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Novel polymer materials for low-cost nitro vapor detection sensors

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Abstract— Current commercial sensors for explosive vapours are high cost bulky equipment not amenable to mass production and thus prevents their mass deployment within society. Our research objective is to create compact sensors that are not only portable but of such low cost that they can be installed in buildings in the same way as smoke detectors. We have developed novel polymers whose properties have been tailored to give them a higher affinity to target nitro group (NO₂) bearing molecules associated with explosives. The polymers have been grown electrochemically onto miniature interdigitated electrode platforms yielding miniature sensors. Novel porous polymers based sensors are demonstrated which yield a detection level of 200 ppb of nitro vapours and can be manufactured at low-unit-cost.

Keywords—explosives; nitro compounds; microsensor; nanoporous materials

I. INTRODUCTION

The threat of terrorist attacks involving latent explosive devices is ever-present, both domestically and internationally. High sensitivity detection of explosive compounds using low-cost, compact sensors is required to increase security for users of public transport and at public places which have open or easy access. For the detection of explosives either sniffer dogs or a developed technology is employed [1]. Sniffer dogs cost tens of thousands of dollars to train, a handler is required and they can only be deployed for a limited time. Alternatively, a range of developed technologies such as ion mobility, infra-red spectroscopy, fluorescent polymers, and colorimetric kits 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) again requires an operator and can only be used for a limited time (a few hours), as well as not amenable for mass-production and/or low-cost. The current sensitivity of this system is quoted as low ppm nitro vapours.

Our research objective is to create small sensors that are not only portable but of such low cost that they can be installed in a building like a smoke detector. The technology we are developing is based on capacitance measurements on polymer films (commonly known as chemicapacitors). The basic sensor platform is a metallic interdigitated electrodes

(IDEs) which can be mass produced at low cost. Upon the electrodes we can deposit a polymer whose properties can be tailored so that the electronic properties are modified in the presence of the target chemicals.

Organic semiconductor polymers can be tailored to attain specific chemical functionalities whilst capable of being deposited by the low-cost manufacturing route of electrochemistry [2]. Electrochemical deposition from a solution of monomers has several advantages over other methods such as photolithography and ink-jet printing. 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 wafer scale production. Thus chemicapacitors fabricated through electrochemical deposition is an enabling technology towards creating low cost microsensors that can be widely deployed throughout society.

The authors have previously developed miniature chemicapacitor sensors and demonstrated a sensitivity and selectivity to nitro-bearing compounds [3,4]. During the previous study, derivatives of 3,4-propylenedioxythiophene (ProDOT) and terthiophenes were synthesised in order to sense nitro-bearing compounds. The microsensors were based on novel brominated-ProDOT (BP) monomers which were then electrochemically grown on IDEs to form a polymer. A selective and reversible response to vapours 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 sizeable cross-sensitivity to a wide range of non-targeted compounds [5].

The sensors we developed previously demonstrated sensitivity to nitro-bearing compounds to a concentration of around 20 ppm. This first generation of synthesised polymers was essentially planar non-porous types. The aim of the present research is to investigate the synthesis of new copolymer materials with a more three dimensional topology with the potential of increasing the number of nitro detecting sites available to the atmosphere being tested, thus creating a more sensitive material and creating a sensor that will exhibit sub-ppm sensitivity in air.

II. EXPERIMENTAL

A. Synthesis of 3D nitro-sensitive polymers

Our previously reported material was a polymer of brominated-ProDOT (BP), which is a linear non-porous material. Here we synthesise novel copolymers of BP with a spiro centred (SC) comonomer containing a three dimensional porous scaffold to increase the number of nitro detecting sites available. Compared to an alternating polymer a random copolymer will require fewer synthetic steps, but may still provide the sensing capabilities required. Additionally, this method will allow for manipulation of pore size without the need to investigate polymers with different types of core structures.

Electropolymerisation of these materials onto the electrodes from their respective monomer solutions in dichloromethane was undertaken. 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. A series of electrochemically prepared random copolymers (mixtures of BP:Spino ratios 4:1, 6:1, 8:1, 10:1, 14:1 and 19:1 of the two monomers) were grown on ITO slides from their respective monomer solutions in dichloromethane using cyclic voltammetry. This was also performed for a BP only polymer which would act as a reference. An attempt was made with a copolymer of ratio of 2:1, however after only a few cycles of polymer growth the current response decreased rapidly until no current was measurable with further cycles, indicating that the resulting polymer was insulating. All the films were subsequently dedoped in a region with no redox activity.

B. Porosity measurement on BP:Spino polymers

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 120°C for 16 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.

C. Evaluation of polymers to vapour concentrations

These polymers were evaluated in a test-bed (described previously [3]) for their response to dynamic vapour concentrations containing target molecules and common VOCs (Fig. 1). The test-bed was modified to include air pumps and a third flowmeter F3 (1 L/min, FLDA3211G, Omega, UK) to subsequently dilute vapour streams to sub-

ppm levels as required. The chemicapacitor sensors were placed into a test chamber and changes in capacitance of the polymers was measured in the presence of varying concentrations of nitroaromatic compounds nitrobenzene and 2-nitrotoluene. These liquid chemicals were placed into a fritted-glass bubbler and an air flow stream controlled by flowmeter F1 (up to 250 ml/min) was bubbled through each sample to create a vapor flow for each chemical. A second flowmeter F2 (up to 250 ml/min) directed through a second bubbler containing VOCs (toluene, THF, hexane) commonly found in the atmosphere was used to test for cross-sensitivity to these VOCs.

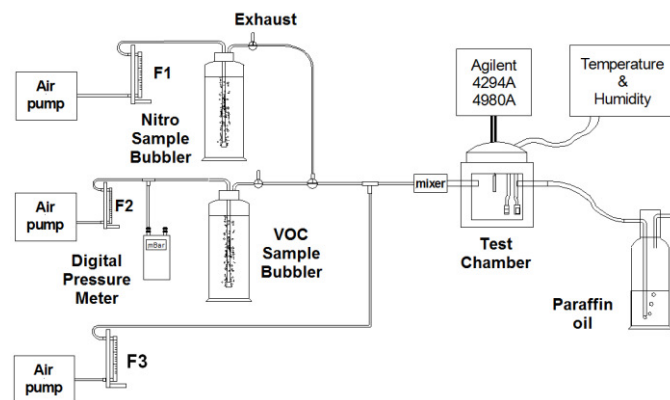


Fig. 1. Apparatus for creating a dynamic vapor flow. Flow controller F1 regulates the flow of nitro vapours, F2 controls the VOC vapour flow, and a pure air stream is controlled by F3 for dilution.

III. RESULTS

A. Porosity results

Table I shows the results of surface area and porosity measurements on the developed random copolymers. 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 BP only polymer, and 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 BP only polymer. The 4:1 copolymer has a vast increase in surface area in comparison to the BP only polymer, while only a small increase in pore volume and pore size was measured. The 10:1 copolymer does not have as great an increase in surface area over the BP only polymer; however it has a larger pore volume and much larger pore size. Meanwhile, the 19:1 copolymer has a low surface area with a pore volume similar to the 10:1 copolymer. A general trend can be observed in the varying ratios of the copolymer compositions. As the ratio moves from 4:1 to 19:1, the surface area decreases, while the pore volume initially shows an increase, with the 8:1 copolymer showing the greatest pore volume, which then decreased towards the 19:1 copolymer. A similar trend is observed for pore size, with an increase 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. 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. TABLE OF POROSITY VALUES MEASURED FOR VARYING COMPOSITION RATIO OF COPOLYMERS. 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 (BP)	0.2003	523.30	1.07	2.7
4:1 copolymer	0.0352	11580.16	9.97	5.3
6:1 copolymer	0.0702	5957.26	40.57	21.9
8:1 copolymer	0.0477	1822.42	46.02	13.8
10:1 copolymer	0.0625	862.47	34.84	86.7
14:1 copolymer	0.0503	267.01	36.65	2.2
19:1 copolymer	0.0445	503.09	32.48	5.4

B. Capacitance response of BP:Spiro copolymers to nitro vapours

The copolymers with monomer ratios of BP:Spiro ranging from 4:1 to 19:1 were individually grown electrochemically onto the IDE platforms supplied by Micrux Technologies Inc (Spain) to form a miniature chemicapacitor sensor (Fig. 2). Each IDE platform had 15 pairs of electrodes with an electrode gap of 10 μm . These sensors were placed in the test chamber and evaluated for their response to nitro bearing vapors.

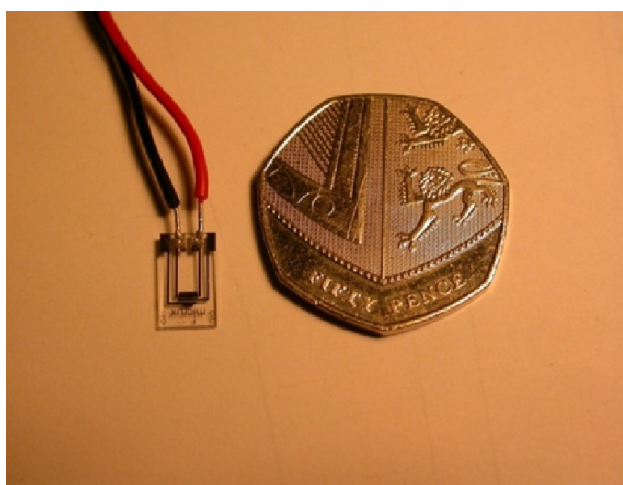


Fig. 2. Photograph showing the developed polymer electrochemically grown onto miniature electrodes.

Fig. 3 shows the average capacitance change for each copolymer for vapours of 83 ppm of nitrobenzene. The 10:1 copolymer was found to be the most sensitive to nitro-vapours. Whilst this polymer did not have the highest 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. These conclusions were consistent with observations of AFM images of the polymers. We conclude that the 10:1 copolymer has pores least likely to be easily blocked compared to the other copolymers, and therefore can maximise the potential of available surface area within the pores better than the other copolymers. Therefore, the 10:1 ratio BP:spiro was the polymer used in subsequent experiments.

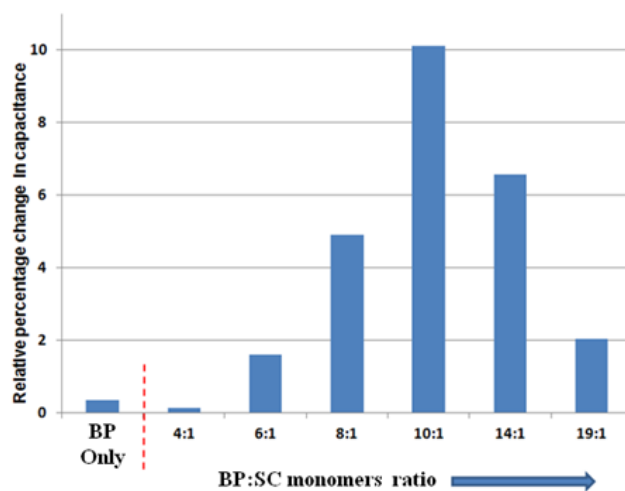


Fig. 3. Measured percentage capacitance response of polymers to nitrobenzene vapor for changing BP:Spiro ratio.

The developed porous nitro sensitive copolymers were tested to determine a lower limit of sensitivity. These chemicapacitor sensors demonstrated a selective and reversible detection of nitrotoluene and nitrobenzene vapours to a concentration of around 200 ppb in room air (Fig. 4).

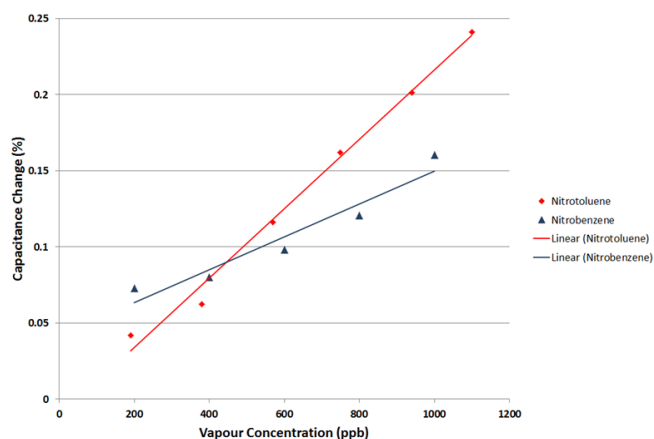


Fig. 4. Linear response of developed 10:1 Br-ProDOT:Spiro coated sensor to nitrotoluene and nitrobenzene vapours down to 200 ppb in room air.

IV. CONCLUSIONS

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

A demonstration of sub-ppm sensitivity to nitro vapours was shown, and overall these results demonstrate promising

materials for the construction of low-cost portable sensors. We envision 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 readout circuitry (capacitance to digital converter).

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 our sensors can be adapted to meet these challenges.

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