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Study of Poly(3-hexyltiophene) Polymer Sensing Properties in Nerve Agent Simulant (DMMP) Detection †

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Abstract: In the present work we report the use of regioregular poly(3-hexyltiophene) polymer (RR-P3HT) as a resistive sensor for the detection of chemical nerve agent simulant, dimethyl methylphosphonate (DMMP). The electrical response to DMMP vapour of RR-P3HT film deposited on ceramic (Al_2O_3) substrate in the room temperature was investigated. Results show that studied material is sensitive to DMMP trace amounts and selective against acetone and methanol. It also exhibits fast response and recovery times, repeatability and short-term stability.

Keywords: chemical sensor; DMMP; nerve agents; polymer; P3HT; semiconductor gas sensor

1. Introduction

Chemical warfare agents (CWA), especially nerve agents (e.g., sarin and soman) are highly lethal compounds. Sarin is one of the best-known chemical weapons of mass destruction. This odourless and colorless compuound causes neuromuscular paralysis and death by suffocation. Since they are used for military tests and against civilians, the development of fast CWA sensors with low detection limit has become an urgent issue. The studies are usually carried out using simulants, e.g., dimethyl methylphosphate (DMMP) that is non-toxic organophosphorus compound with a similar structure to sarin.

The effective medium for sensing organophosphates, can be conductive polymers e.g., polyaniline and P3HT [1–5]. Gas adsorption of electronoactive vapors (DMMP) causes electronic changes that come about in thin films of these polymers. Regioregular P3HT is of particular interest, because it posseses a large hole mobility. Moreover it exhibits strong photoconductivity [6], hence its sensing properties can be enhanced by the light. Öztürk et al presented sensitivity of P3HT to DMMP by quartz crystal microbalance method [5]. In this work we studied P3HT sensing properties in DMMP detection using resistance method.

2. Materials and Methods

2.1. Synthesis of P3HT Polymer

2,5-dibromo-3-hexylthiophene (>97%) (TCI Chemicals), t-butylmagnesium chloride (2M diethyl ether solution) (Sigma Aldrich) and [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (99%) (Acros Organics) were used as commercially available, without further purification. Anhydrous THF (99.9%) (Acros Organics) was distilled right prior to use. All reactions were conducted under dry nitrogen flow, in oven-dried glassware.

To synthesis hydrogen/bromine terminated regioregular poly(3-hexylthiophene) a McCullough GRIM method was used [7] with some modifications taken from De Girolamo et al. article [8]. Dry 100 mL three-necked flask equipped with septum, condenser (end-capped with a trap to seal the re action Lessel), gas capillary and magnetic dipole was flushed with nitrogen and charged via syringe with 2,5-dibromo-3-hexylthiophene (6.13 mmol, 2 g), anhydrous THF (21.5 mL) and t-butylmagnesium chloride (7.46 mmol, 3.7 mL). Reaction mixture was refluxed for 2 hrs followed by addition of Ni(dppp)Cl2 catalyst (0.0318 mmol, 0.0172 g) and refluxed for next 1 h. Crude polymer was precipitated by quenching reaction mixture in metanol, filtered and purified by sequential Soxhlet extraction with methanol, hexane and chloroform. Polymer fraction was isolated from the extract as described above, yielding 0.411 g (yield 41%) of dark green, brittle product.

3.2. Preparation of Sensing Layer

Thin layer of RR-P3Ht with dimensions 1.5 × 1.0 cm was deposited on the porous ceramic (Al_2O_3) substrate with interdigitated electrodes by spray coating method. The P3HT solution with approximately 1 mg/mL in chloroform was loaded into commercially available pistol-type airbrush with a nozzle size of 0.4 mm and sprayed onto substrate using synthetic air pressuse of 15 psi. The nozzle-to-substrate distance during all the process was 2 cm and deposition time was approximately 10 s.

3.3. Gas Detection Measurement

Fabricated sample was placed in a test chamber possessing inlet and outlet and electrical feedthrough. DMMP, acetone and methanol vapours were prepared from an Owlstone vapor generator (OVG-4), with certified permeation tubes. Synthetic dry air (~5% relative humidity, Air Liquide) was applied as a carrier gas. Humidity of flowing air was controlled and measured with Owlstone Water Vapor Generator OHG-4. Resistance of samples was monitored with Agilent Multimeter type 34401a. Sensing properties were investigated at room temperature and under white room light with two maximums in the spectrum (540 nm and 610 nm).

3. Results and Discussion

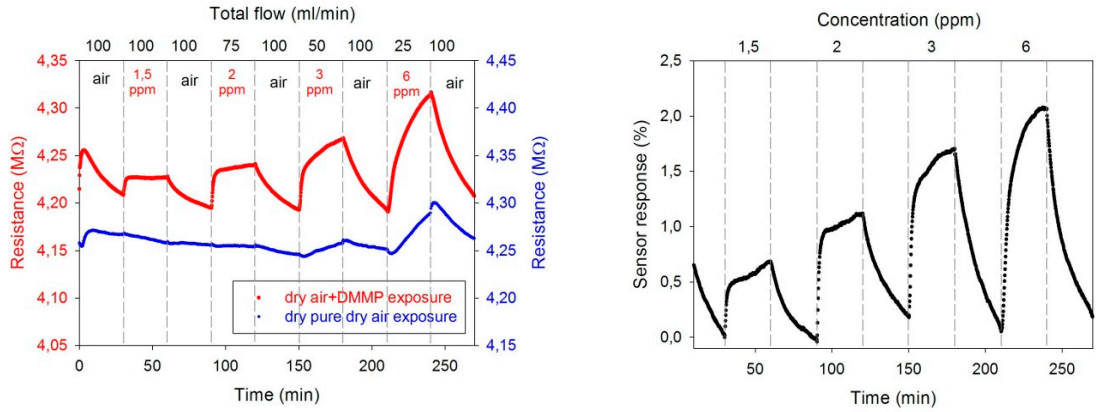
3.1. Sensing Properties

Figure 1a presents electrical response of studied sensor to the DMMP/air mixture and to the pure air. Concentration of DMMP vapour was regulated by changing total flow rate according to the following formula:

$$c = \frac{22.4 q_D}{MQ} \quad (1)$$

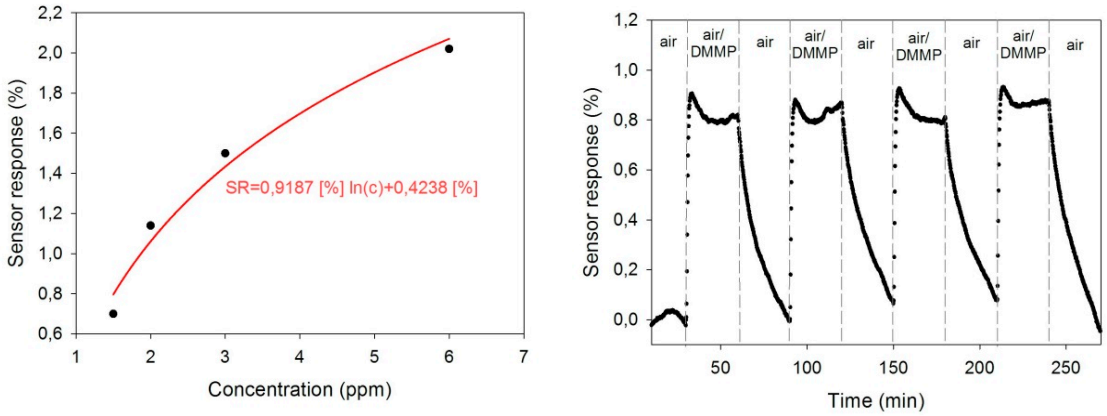
where c is DMMP concentration (ppm), q_D—permeation rate (747 ng/min), M—DMMP molar mass (M = 124.08 g/mol) and Q is a flow rate (mL/min).

Air flow rate during regeneration cycles was constant (100 mL/min). It can be observed that investigated sample exhibits dependence of resistance on the air flow rate. However, its electrical response to DMMP vapour is significantly higher than to the pure air. It can be seen at the Figure 1b, which shows the sensor response (SR) obtained from the difference between resistance in the presence of DMMP vapour and in the pure air. The dependence of sensor response on DMMP concentration (c) is depicted at the Figure 2a. Limit of detection (LOD) can be estimated from the interpolated curve. Considering 0.5% as the lowest detectable SR, we obtain 1.1 ppm. Figure 2b presents repeatability and short-term stability of the sensor under exposition to the 2 ppm of DMMP. The studied material was found to be highly selective against other organic vapours, like methanol and acetone. The response of the sensor to 6 ppm of DMMP, acetone and methanol is depicted at the Figure 3.



(**a**) (**b**)

Figure 1. (**a**) Electrical response of studied sensor to the DMMP/air mixture (red curve) and to the pure air (blue curve), (**b**) Sensor response to the different concentrations of DMMP.



(**a**) (**b**)

Figure 2. (**a**) Dependence of the sensor response (SR) on the DMMP concentration (**c**), (**b**) Sensor response to the constant concentration (2 ppm) of DMMP.

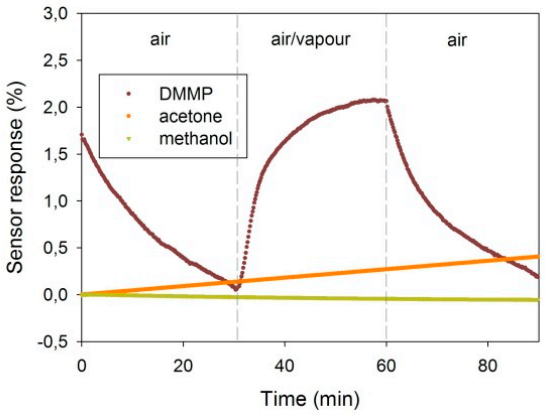


Figure 3. Sensor response to 6 ppm of DMMP, acetone and methanol vapours.

3.2. Sensing Mechanism

P3HT contains delocalized π bonds, which permit the easy flow of electrons within the delocalized π system. The relative response of P3HT to analyte species depends on their Lewis acidity or basicity: stronger acids or bases have a larger effect on polymer resistance, with acids decreasing resistance and bases increasing resistance. For DMMP, there is a phosphorous oxygen double bond. The electronegativity of the oxygen atom is stronger than that of the phosphorus atom, resulting in the increase of the electron density of the oxygen, so DMMP shows alkalescence. The p-type semiconducting behavior of P3HT promotes holes in the valence band of P3HT which play a key role in sensing properties. The DMMP is a strong electron donor which depletes holes from the valence band of P3HT, resulting in an increase in resistance after being adsorbed on the P3HT surface.

3. Conclusions

In summary, we investigated regioregular poly(3-hexyltiophene) photoconductive polymer as a potential material for sarin simulant DMMP detection by resistive method. The studied thin layer of RR-P3HT exhibited sensitivity to trace amounts of DMMP in the room temperature. The estimated limit of detection is 1.1 ppm. Investigated sensor reveals fast response and recovery times for low concentrations, as well as repeatability and short-term stability. The electrical responses of RR-P3HT to other organic vapours were also studied and the material was found to be highly selective against acetone and methanol.

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