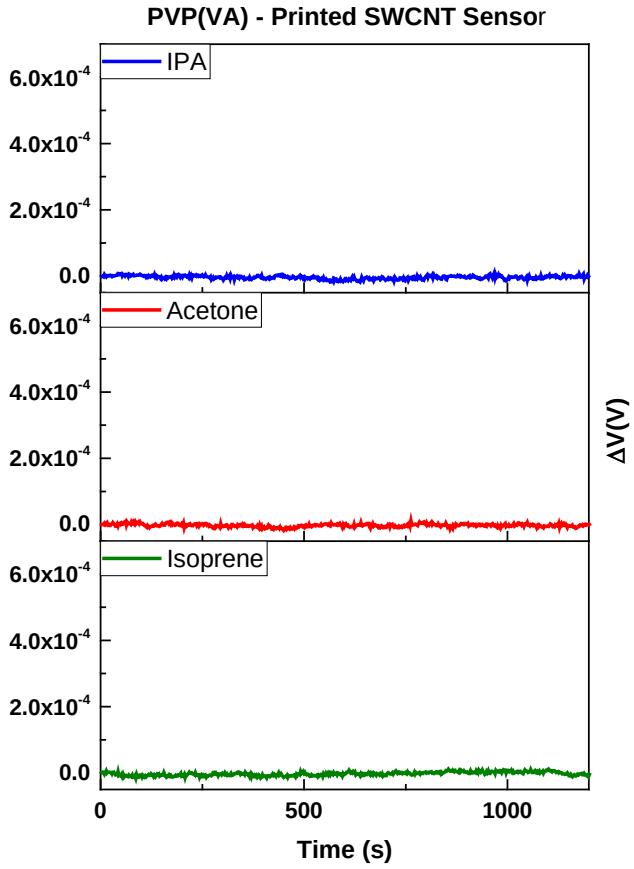
Polymer	Wt%	Thickness (nm)
poly(1-vinylpyrrolidone-co-vinyl-acetate)	0.25	35
	0.30	12
	0.55	53
poly(1-vinylpyrrolidone-co-styrene)	0.11	75
	0.38	75
Poly(1-vinylpyrrolidone-co-2-dimethylaminoethyl-methacrylate)	0.08	15
	0.15	20
	1.9	200
Poly-vinylpyrrolidone	0.2	15

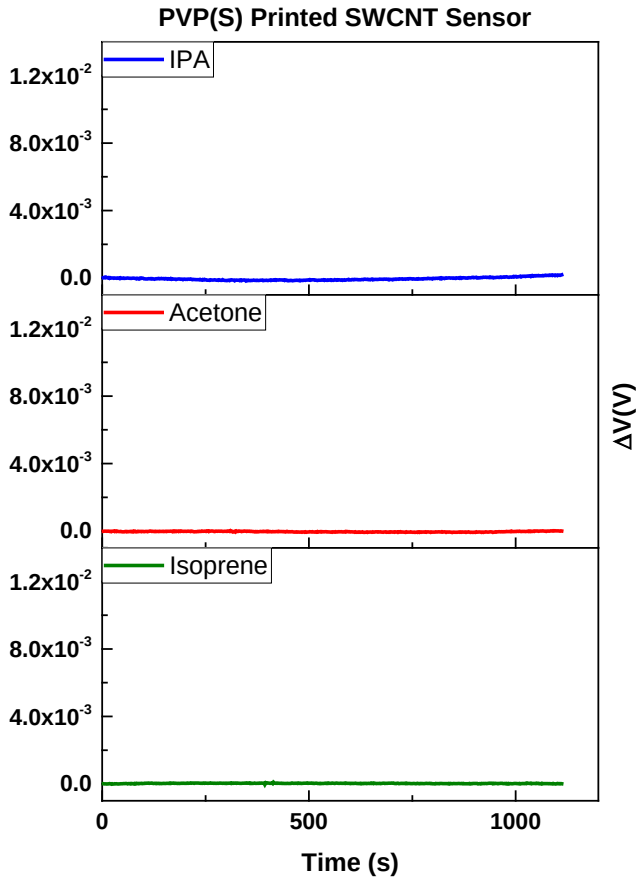
SI1: Summary of different polymers and film thickness after dip coating technique.



SI2: Voltage changes vs time of printed SWCNT sensor post exposure to IPA, Acetone, Isoprene for PVP-DAM copolymer at 0.27 wt% concentration. IPA (100ppm) injected at 300s time frame showed no response after baseline subtraction.



SI3: Voltage changes vs time of printed SWCNT sensor post exposure to IPA, Acetone, Isoprene for PVP-VA copolymer at 0.55 wt% concentration. IPA (100ppm) injected at 300s time frame showed no response after baseline subtraction.



SI4: Voltage changes vs time of printed SWCNT sensor post exposure to IPA, Acetone, Isoprene for PVP-S copolymer at 0.65 wt% concentration. IPA (100ppm) injected at 300s time frame showed no response after baseline subtraction.