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Miniature nitro and peroxide vapor sensors using nanoporous thin films

Robert Blue, *Member IEEE*, Neil Thomson, Stewart J. Taylor, Ashleigh J. Fletcher, Peter J. Skabara, and Deepak Uttamchandani, *Senior Member IEEE*

Abstract— With the increased and continuous threat of terrorist attacks in public areas, new sensors are required to safeguard the public from home-made explosive devices. Current commercial sensors for explosive vapors are high-cost, bulky equipment not amenable to mass production, thus limiting their widespread deployment within society. We are conducting research on polymer-based microsensors that can overcome these limitations. Our devices offer an approach to the realization of low-cost sensors that can readily be placed as a network of electronic sentinels that can be permanently located in areas of public access. The polymers are chemically tailored to have a high affinity for nitro and peroxide vapors and are grown electrochemically on microelectrodes. Novel nanoporous polymer-based sensors are demonstrated with a detection level of 200 ppb of nitro vapors. In addition, a prototype reversible sensor for peroxide vapors is demonstrated to low ppm concentrations.

Index Terms— Explosive sensors, nitro-group, peroxides, microsensors, nanoporous polymers

I. INTRODUCTION

The threat of terrorist attacks involving latent explosive devices is ever-present, both domestically and internationally [1]. High sensitivity detection of explosive compounds using low-cost, compact, rapidly-responding smart sensors are required to increase security for users of transport hubs, shopping malls and other public places which have uncontrolled access. As well as traditional explosives containing nitro-bearing compounds such as trinitrotoluene (TNT), peroxide-based explosives, such as triacetone triperoxide (TATP), are increasingly being employed in terrorist incidents (Fig. 1). Peroxide is an ingredient often used in home-made explosives because of its ease of manufacture or legitimate supply, as well as being difficult to detect [2].

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For the detection of explosives either sniffer dogs or a developed technology are currently employed [3]. Sniffer dogs cost tens of thousands of dollars to train, a handler is required and they can only be deployed for a limited time before being rested. Alternatively, a range of developed technologies such as ion mobility [4], infra-red spectroscopy [5], fluorescent polymers [6], and colorimetric kits [7] have been utilized. Such systems range from static walk-through machines to portable devices such as the state-of-the-art SABRE™ 5000 (Smiths Group plc). This portable system, weighing several pounds with a 4hr battery life, is not amenable to mass-production and/or low-cost. The current sensitivity of this system is quoted as low ppm nitro vapors [8].

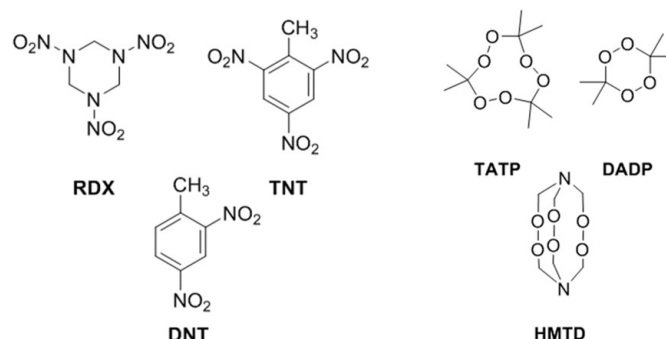


Fig. 1. Chemical structures of nitro-based and peroxide-based explosive compounds:

Our research objective is to create miniature sensors that are not only portable, but of such low cost that they can be employed unattended in a building in a similar manner to smoke detectors. The approach we are investigating is based on capacitance measurements of thin polymer film capacitors. The basic sensor platform is metallic interdigitated electrodes (IDEs) which can be mass produced at low cost. Upon the electrodes we deposit a tailored polymer whose electronic properties are changed by the presence of the target chemicals, but are much less responsive to non-targeted chemicals. If the sensing mechanism is based on measuring changes in capacitance then these miniature chemical sensors are called chemicapacitors (Fig. 2).

Organic semiconductor polymers can be tailored to attain specific chemical functionalities whilst still capable of being deposited by the low-cost manufacturing route of electrochemistry [9]. Electrochemical deposition from a solution of monomers has several advantages over other methods such as photolithography and ink-jet printing [10,11].

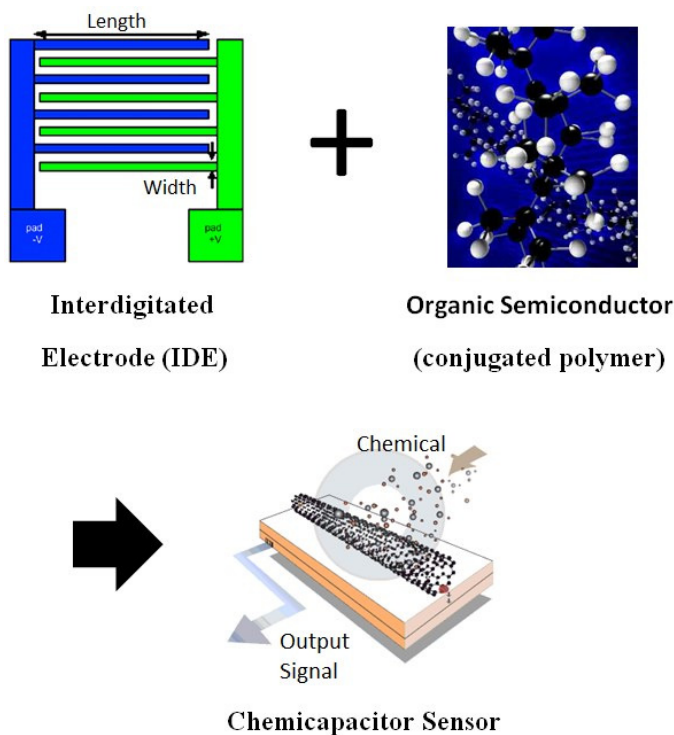


Fig. 2. Concept of deposition of a polymer upon metallic electrodes to create a miniature chemicapacitor sensor.

These include the coating of multiple devices in a single step, being amenable to a wide range of solvents, the growth of films on the nanoscale, and being a low-cost high yield process applicable to silicon wafer production. Multiple discrete devices on the wafer can be simultaneously coated by the simple application of a current to each device. Thus chemicapacitors fabricated through electrochemical deposition is an enabling technology towards creating low-cost microsensors.

Other explosives sensors that have been reported are based on fluorescent receptors (for example, ICX Technologies Inc). Overall, such optical sensors are more complex and expensive systems, requiring the integration of light sources, optical filters, sensitive photodetectors and electronics [12], while a chemicapacitor system is based purely on electronic read-out. The majority of publications describing the use of biosensors for explosives detection deal with liquid-mediated formats and optical readout [13], but these techniques are generally not reversible, and thus the sensor is not reusable. Chemicapacitors incorporating polymer films are known to have good reversibility when the analyte concentration reverses [14]. Thus, overall, the chemicapacitor is a suitable sensor format that offers an approach to the development of low-power and low-cost stand-alone sensors.

We have previously reported miniature chemicapacitor sensors which demonstrated a sensitivity and selectivity to nitro-bearing compounds [15,16]. During the previous study, derivatives of 3,4-propylenedioxythiophene (ProDOT) and terthiophenes were synthesized in order to sense nitro-bearing vapors. The chemicapacitors were based on novel brominated-ProDOT (Br-ProDOT) monomers which were then

electrochemically grown on IDEs to form a polymer. A selective and reversible response to vapors of nitro-bearing compounds was demonstrated with up to three orders of magnitude higher response to the targeted nitro-bearing compounds compared to the response to other common volatile organic chemicals (VOCs) interferences. Similar sensors demonstrated by other research groups have used non-specific, i.e. off-the-shelf, polymer films which show sensitivity to a target analyte, but also exhibit undesired and sizeable cross-sensitivity to a wide range of non-targeted compounds [17-19]. The sensors reported previously [16] demonstrated sensitivity to nitro-bearing compounds to a concentration of around 20 ppm. This first generation of synthesized polymers was essentially planar non-porous types.

The aim of the present research is to synthesize and investigate new copolymer materials with a three dimensional topology. Such materials have the potential of increasing the number of nitro detecting sites available, thus creating a more sensitive material and a sensor that will exhibit sub-ppm sensitivity. In addition, our technology is flexible and can be adapted to meet new threats by incorporating new specific functional groups in our base polymers. We demonstrate this here by synthesizing and developing another novel polymer, this time targeting peroxide vapors in air.

II. EXPERIMENTAL

A. Theoretical basis of a chemicapacitor sensor

Igreja and Dias [20] derived equations for an IDE structure having one sensing layer of dielectric constant ϵ_{Layer} and a thick substrate of dielectric constant ϵ_{sub} and showed that the total capacitance is given by:

$$Cap = (N-3) \frac{C_I}{2} + 2 \frac{C_I C_E}{C_I + C_E} \quad (1)$$

where N is the number of electrodes and C_I and C_E are the half capacitance of one interior electrode and the capacitance of one outer electrode given by:

$$C_I = \epsilon_0 L \left[\frac{K(k_{I-\infty})}{K(k'_{I-\infty})} + (\epsilon_{\text{Layer}} - 1) \frac{K(k_{I-\text{Layer}})}{K(k'_{I-\text{Layer}})} + \epsilon_{\text{Sub}} \frac{K(k_{I-\infty})}{K(k'_{I-\infty})} \right] \quad (2)$$

$$C_E = \epsilon_0 L \left[\frac{K(k_{E-\infty})}{K(k'_{E-\infty})} + (\epsilon_{\text{Layer}} - 1) \frac{K(k_{E-\text{Layer}})}{K(k'_{E-\text{Layer}})} + \epsilon_{\text{Sub}} \frac{K(k_{E-\infty})}{K(k'_{E-\infty})} \right] \quad (3)$$

where ϵ_0 is the relative permittivity of free space, L is the length of the electrodes, and $K(\cdot)$ is the complete elliptical integral of the first kind. The first term in square brackets represents the contribution to capacitance of an infinite air layer, the second term the sensing polymer, and the third term the thick substrate. From these equations it is clear that for other parameters remaining fixed, the capacitance is directly

proportional to the dielectric constant of the sensing layer (ϵ_{Layer}).

B. Synthesis of 3D nitro-sensitive copolymers

The creation of a three dimensional polymer matrix is based upon the synthesis of two intermediates shown in Fig. 3. These compounds have the potential to be electropolymerized to form a random copolymer. By copolymerization with a spiro compound, which is a bicyclic organic compound with rings connected through just one atom (the spiro atom), a non-planar, crosslinked polymer is produced. By altering the ratio of the two co-monomers the surface area and pore size can be easily altered. To allow for simple electro-copolymerization the spiro compound selected was spiro bipropylenedioxythiophene (spiro biProDOT).

Synthesis of compounds Br-ProDOT (**1**) and the spiro compound (**2**) was achieved. By variation of the ratio of compounds **1**:**2**, the sensitivity towards nitro groups can be altered, which will allow for some optimization of the chemicapacitor sensor. This Br-ProDOT:spiro (BP:Spino) ratio was varied over the range 4:1 to 19:1.

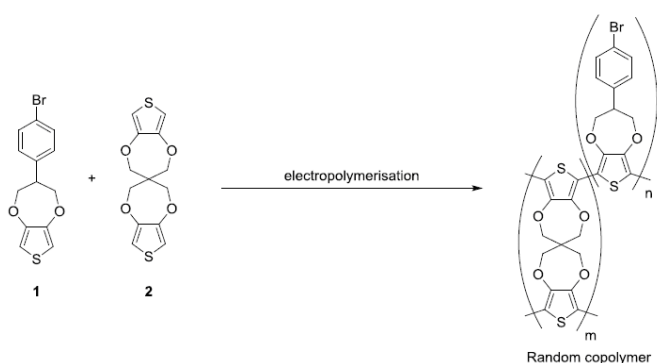


Fig. 3. Synthesised monomer sub units **1** (Br-ProDOT) and **2** (Spiro biProDOT) to form a random copolymer.

Electropolymerization of these materials onto interdigitated electrodes (IDEs) was carried out from their respective monomers in 1 mM dichloromethane solutions containing *n*-tetrabutyl-ammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte using cyclic voltammetry (BAS model CV50W Voltammetric Analyzer, Bioanalytical Systems Inc., USA). The IDE chips were used as the working electrode, while Pt wire was a counter electrode, and Ag wire was a pseudoreference electrode referenced to ferrocene (Fig. 4). Polymers were produced by cyclic voltammetry between 0 V and 1.8 mV for 50 cycles. As the conjugation increases when forming oligomer and polymer chains, the oxidation potential shifts to a lower value and the current response increases with each cycle. The chips were fully immersed into the monomer solution and electropolymerization was localized to the individual electrodes connected to the potentiostat, thus forming discrete functionalized sensors. The films were subsequently dedoped in a monomer-free acetonitrile solution of *n*-tetrabutylammonium hexafluorophosphate (TBAPF₆). The thickness of the polymer films grown on the electrodes was typically less than 500 nm, measured with an Alpha-Step IQ Surface Profiler (KLA Tencor Corp.). The

electropolymerized film was noted as being strongly bonded to the gold electrodes and was physically robust.

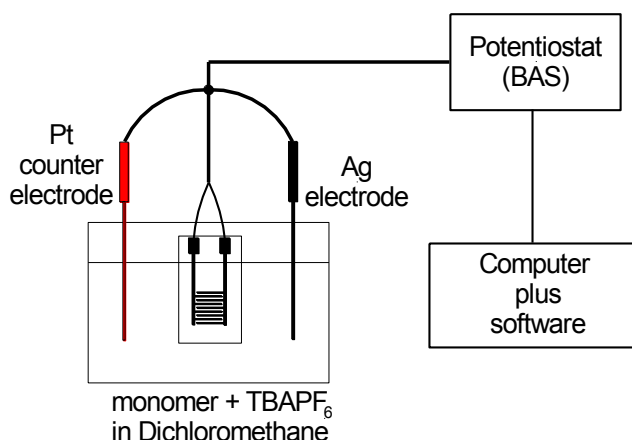


Fig. 4. Electropolymerization of monomers from solution onto gold IDEs set-up as a working electrode in dichloromethane solution, using a Pt wire counter electrode, Ag wire pseudoreference electrode referenced to ferrocene, and *n*-tetrabutylammonium hexafluoro-phosphate as the electrolyte (0.1 M).

C. Synthesis of polymer targeting peroxide vapors

To address new threats such as home-made explosives based on peroxides, we also synthesized and investigated another novel polymer (BE-ProDOT) which was chemically synthesised to have a high specificity towards peroxide vapors (Fig. 5). This was achieved by creating a monomer containing a moiety which is stable towards organic compounds commonly found in the atmosphere, but which will oxidise in contact with peroxides. Here, the bromide functionality of the monomer was converted, to a boronate ester functionality, transforming the Br-ProDOT monomer to BE-ProDOT. The BE-ProDOT monomer was electropolymerized onto a standard glassy carbon electrode and the oxidation peak for the polymer was observed at 0.21 V. This is significantly lower than the oxidation peak of the monomer, which was observed at 1.23 V, and is a good indication of successful polymer growth.

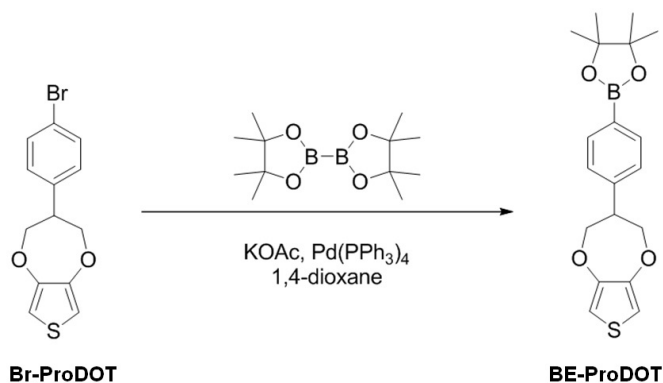


Fig. 5. Synthesis of BE-ProDOT monomer which has an increased affinity towards peroxide vapors.

D. Process of porosity measurement on 3D nitro-sensitive copolymers

A series of electrochemically prepared random copolymers (mixtures of BP:Spio ratios 4:1, 6:1, 8:1, 10:1, 14:1 and 19:1 of the two monomers) were grown on ITO coated slides from their respective monomer solutions in dichloromethane using cyclic voltammetry. This was also performed for a Br-ProDOT only polymer which would serve as a non-porous reference. All the films were subsequently dedoped in a region with no redox activity. Brunauer-Emmett-Teller (BET) surface area measurements were performed using an accelerated surface area and porosimetry system (Micrometrics ASAP 2420). Samples were outgassed within the system at 110 °C for 2 hours. The porosity values were obtained *via* nitrogen adsorption, performed on the degassed sample using pressure increments between vacuum and the saturated vapor pressure. A Dewar of liquid nitrogen to hold the sample temperature constant at -196 °C and zero grade nitrogen with a minimum purity of 99.998% was used (supplied by BOC Gases, UK). In each of the polymer cases, porosity measurements were run on the polymer coated slides, followed by removal of the polymer from the slides. Porosity measurements of the blank ITO slides were then taken in order to correct for any porosity provided by the ITO slide itself. Results are presented and discussed in section IIIA.

E. Process of evaluation of chemicapacitor sensors to vapor concentrations

The copolymers with monomer ratios of BP:Spio ranging from 4:1 to 19:1 were individually grown electrochemically onto IDE platforms supplied by Micrux Technologies Inc (Spain) to form a miniature chemicapacitor sensor (Fig. 6). Each IDE platform covered an area of approximately 2 mm and consisted of 15 pairs of gold electrodes (with an electrode gap of 10 μm) fabricated on a glass substrate of dimensions 10 x 6 x 0.75 mm.

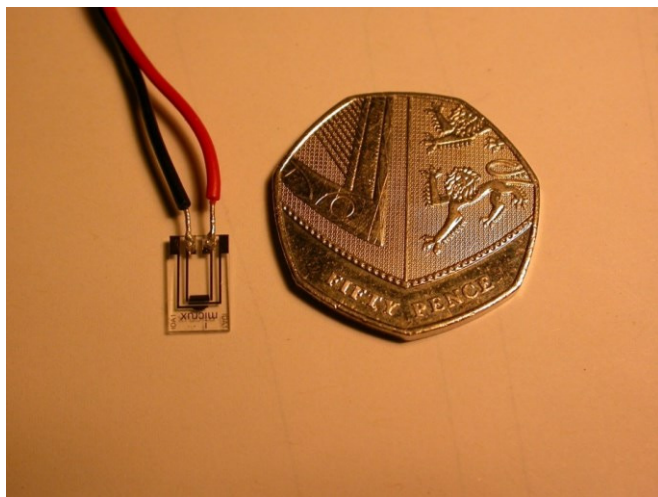


Fig. 6. Photograph showing the developed polymer electrochemically grown onto miniature electrodes.

These sensors were evaluated in a test-bed for their response to dynamic vapors concentrations containing target molecules and common VOCs (Fig. 7). The test-bed consisted of a glass test chamber of diameter 60 mm and height 55 mm. A humidity sensor (HIH-4000, Honeywell) and temperature sensor (HEL-775-B-T-1, Honeywell) were inserted into the chamber to monitor the stability of these quantities. Due to health and safety issues the direct use of explosives in our laboratory was not possible. Therefore, nitroaromatic compounds nitrobenzene and 2-nitrotoluene were employed to generate test vapors containing nitro groups. Nitrobenzene was distilled and stored on 4 angstrom molecular sieves. The chemicapacitor sensors were placed into the test chamber and changes in capacitance was measured in the presence of varying concentrations of nitroaromatic compounds nitrobenzene and 2-nitrotoluene. An E4980A Precision LCR meter and a 4294A Impedance Analyzer (Agilent Technologies Ltd) both operating at excitation frequency 100 kHz were used to measure capacitance of the sensors. These liquid chemicals were placed into a fritted-glass bubbler and an air flow stream controlled by flowmeter F1 (Platon NGX, Roxspur Measurement & Control Ltd., UK) up to 250ml/min was bubbled through each sample to create a vapor flow for each chemical. A second flowmeter F2 (up to 250ml/min) directed air flow through a second bubbler containing VOCs (toluene, THF, hexane) commonly found in the atmosphere was used to test for cross-sensitivity to these VOCs. A third flowmeter F3 (1L/min, FLDA3211G, Omega, UK) was included to subsequently dilute vapor streams to sub-ppm levels as required. Glass tubing was used throughout as an inert material to avoid any absorption from the vapor stream. An exhaust tap was included after the bubbler to allow a stable vapor concentration emerging from the bubbler to develop before the vapor was directed into the test chamber. In the case of high boiling point liquids such as the nitroaromatic compounds, bubbling occurred for at least 2 hours at room temperature prior to taking measurements in order to achieve stability in the vapor concentration. Quite often these chemicals were bubbled overnight before being used for experimentation. At the time of introduction of an analyte species into the test chamber no significant fluctuations of humidity and temperature occurred beyond the baseline noise. The exhaust tap also allowed on and off cycling of vapors entering the chamber to investigate sensor reversibility. Additionally, a mixer, consisting of a 25 mm long section of SiO₂ glass wool (Sigma Aldrich Cat. No. 18421) was included within the glass tubing prior to the test chamber to increase flow turbulence and maximize mixing of the vapor and diluting streams. The sensor performance results are presented and discussed in section IIIB.

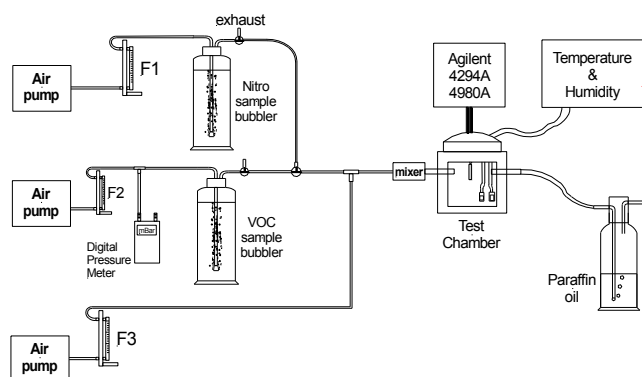


Fig. 7. Apparatus for creating a dynamic vapor flow. Flow controller F1 regulates the flow of nitro vapors, F2 controls the VOC vapor flow, and a pure air stream is controlled by F3 for dilution.

III. RESULTS

A. Porosity results for 3D nitro-sensitive copolymers

Table I shows the results of surface area and porosity measurements on the developed random copolymers deposited on ITO slides. Due to the nature of the samples undergoing BET analysis, the values presented in Table I should not be considered to be absolute values, and are instead compared relatively to each other and the poly(Br-ProDOT) reference. It can be seen that the surface area, pore volume and pore size vary across the different copolymers. In all cases the pore volume is greater for the copolymers than the Br-ProDOT only polymer. Since porosity is defined as the ratio of pore volume to total volume of sample, it can be assumed that all copolymers are more porous than the Br-ProDOT only polymer. The 4:1 copolymer has a vast increase in surface area in comparison to the Br-ProDOT only polymer, more modest increases were observed for both pore volume and pore size; and it is notable that all samples but the 10:1 copolymer exhibited mesoporous character throughout the series. The 10:1 copolymer does not have as great an increase in surface area over the Br-ProDOT only polymer; however it has a larger pore volume and much larger pore size. Meanwhile, the 19:1 copolymer has a surface area similar to the Br-ProDOT only polymer but with a pore volume similar to the 10:1 copolymer. In some areas of Table I trends can be observed in the varying ratios of the copolymer compositions. As the ratio moves from 4:1 to 14:1, the surface area decreases, after which a slight increase is then observed for the 19:1 copolymer. Whilst the pore volume initially shows an increasing trend from the 4:1 copolymer to the 8:1 copolymer, which shows the greatest pore volume, thereafter no overall increasing or decreasing trend is observed. The figures for pore size show an increasing trend moving from the 4:1 copolymer to the 10:1 copolymer, which has by far the greatest pore size at 86 nm. Thereafter, the pore size of the copolymers is significantly less for the 14:1 and 19:1 copolymers, with the 19:1 copolymer found to have a slightly larger value. Pore size is defined as the distance between two

opposite walls of a pore (on the assumption that the pores are slit-shaped) or the diameter of a pore (on the assumption that the pores are cylindrical) and can be an indication of how easily pores can become accessed - a small pore size can lead to blockages at the mouth of pores, reducing the apparent pore volume and also contribute to long desorption times.

TABLE I
POROSITY VALUES MEASURED FOR VARYING COMPOSITION RATIO OF COPOLYMER. SA – SURFACE AREA, PV – PORE VOLUME.

Polymer	Film Weight (mg)	Corrected SA (m ² /g)	Corrected PV (cm ³ /g)	Pore Size (nm)
Br-ProDOT	0.2003	523.3	1.07	2.7
4:1 copolymer	0.0352	11580.2	9.97	5.3
6:1 copolymer	0.0702	5957.3	40.57	21.9
8:1 copolymer	0.0477	1822.4	46.02	13.8
10:1 copolymer	0.0625	862.5	34.84	86.7
14:1 copolymer	0.0503	267.0	36.65	2.2
19:1 copolymer	0.0445	503.1	32.48	5.4

B. Capacitance response of different BP:Spino copolymers to nitro vapors

The copolymer chemicapacitive sensors were placed in the test chamber and evaluated for their response to nitro bearing vapors as described in section III. Fig. 8 shows the average capacitance change for each copolymer for vapors of 83 ppm of nitrobenzene.

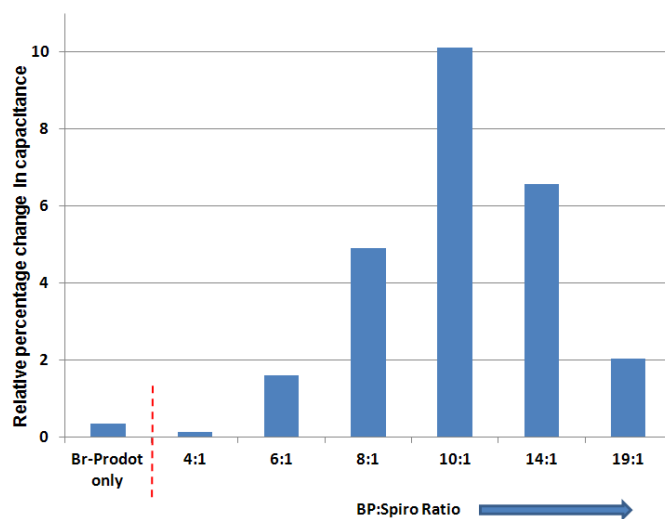


Fig. 8. Measured percentage capacitance response of polymers to nitrobenzene vapor for changing BP:Spino ratio.

The 10:1 copolymer was found to be the most sensitive to nitro-vapors. Whilst this polymer did not have the largest pore volume, the pore volume was still significantly high.

Additionally, this polymer had by far the greatest pore size. While the 4:1 copolymer has by far the greatest surface area it has a small pore volume and small size of pores. Our conclusion from this is that the 4:1 copolymer has a large number of pores which have a small volume, consistent with small pore size but larger surface area. The 10:1 copolymer on the other hand consists of fewer pores which are of larger volume, consistent with a smaller surface area, but which have a greater pore size. At the other end of the scale, the 19:1 copolymer has a low surface area but with a large pore volume. We conclude that the 10:1 copolymer has pores least likely to be easily blocked compared to the other copolymers, and therefore can maximize the potential of available surface area within the pores better than the other copolymers.

Therefore, the 10:1 ratio BP:spiro chemicapacitor sensors were used in subsequent experiments. They were tested for their cross-sensitivity to other VOCs that may be found in the atmosphere. Fig. 9 summaries the change in capacitance per ppm of vapor chemical measured clearly showing the high sensitivity towards nitro-bearing compounds.

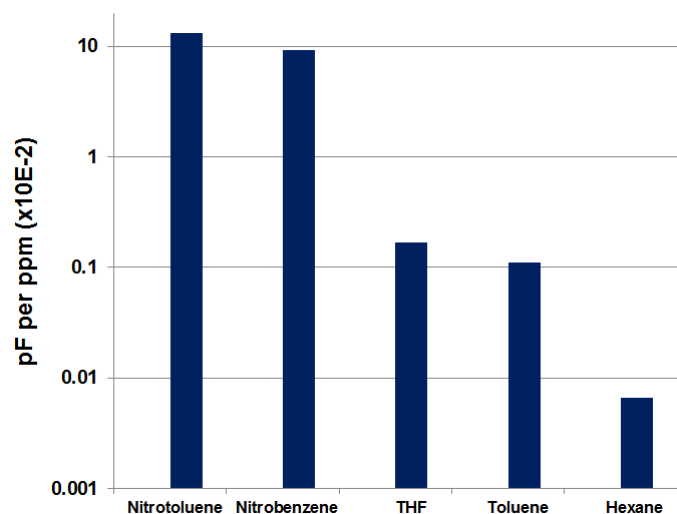


Fig. 9. Relative change in capacitance of copolymer BP:Sprio (10:1) sensor to different chemical vapors.

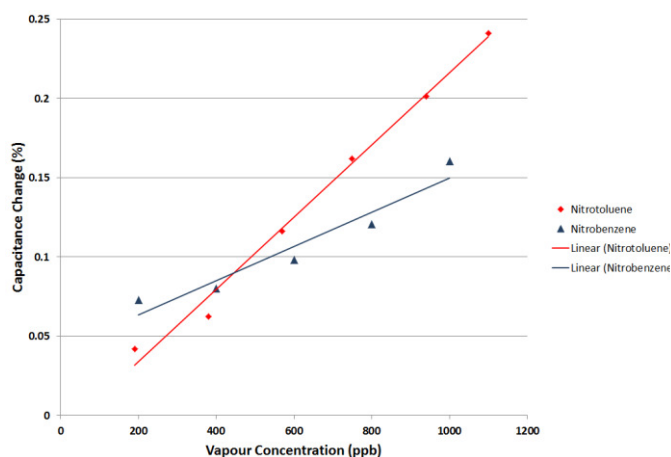


Fig. 10. Linear response of developed 10:1 BP:Sprio coated sensor to nitrotoluene and nitrobenzene vapors down to 200 ppb in room air.

The developed porous nitro-sensitive copolymers were then tested to determine a lower limit of sensitivity. These chemicapacitor sensors demonstrated a selective and reversible detection of nitrotoluene and nitrobenzene vapors to a concentration of around 200 ppb in room air (Fig. 10).

C. Evaluation of new sensor for peroxide vapors

Electropolymerization of the BE-ProDOT monomer of section IIC onto IDE chips was successfully undertaken to form peroxide vapor sensors. To generate peroxide vapors, urea-hydrogen peroxide adduct was obtained and placed in a Dreschel bottle with a flow of air through this powder. A flow of 50 ml/min of air through the urea-hydrogen peroxide powder generated a hydrogen peroxide (H_2O_2) concentration of 17 ppm measured on a PortaSens II hydrogen peroxide sensor (Analytical Technologies Inc). The test-bed was adapted to incorporate this H_2O_2 stream. Fig. 11 shows the response of a poly(BE-ProDOT) and a non-porous poly(Br-ProDOT) sensor to H_2O_2 vapor. Poly(Br-ProDOT) is not expected to have any sensitivity towards peroxide vapors and is therefore a suitable reference. In addition, air was bubbled through a sample of water to create a water rich vapor that was directed into the test chamber to gauge the sensitivity of the sensor to a large change of humidity only.

Fig. 11a shows the response of the peroxide sensor poly(BE-ProDOT) to this water vapor in relation to peroxide vapors and also to toluene (2700 ppm) used as a test VOC. Fig. 11b shows the corresponding changes in humidity within the test chamber during the course of the experiment. At a time of approximately 130 mins 2,700 ppm toluene vapor enters the test chamber and induces a small drop in the capacitance measurement on the H_2O_2 sensor (Fig. 11a) and very little change in the measured humidity in the chamber (Fig. 11b). Subsequently two on/off cycles of 17 ppm H_2O_2 vapor were directed into the test chamber resulting in two larger upwards changes in capacitance of the peroxide sensor and two sharp rises in response from the humidity sensor. A short time later at approximately 380 mins pure water vapor was injected into the test chamber which now caused a smaller fall in capacitance of the H_2O_2 sensor but another larger rise of the humidity sensor. Finally, two more on/off cycles of 17 ppm H_2O_2 vapor were directed into the test chamber and once more resulted in two large upwards changes in capacitance of the H_2O_2 sensor and two sharp rises in response from the humidity sensor.

However, throughout these experiments it was observed the prototype peroxide sensor was significantly more prone to long term drifts in signal compared to other developed sensors. The urea peroxide powder was untreated and significantly affected the humidity over the short and long term. As shown in Fig. 11b, air flow through either the urea-hydrogen peroxide powder or through the water sample induced a change in humidity in the test chamber, but the peroxide sensor shows a larger and reversed change to the H_2O_2 vapor. The response of the H_2O_2 sensor to 17 ppm H_2O_2

was also reversed and 8.8 times greater than that for 2,700 ppm toluene in air. This reversed behavior was also observed for vapors of hexane and acetone. The different response of the H_2O_2 sensor may be a method to distinguish H_2O_2 vapor from others. For sensors with problems of long term drift, algorithms have been employed to address this issue [21]. Future experiments will investigate this drift and attempt to minimize this effect. In addition, the developed peroxide sensor was expected to have poor or no reversibility, but from these experiments a reversibility of the response to peroxide of these sensors was also evident. The reversibility is hypothesized to be due to the boronic ester and hydrogen peroxide form an adduct that is reversible. However, as shown in Fig 11a the response to 17 ppm H_2O_2 can decrease for subsequent cycles which may be due to a slow or incomplete reversibility. Overall, this new polymer is a promising candidate for future development of a reusable microsensor for peroxide vapors.

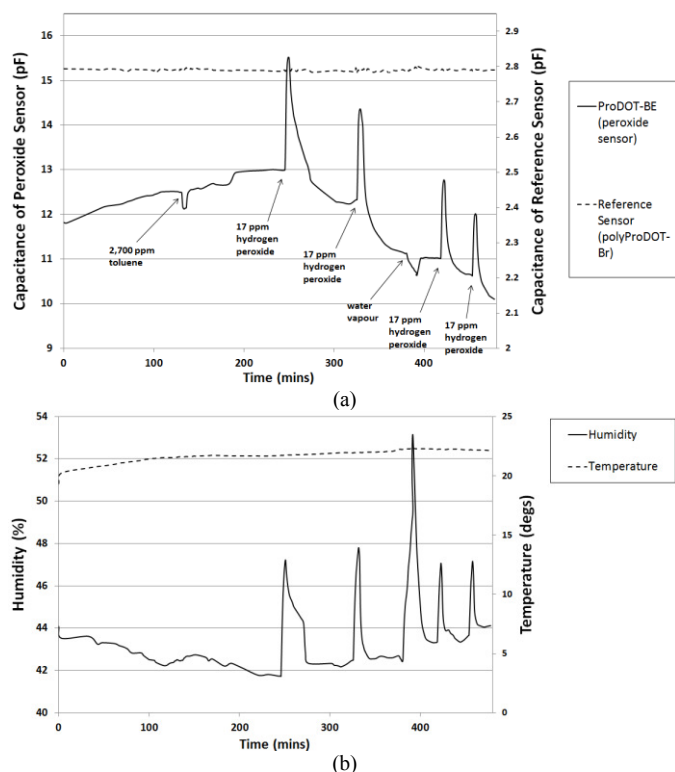


Fig. 11. (a) Sensor developed for hydrogen peroxide exposed to vapors containing toluene, hydrogen peroxide, and water. (b) Measured temperature and humidity in test chamber during experimental time period shown in Fig. 11a.

IV. CONCLUSION

We have investigated a route to the creation of miniature low-cost sensors targeting nitro and peroxide vapors released from compounds commonly found in home-made explosive devices. Novel polymers were synthesized that can be electrochemically grown via a one-step process onto mass produced IDEs. Such technology can be readily adapted to the

formation of numerous discrete sensors using photolithography/microfabrication on glass or silicon.

We have synthesized a novel BP:Spino copolymer sensor which demonstrates a greater sensitivity to nitro vapors than a previously used Br-ProDOT polymer sensor, whilst retaining the high selectivity and reversibility. It is theorized that the improvement in sensitivity is due to the change from a two dimensional film (with only the surface sensing sites) to a three dimensional matrix where we have a structure that has pores, and therefore has a greater number of sensing sites on the internal surfaces. Porosity measurements of the BP:Spino copolymers show an increase in overall porosity of the copolymers in relation to the Br-ProDOT only polymer. A ratio of 10:1 of Br-ProDOT to Spino composition was found to be the best balance between increased porosity and increased Br-ProDOT sensing units to achieve the best sensitivity.

A demonstration of sub-ppm sensitivity to nitro vapors was shown, and overall these results demonstrate promising materials for the construction of low-cost portable explosives sensors. We envisage that the sensitivity of our nitro sensors can be improved further by adding repeat units with enhanced redox activity (for example the molecule tetrathiafulvalene), by bespoke design of IDEs geometries (such as 3D arrays), and the use of dedicated on-chip readout circuitry. The introduction in recent years of $\Sigma\Delta$ capacitive to digital converters (CDCs) that are directly integrated with a chemicapacitor sensor has reduced the low frequency quantization noise introduced and improved the accuracy during the conversion process [22]. This technology offers a low-power, high-speed and high resolution method of sensor signal readout.

In addition, a novel electrochemically deposited polymer with enhanced affinity to peroxide vapors is reported for the first time. This polymer demonstrated good discrimination for peroxide vapor and general reversibility and thus forms the basis for the development of a future chemicapacitor sensor for peroxide vapors. It is anticipated that the peroxide sensor sensitivity can be moved from ppm to ppb concentrations by modifying the structure of the polymer to that of a highly porous polymer as was successfully achieved for the nitro sensor.

Furthermore, our technology can also be adapted to incorporate new target specific functional groups in our base polymers with minimal synthetic effort. Threat materials such as the explosive precursor materials ammonia and formaldehyde are gaining importance within the security community and there is scope for our sensors to be adapted to meet these challenges.

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