

REPORT DOCUMENTATION PAGE				<i>Form Approved OMB No. 0704-0188</i>	
The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YY) 02 03 18		2. REPORT TYPE Journal		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Chemically Enhanced Polymer-Coated Carbon Nanotube Electronic Gas Sensor for Isopropyl Alcohol Detection				5a. CONTRACT NUMBER In-House	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER 61102F, 62202F	
6. AUTHOR(S) Yen H. Ngo, ^{†,‡} Michael Brothers, ^{†,‡} Jennifer A. Martin, [†] Claude C. Grigsby, [†] Kathy Fullerton, [†] Rajesh R. Naik, [†] and Steve S. Kim*, [†]				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER H0SL	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) ‡UES Inc., Beavercreek, Ohio 45432				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) †Air Force Materiel Command Air Force Research Laboratory 711 th 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-JA-2018-0019	
12. DISTRIBUTION/AVAILABILITY STATEMENT Distribution A: Approved for public release. 88ABW-2018-1040, CLEARED on 02 Mar 2018					
13. SUPPLEMENTARY NOTES ACS Omega 2018, 3, 6230–6236 DOI: 10.1021/acsomega.8b01039					
14. ABSTRACT Breathing-air quality within commercial airline cabins has come under increased scrutiny because of the identification of volatile organic compounds (VOCs) from the engine bleed air used to provide oxygen to cabins. Ideally, a sensor would be placed within the bleed air pipe itself, enabling detection before it permeated through and contaminated the entire cabin. Current gas-phase sensors suffer from issues with selectivity, do not have the appropriate form factor, or are too complex for commercial deployment. Here, we chose isopropyl alcohol (IPA), a main component of de-icer spray used in the aerospace community, as a target analyte: IPA exposure has been hypothesized to be a key component of aerotoxic syndrome in pre, during, and postflight. IPAs proposed mechanism of action is that of an anesthetic and central nervous system depressant. In this work, we describe IPA sensor development by showing (1) the integration of a polymer as an IPA capture matrix, (2) the adoption of a redox chemical additives as an IPA oxidizer, and (3) the application of carbon nanotubes as an electronic sensing conduit. We demonstrate the ability to not only detect IPA at 100–10 000 ppm in unfiltered, laboratory air but also discriminate among IPA, isoprene, and acetone, especially in comparison to a typical photoionization detector. Overall, we show an electronic device that operates at room temperature and responds preferentially to IPA, where the increase in the resistance corresponds directly to the concentration of IPA. Ultimately, this study opens up the pathway to selective electronic sensors that can enable real-time monitoring in a variety of environments for the force health prevention and protection, and the potential through future work to enable low parts-per-million and possibly high parts-per-billion selective detection of gas-phase VOCs of interest					
15. SUBJECT TERMS volatile organic compounds, isopropyl alcohol, gas sensors					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT: SAR	18. NUMBER OF PAGES 8	19a. NAME OF RESPONSIBLE PERSON (Monitor) Steve Kim 19b. TELEPHONE NUMBER (Include Area Code) N/A
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			

Chemically Enhanced Polymer-Coated Carbon Nanotube Electronic Gas Sensor for Isopropyl Alcohol Detection

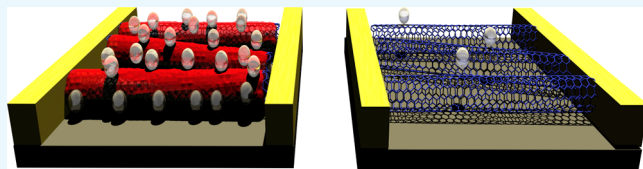
Yen H. Ngo,^{†,‡} Michael Brothers,^{†,‡} Jennifer A. Martin,[†] Claude C. Grigsby,[†] Kathy Fullerton,[†] Rakesh R. Naik,^{†,§} and Steve S. Kim^{*,†,§}

[†]711th Human Performance Wing, Air Force Research Laboratory, Wright-Patterson AFB, Ohio 45433, United States

[‡]UES Inc., Beavercreek, Ohio 45432, United States

Supporting Information

ABSTRACT: Breathing-air quality within commercial airline cabins has come under increased scrutiny because of the identification of volatile organic compounds (VOCs) from the engine bleed air used to provide oxygen to cabins. Ideally, a sensor would be placed within the bleed air pipe itself, enabling detection before it permeated through and contaminated the entire cabin. Current gas-phase sensors suffer from issues with selectivity, do not have the appropriate form factor, or are too complex for commercial deployment. Here, we chose isopropyl alcohol (IPA), a main component of de-icer spray used in the aerospace community, as a target analyte: IPA exposure has been hypothesized to be a key component of aerotoxic syndrome in pre, during, and postflight. IPAs proposed mechanism of action is that of an anesthetic and central nervous system depressant. In this work, we describe IPA sensor development by showing (1) the integration of a polymer as an IPA capture matrix, (2) the adoption of a redox chemical additives as an IPA oxidizer, and (3) the application of carbon nanotubes as an electronic sensing conduit. We demonstrate the ability to not only detect IPA at 100–10 000 ppm in unfiltered, laboratory air but also discriminate among IPA, isoprene, and acetone, especially in comparison to a typical photoionization detector. Overall, we show an electronic device that operates at room temperature and responds preferentially to IPA, where the increase in the resistance corresponds directly to the concentration of IPA. Ultimately, this study opens up the pathway to selective electronic sensors that can enable real-time monitoring in a variety of environments for the force health prevention and protection, and the potential through future work to enable low parts-per-million and possibly high parts-per-billion selective detection of gas-phase VOCs of interest.



INTRODUCTION

The degree of exposure to the volatile organic compounds (VOCs), gases, and airborne particles for a human subject can significantly vary from others because of his/her differences in work, recreational, and residential settings. Breathing-air quality within commercial airline cabins has come under increased scrutiny because of the identification of VOC contaminants from the engine bleed air used to provide oxygen to cabins. Ideally, a sensor would be placed within the bleed air pipe itself, enabling detection before it permeated through and contaminated the entire cabin.

We chose isopropyl alcohol (IPA), a main component of de-icer spray used in the aerospace community, as a target analyte that has to be selectively detected; IPA exposure has been hypothesized to contaminate breathing air and to be a key component of aerotoxic syndrome pre, during, and postflight.¹ 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.² 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.³ More explicitly, competing technologies, primarily semiconductor platforms, infrared (IR) detectors, and

photoionization detectors (PIDs) lack any recognition element specific for IPA. Photoionization detectors rely on the ionization of hydrocarbons but provide no selectivity or specificity for any functional groups. Semiconductor- and/or absorbance-based sensors use a heating element in conjunction with a metal oxide with preferential binding to specific chemical classes and lack the ability of selectively discriminating IPA from the ambience. Finally, most miniaturized IR systems only provide feedback at one wavelength, being vulnerable to the interferences from the gas compounds with similar absorption peaks. Even when obtaining true Fourier-transform infrared spectra, the ability of selectively identifying a compound of interest among a complex mixture is near impossible because of the overlap in the chemical structure of many volatile compounds, including water.

In addition to their lack of specificity, these gas sensors often have one or more of the following negative characteristics: (1) they are bulky, (2) they suffer from sensor drift, (3) they are chemically unstable, (4) they require optical/electrical components (cost/size), and/or (5) they have a slow response

Received: May 21, 2018

Accepted: May 31, 2018

Published: June 11, 2018

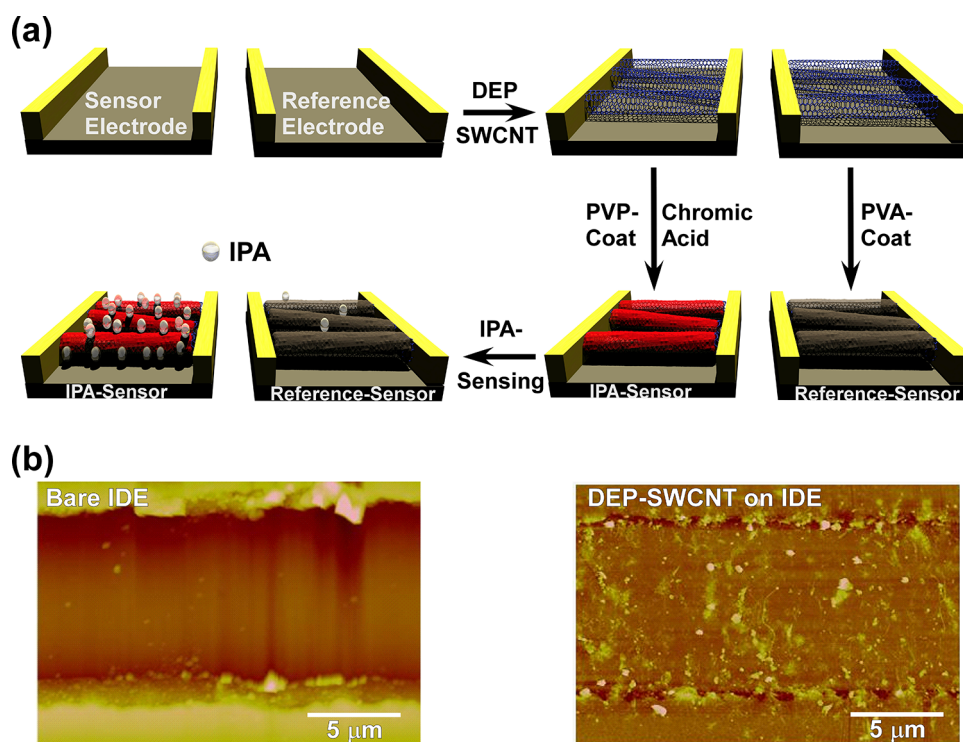


Figure 1. (a) Scheme showing IPA sensor fabrication process based on dielectrophoresis (DEP)-SWCNT device using PVP polymer matrix and chromic acid (CA)-based chemical enhancement. (b) Atomic force microscopy (AFM) topography image showing the bare interdigitated electrode (IDE) and DEP-SWCNT assembled on the IDE.

time.⁴ Thus, it is necessary to develop a noiseless, low-power, 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.^{5,6} The single-atom thin cylindrical semiconductor/semimetal/metal CNTs change their resistance as a function of ion concentration, doping level, and solvent conditions with unmatched sensitivity compared to those of the most bare metal-oxide or inorganic semiconductors, offering ultimate sensitivity as nanoelectronic sensors.⁷ CNTs often serve as p-type semiconductors in ambience, and thus their resistance should change as a function of ionic content and/or redox ambience. 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.⁸ Previous work has identified ultrathin, polymeric coatings covalently bound to carbon nanotubes as a way to disperse them and enable easy assembly of networks; however, thicker layers have been demonstrated to serve as recognition elements on the basis of the polarity of the compound.⁹

Lee et al. demonstrated IPA absorption into the poly(vinylpyrrolidone) (PVP)-coating matrix, followed by subsequent absorption into the base layer solvatochromic sensor. The solvatochromic 10,12-tricosadynoic acid/polydiacetylene copolymer was selective for alcohols, making this particular solvent-gated solvatochromic sensor highly selective to IPA.

The above solvatochromic 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.¹⁰ Therefore, using PVP polymers as surface modifications to single-walled carbon nanotubes (SWCNTs)

has a potential to improve sensing performance to IPA as a suitable molecular recognition element.¹¹ Moreover, other work demonstrated that the PVP-SWCNT interaction was proven to form molecular level interactions that could produce an individually dispersed carbon nanotube solution, in which the nanotubes overcame their immense inter-tube cohesive (bundling) energy.⁹ Therefore, we were motivated to look into an electronic field-effect transistor (FET)-sensor based off of this methodology, where upon the concentration of gas-phase IPA can thus be correlated directly to the transconductance of the carbon nanotubes embedded within the PVP matrix, resulting in a shift in the source-drain voltage operating at constant drain current mode.

In addition to using PVP polymer as a SWCNT dispersant and recognition elements,¹⁰ we further looked into improving the IPA sensor response by incorporating a doped matrix to trigger a chemical reaction originally used in breathalyzers and measured the reaction progression using a field-effect transistor (FET) (Figure S1). By coupling these elements together, we have formulated a platform that results in a change in electrical output corresponding to a specific analyte concentration. In summary, in this work, we describe an IPA sensor development process that we believe can be applied to a wide range of analytes. Figure 1a shows the sensor development process that consists of (1) forming carbon nanotube FETs, where the source-drain voltage necessary to maintain a constant current changes as a function of ion content/concentration, (2) applying a polymer matrix that serves as an analyte capture matrix,¹⁰ and (3) adding oxidizing agents that react with isopropanol.¹² Through this process, we analyzed and modified various components to improve the quality of the sensor, including how best to fabricate the carbon nanotubes as well as apply the solvent-selective coatings. As a result, we formulated

an electronic device that responds preferentially to IPA, where the increase in the resistance corresponds directly to the concentration of IPA. We demonstrated the detection of IPA using the sensor in unadulterated, ambient laboratory air in ranges relevant to Occupational Safety and Health Administration (OSHA) limits. Later, we provide an insight into future work to enable lowering the limit of detection from 100 to 1 ppm and potentially parts-per-billion levels of IPA. Each component was carefully selected to optimize sensor performance as described below.

RESULTS AND DISCUSSION

SWCNT Channels Generated by Dielectrophoresis.

The carbon nanotubes employed 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.¹² 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 the deposition of SWCNTs among electrodes as a function of the applied voltage and frequency. We found that an alternating current (AC) voltage of $6 V_{p-p}$ at 10 MHz frequency applied for 1 min to the electrode pair in a probe station yielded repeatable $1.5 \pm 0.88 \text{ k}\Omega$ resistance SWCNTFET at $0 V_g$. The $1.5 \pm 0.88 \text{ k}\Omega$ DEP-SWCNT assembly was used for further experiments in formulating and testing IPA sensors. The AFM images obtained from bare IDE and DEP-SWCNT IDE, shown in Figure 1b, confirmed that the DEP effectively assembled carbon nanotubes onto the $10 \mu\text{m}$ gap gold electrodes.

Polymer Coating on DEP-SWCNTFET. Solvent semi-selective polymer films have been demonstrated in the liquid phase to act as a diffusion barrier for solvatochromic solvent sensors. Both the poly(acrylic acid) and PVP coatings served as a solvent-selective gate, whereupon only solvents with the correct polarity would reach the colorimetric reagent, as described in the Introduction section.¹⁰ To simplify the fabrication, as well as to likely enhance response times, we attempted to optimize the polymer composition by adding copolymers and determining 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.¹⁷ When exposed to a VOC, the vapor penetrates into the polymer layer and causes the film to expand; absorption of the solvent of interest by itself oftentimes changes charge density and therefore influences the electrical resistance of the device.¹⁸ As the solvent must be in close proximity to the single-walled nanotube (SWNT) to generate a sensor response, a thicker polymer film may impose a larger diffusion barrier, reducing sensitivity and providing a time-lag in sensing a response. Meanwhile, a thinner film may exhibit pin-hole and 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 need to be controlled to produce conductive polymer films.¹⁹ 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. As indicated in Supporting Information (SI) Table S2, 0.25 and 0.55 wt % poly(1-vinylpyrrolidone-co-vinyl-acetate)

dip-coated samples resulted in film thickness of 35 and 53 nm, respectively. Dip coating with 0.08 wt % poly(1-vinylpyrrolidone-co-2-dimethylaminoethyl-methacrylate) resulted in a film thickness of 15 nm and 0.152 wt % with 20 nm (Figure 2). Because of the viscosity of poly(1-vinylpyrrolidone-co-

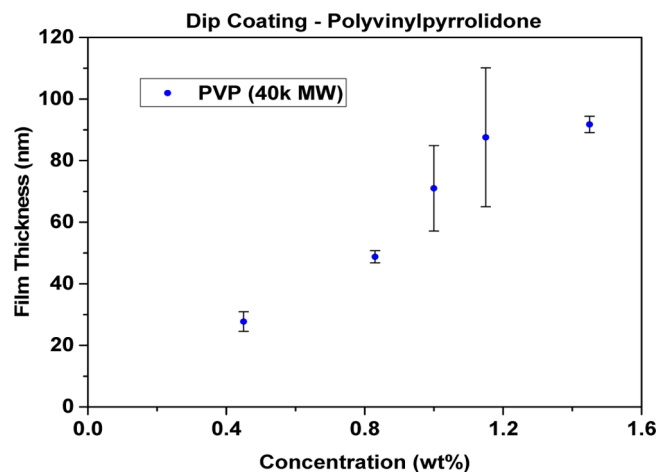
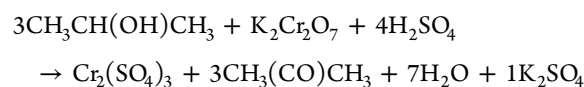


Figure 2. Dip-coated PVP film thickness profile as a function of the polymer weight percentage in water.

styrene), the majority of the film thickness was 75 nm or higher regardless of the weight percentage concentration used. Of the polymers previously mentioned, PVP (40k MW) provided the thinnest uniform coating (15 nm at 0.2 wt % concentration). As expected, higher PVP concentrations resulted in higher film thickness. On the basis of these, using PVP in the dip-coating technique emerged as the method of choice for producing better film results and sensor responses (Figure 2).

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 the subsequent CA treatment process (Figure 3). This implies that the device operates as a general resistor mode, enabling its use in a sensor to detect changes in the ion composition.

Polymer-Coated SWCNTFET with CA Dopant. Selectivity based solely on polymer absorption of solvent is limited because many solvents have similar dielectric constants and/or polarities, that is, one polymer can absorb many solvents. We sought to introduce selectivity using a dopant that can react with the isopropanol, which would result in creating a change in the ionic environment. On the basis of the known breathalyzer chemistry,²⁰ we decided to dope PVP with a CA mixture containing 1 M sulfuric acid. Oxidizers prepared from the CA chemistry have been studied extensively and most commonly used for the detection of the reducing agents.²¹ The putative reaction for IPA is as follows



Using CA as the dopants, the 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.²⁰ In the case of IPA, which is a secondary alcohol, the reaction can only progress to the ketone,

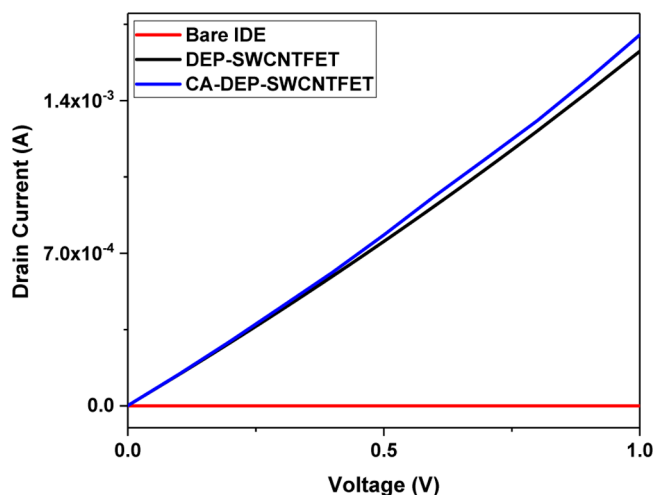


Figure 3. Representative drain current vs drain–source voltage gram at $V_g = 0$ V for bare IDE, DEP-deposited SWCNTFET, and the DEP-SWCNTFET exposed to CA.

resulting in the generation of acetone, water, and chromium sulfate. The net result is a modification of the ion concentration (reduction in sulfuric acid content), modification of the ion content, and change in the solvent composition that can possibly be exploited for measurement. In this article, it is presumed that the IPA molecule absorbs into the PVP, reacts with the immobilized dichromate and sulfuric acid, and causes a decrease in the concentration of protons. The decrease in protons immobilized within the PVP matrix, in theory, should result in an increase in the resistance for the p-doped SWCNT.¹² As predicted, we have observed upon the exposure of our sensor to IPA, a decrease of nearby protons as indicated by resistance increase of IPA sensor responses.

IPA 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 100, 1000, and 10 000 ppm for IPA, acetone, and isoprene, respectively. We chose 100–10 000 ppm as the range of interest because of Occupational Safety and Health Administration (OSHA) permissible exposure limit for IPA being 400 ppm. Prior to the VOC testing, sensors were equilibrated for 10 min or until the drift in applied voltage was less than 0.01 V/min. The source–drain voltage was then collected in real time with 1 s intervals and used as the sensor response data.²²

Poly(1-vinylpyrrolidone-*co*-2-dimethylaminoethyl-methacrylate), poly(1-vinylpyrrolidone-*co*-vinyl-acetate), and poly(1-vinylpyrrolidone-*co*-styrene) did not give noticeable responses to the IPA vapors regardless of the concentration (Figures S3–S5). Even with poly(1-vinylpyrrolidone-*co*-2-dimethylaminoethyl-methacrylate) being the thinnest film (approximately 15 nm), 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. Meanwhile, it was determined that PVP was the better candidate vs its copolymer counterparts in responding to IPA. A nearly instantaneous response was observed from the PVP-coated SWCNTFET at gate voltage of 0 V just after adding the IPA into the chamber. Therefore, we proceeded with all further tests only using the optimized PVP coating.

To test the impact of CA on IPA sensing, we compared the DEP-SWCNTFET sensors in the presence and the absence of

the chromic acid dopants. A commercial PID was used as a control in both experiments. A less than 5% change in resistance was observed in the absence of CA even at 10 000 ppm IPA (Figure 4a). However, upon addition of CA dopants,

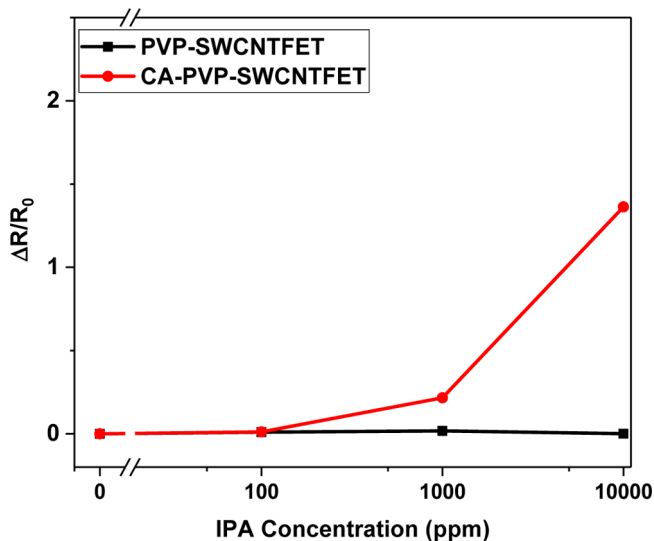


Figure 4. Drain–source resistance changes from the PVP-coated SWCNTFET sensors exposed to IPA vapor, showing the effect of CA treatment. The PVP-coated SWCNTFET IPA sensor displayed a greater signal response change upon the application of CA as compared to the pre-CA treatment.

a greater than 100% change in resistance was observed at the highest concentrations of IPA (Figure 4b), supporting the CA chemical reaction as the key mechanism for achieving a high-sensitivity SWCNT IPA sensor, which when combined with the semiselective polymeric PVP coating, confers both enhanced selectivity and reasonable sensitivity compared to that of the traditional SWCNT sensors. Subsequent repeated additions of 100 ppm IPA into the chamber after a 10 000 ppm IPA test and a complete purge exhibited similar sized responses to the first 100 ppm additions. Although the putative CA oxidation is irreversible, this repetitive sensor response indicates the sensor works in a reversible fashion. One proposed mechanism is as follows: (1) PVP is diffusion-limiting the IPA to the embedded CA reaction sites; (2) SWCNTFET sensor (gate voltage = 0) responds to the IPA oxidation to the highest extreme; (3) diffusion replenishes the CA at sites close to the SWCNT. Overall, these provide a potential tool to enhance the sensor lifetime and accuracy by systematically investigating the target VOC diffusion mechanism and redox reagent chemistry.

Sensor Performance Comparison with a Commercial PID. Using the key parameters identified to generate an IPA sensor on a hard glass IDE substrate, we proceeded to triplicate-test the protocol to a commercial PID. The PID was used off the shelf according to instructions. CA-treated SWCNTFET showed a higher response to IPA compared with that of the other VOCs (acetone and isoprene), and outperformed the PID with regards to selectivity in all trials (Figure 5a,b). It is obvious that PIDs use only the absorption of UV light to generate ions that can be detected, which is inherently selective only toward aromatic or conjugated moieties that would absorb UV light. The sensor response time it requires to reach saturation for IPA was less than 2 min for 100 ppm concentration and less than 3 min for 1000 ppm.

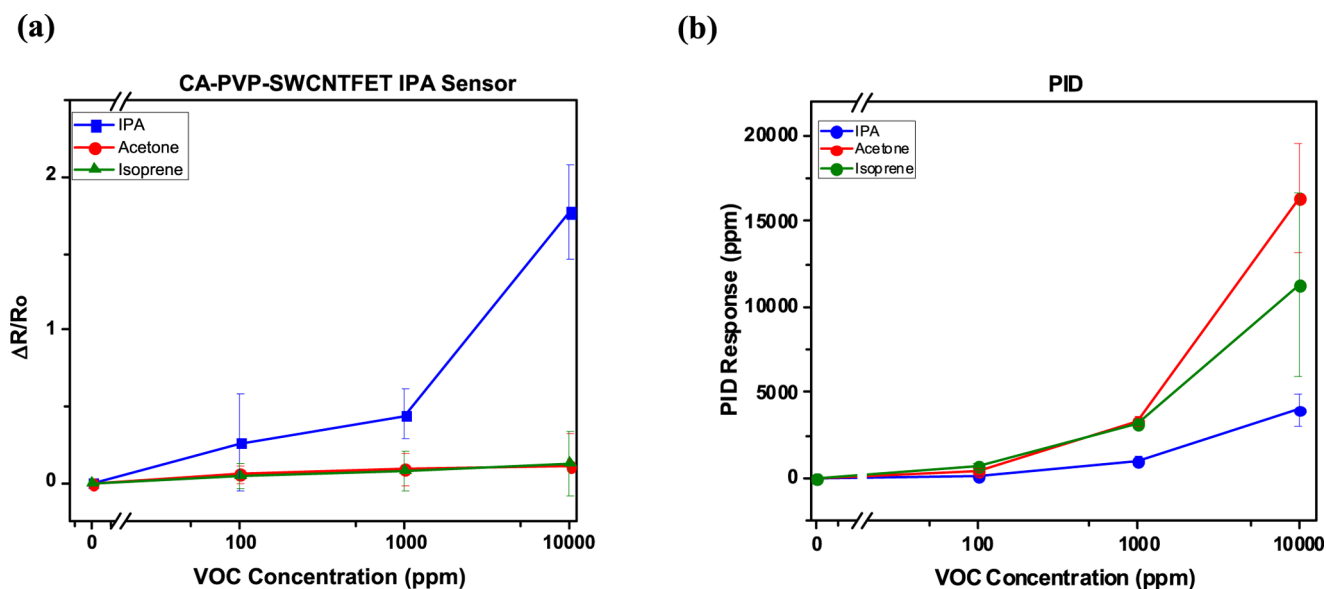


Figure 5. a) CA–PVP–SWCNTFET and (b) commercial PID sensor responses at various chemical concentration point injections. CA–PVP–SWCNTFET shows higher responses to IPA as compared to the equivalent concentrations of acetone and isoprene gases. Commercial PID displays no specificity to IPA.

CONCLUSIONS

Recent work demonstrating a colorimetric output upon solvent binding¹⁰ provided a novel proof of the principle assay; however, colorimetric techniques are difficult for quantitation and/or real-time detection because of 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 because resistance can be measured continuously and translated by a program to provide real-time alerts of solvent contamination. Here, we examined how polymer composition and coating, SWCNT deposition, and CA chemical additives impact the performance of a sensor designed to be selective for IPA.

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

In summary, the development of a novel sensor platform, coupling polymeric solvatoselective capture elements coating for IPA into a carbon nanotube electronic sensor, has been demonstrated. We have successfully constructed a sensor on the basis of the protocol described above and 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. The results showed improved signal responses demonstrating that the device is selective enough to detect IPA, exceeding the level of performance from a commercial PID. Although much progress has been done to display selective responses to high-parts-per-million-level IPA, there are still challenges that need to be addressed being precise control of CA concentration, increasing signal-to-noise ratio, miniatur-

ization of sensor, multiplexing data acquisition, and more detailed chemical vapor chamber work. Future research needs to be done to optimize the chemistry and the device geometry to further improve the limit of detection to the low parts-per-million/parts-per-billion level. Additional studies will also look toward additional polymeric gating that should provide enhanced selectivity at the potential expense of time resolution and/or sensitivity. Finally, in the future, this approach can also be applied to other gaseous compounds of interest using orthogonal chemistries for the specific detection of VOCs or classes of VOCs. Regardless, this proof of principle demonstration opens up the pathway to sensitive and selective electronic sensors that can enable real-time monitoring in a variety of environments.

EXPERIMENTAL METHODS

Interdigitated Electrode (IDE) Preparation. IDEs with 10 μm gap, 20 μm width on 28×5 mm glass supported with 150 nm 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.

SWCNTFET Preparation. The SWCNT (Southwest Nanotechnologies, Norman, OK) purchased were special grade 90% purity with 0.83 nm mean diameter. SWCNTs were ultrasonicated into a water-based suspending medium of PVP or PVP–copolymer 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 the electrical contact was made through the Au electrodes. Using the top layer of the PVP–SWCNT suspension, 5 μL was pipetted and the droplet was placed over the area of interest. Because of the nature of the process being solution based, the solution should be aligned across the gap between the pair of electrodes.¹³ AC electrophoresis retains CNT bundles in the electron gap thus

enabling them to serve as good candidates for gas-sensing elements¹⁴ using dielectrophoretic forces to propagate the CNT along the electric field lines onto the electrodes.¹⁵ Various voltages and frequencies were used to test the conductivity of the DEP process. Parameters with either 1 or 10 peak-to-peak voltages (V_{p-p}) did not result in conductive current vs voltage measurements (SI Table S1 and Figure S2). We concluded that optimal conditions were 60 s deposition time at a frequency of 10 MHz with a V_{p-p} of 6 V. After the DEP step, the substrates were rinsed with distilled water and then dried with house air. Reproducibility of the CNT arrangements is determined by the electrode dimensions and deposition conditions.¹⁶

Polymer Coating to SWCNTFET. Commercial grade polymer coatings such as poly(vinylpyrrolidone) (PVP), poly(vinyl 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 a polymer film onto the SWCNT device. The dip coating comprised of hand dipping the sensor into the polymer solution for 10 min followed by drying inside a heated vacuum chamber (<60 °C) for 5 min. The thickness of the polymer coatings was then characterized using Bioscope II (Bruker, Billerica, Massachusetts) atomic force microscopy (AFM).

Chromic Acid Treatment of Polymer-Coated SWCNTFET. After the polymer-coating process, water-based chromic acid (CA) solution was added to the polymer coating to enhance device sensitivity. The CA was prepared by making an aqueous solution containing potassium dichromate ($K_2Cr_2O_7$) in distilled water with 1 M sulfuric acid (H_2SO_4). The PVP-coated CNT devices were then placed in the solutions for 1 min and allowed to dry via air.

SWCNTFET Sensor Testing. These sensors were mounted onto a breadboard inside of the custom built chamber (17.43L) 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. Acetone, IPA, and isoprene were injected with a syringe, and the air circulated in the static chamber at differing concentrations ranges 100, 1000, and 10 000 ppm. Source–drain voltage changes were measured in real time with constant source–drain current and gate voltage of 1 μA and 0 V, respectively. In addition, linear baseline adjustments were applied for each collected data set based on measuring the linear source–drain voltage drift in the sensor's equilibrated state. A blank reference SWCNTFET sensor coated with poly(vinyl alcohol) was used to subtract the variation of the background the PVP-coated CNT IPA sensor signal.

Commercial Sensor Testing. The SWCNTFET IPA sensors were simultaneously tested with a commercial off the shelf piD-TECH plus photoionization detector (PID, MOCON Inc., Brooklyn Park, MN). PIDs are general-use detectors that, in summary, rely on the ionization of the sample by UV light to ionize the sample, increasing the electron flow across the detector when subject to an electric field. Using a manufacturer-provided table that accounts for the degree of ionization, the PID output was calibrated using the gas samples from a standard 100 ppm IPA gas cylinder.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01039.

SWCNTFET DEP parameters; PVP film thickness; DEP-assembled SWCNTFET drain current vs gate voltage; drain current vs drain–source voltage characteristics from DEP SWCNTFET; SWCNT sensor exposed to IPA, acetone, and isoprene for PVP-DAM copolymer, PVP-VA copolymer, and PVP-S copolymer coating; raw data from SWCNTFET IPA sensor devices (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: steve.kim.13@us.af.mil.

ORCID

Rajesh R. Naik: 0000-0002-7677-928X

Steve S. Kim: 0000-0002-9519-077X

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The funding from the Defense Health Program is greatly acknowledged. The authors thank Capt Suarez, C. for helping early stage IPA-sensing demonstration using printed SWCNT electrodes.

■ REFERENCES

- (1) Linakis, M. W.; Job, K. M.; Liu, X.; Collingwood, S. C.; Pangburn, H. A.; Ott, D. K.; Sherwin, C. M. T. Riding (High) into the Danger Zone: A Review of Potential Differences in Chemical Exposures in Fighter Pilots Resulting from High Altitude and G-Forces. *Expert Opin. Drug Metab. Toxicol.* **2017**, *13*, 925–934.
- (2) Center for Disease Control and Prevention. Isopropyl Alcohol. <https://www.cdc.gov/niosh/npg/npgd0359.html> (accessed Oct 8, 2017).
- (3) Liu, X.; Cheng, S.; Liu, H.; Hu, S.; Zhang, D.; Ning, H. A Survey on Gas Sensing Technology. *Sensors* **2012**, *12*, 9635–9665.
- (4) Patel, S. V.; Mlsna, T. E.; Fruhberger, B.; Klaassen, E.; Cemalovic, S.; Baselt, D. R. Chemically Capacitive Microsensors for Volatile Organic Compound Detection. *Sens. Actuators, B* **2003**, *96*, 541–553.
- (5) Wang, J. Carbon-Nanotube Based Electrochemical Biosensors: A Review. *Electroanalysis* **2005**, *17*, 7–14.
- (6) Fennell, J.; Hamaguchi, H.; Yoon, B.; Swager, T. Chemiresistor Devices for Chemical Warfare Agent Detection Based on Polymer Wrapped Single-Walled Carbon Nanotubes. *Sensors* **2017**, *17*, 982.
- (7) Liu, Y.; Dong, X.; Chen, P. Biological and Chemical Sensors Based on Graphene Materials. *Chem. Soc. Rev.* **2012**, *41*, 2283.
- (8) Li, J.; Lu, Y.; Ye, Q.; Cinke, M.; Han, J.; Meyyappan, M. Carbon Nanotube Sensors for Gas and Organic Vapor Detection. *Nano Lett.* **2003**, *3*, 929–933.
- (9) Yoon, B.; Liu, S. F.; Swager, T. M. Surface-Anchored Poly(4-Vinylpyridine)-Single-Walled Carbon Nanotube-Metal Composites for Gas Detection. *Chem. Mater.* **2016**, *28*, 5916–5924.
- (10) Lee, J.; Chang, H. T.; An, H.; Ahn, S.; Shim, J.; Kim, J. M. A Protective Layer Approach to Solvatochromic Sensors. *Nat. Commun.* **2013**, *4*, No. 2461.
- (11) Sarkar, T.; Srinives, S.; Sarkar, S.; Haddon, R. C.; Mulchandani, A. Single-Walled Carbon Nanotube-Poly(porphyrin) Hybrid for Volatile Organic Compounds Detection. *J. Phys. Chem. C* **2014**, *118*, 1602–1610.
- (12) Bushmaker, A. W.; Oklejas, V.; Walker, D.; Hopkins, A. R.; Chen, J.; Cronin, S. B. Single-Ion Adsorption and Switching in Carbon Nanotubes. *Nat. Commun.* **2016**, *7*, No. 10475.

- (13) Banerjee, S.; White, B. E.; Huang, L.; Rego, B. J.; O'Brien, S.; Herman, I. P. Precise Positioning of Single-Walled Carbon Nanotubes by AC Dielectrophoresis. *J. Vac. Sci. Technol., B: Microelectron. Nanometer Struct.* **2006**, *24*, 3173.
- (14) Suehiro, J.; Zhou, G.; Hara, M. Fabrication of a Carbon Nanotube-Based Gas Sensor Using Dielectrophoresis and Its Application for Ammonia Detection by Impedance Spectroscopy. *J. Phys. D: Appl. Phys.* **2003**, *36*, L109.
- (15) Xue, W.; Li, P. Dielectrophoretic Deposition and Alignment of Carbon Nanotubes. In *Carbon Nanotubes—Synthesis, Characterization, Applications*; Yellampalli, S., Ed.; InTech: Vancouver, 2011; pp 171–190.
- (16) Monica, A. H.; Papadakis, S. J.; Osiander, R.; Paranjape, M. Wafer-Level Assembly of Carbon Nanotube Networks Using Dielectrophoresis. *Nanotechnology* **2008**, *19*, No. 08S303.
- (17) Li, B.; Sauv e, G.; Iovu, M. C.; Jeffries-El, M.; Zhang, R.; Cooper, J.; Santhanam, S.; Schultz, L.; Revelli, J. C.; Kusne, A. G.; et al. Volatile Organic Compound Detection Using Nanostructured Copolymers. *Nano Lett.* **2006**, *6*, 1598–1602.
- (18) Arshak, K.; Moore, E.; Lyons, G. M.; Harris, J.; Clifford, S. A Review of Gas Sensors Employed in Electronic Nose Applications. *Sens. Rev.* **2004**, *24*, 181–198.
- (19) Moradi, M. A.; Larrakoetxea Angoitia, K.; Van Berkel, S.; Gnanasekaran, K.; Friedrich, H.; Heuts, J. P. A.; Van Der Schoot, P.; Van Herk, A. M. Bimodal Latex Effect on Spin-Coated Thin Conductive Polymer-Single-Walled Carbon Nanotube Layers. *Langmuir* **2015**, *31*, 11982–11988.
- (20) Borkenstein, R. F. Method for Rapid Quantitative Analysis of Ethyl Alcohol. US3208827A, 1965.
- (21) Hassan, M.; Al-Hakimi, A.; Alahmadi, M. Kinetics of Oxidation of Aliphatic Alcohols by Potassium Dichromate in Aqueous and Micellar Media. *South African J. Chem.* **2011**, *64*, 237–240.
- (22) Hulanicki, A.; Glab, S.; Ingman, F. Chemical Sensors: Definitions and Classification. *Pure Appl. Chem.* **1991**, *63*, 1247–1250.