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Flexible carbon nanotube sensors for nerve agent simulants

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Abstract
Chemiresistor-based vapour sensors made from network films of single-walled carbon nanotube (SWNT) bundles on flexible plastic substrates (polyethylene terephthalate, PET) can be used to detect chemical warfare agent simulants for the nerve agents Sarin (diisopropyl methylphosphonate, DIMP) and Soman (dimethyl methylphosphonate, DMMP). Large, reproducible resistance changes (75–150%), are observed upon exposure to DIMP or DMMP vapours, and concentrations as low as 25 ppm can be detected. Robust sensor response to simulant vapours is observed even in the presence of large equilibrium concentrations of interferent vapours commonly found in battle-space environments, such as hexane, xylene and water (10 000 ppm each), suggesting that both DIMP and DMMP vapours are capable of selectively displacing other vapours from the walls of the SWNTs. Response to these interferent vapours can be effectively filtered out by using a 2 μm thick barrier film of the chemoselective polymer polyisobutylene (PIB) on the SWNT surface. These network films are composed of a 1–2 μm thick non-woven mesh of SWNT bundles (15–30 nm diameter), whose sensor response is qualitatively and quantitatively different from previous studies on individual SWNTs, or a network of individual SWNTs, suggesting that vapour sorption at interbundle sites could be playing an important role. This study also shows that the line patterning method used in device fabrication to obtain any desired pattern of films of SWNTs on flexible substrates can be used to rapidly screen simulants at high concentrations before developing more complicated sensor systems.

(Some figures in this article are in colour only in the electronic version)

M Supplementary data files are available from stacks.iop.org/Nano/17/4123

1. Introduction

We describe the use of network films of single-walled carbon nanotube (SWNT) bundles on flexible substrates such as polyethylene terephthalate (PET) [1] to detect diisopropyl methylphosphonate (DIMP) and dimethyl methylphosphonate (DMMP), simulants for the G series nerve agents Soman and Sarin, respectively. The G-series nerve agents have strong electrophilic phosphorus, sulfur, or nitrogen centres [2], and are among the most toxic chemical warfare agents (CWAs) known. Nerve agents act by first binding with, and then irreversibly inhibiting, acetyl cholinesterase (AChE) and producing a toxic accumulation of acetylcholine (ACh), resulting in symptoms ranging from nausea and dizziness to death. Current methods to detect nerve agents include surface acoustic wave (SAW) sensors [3], conducting polymer arrays [4], vector machines [5], and colour change paper sensors [6].

Carbon nanotubes were first used for organic vapour sensing as chemiresistors, where resistance changes in nanotubes were monitored continuously with time upon exposure to vapours [7]. These studies have now been extended

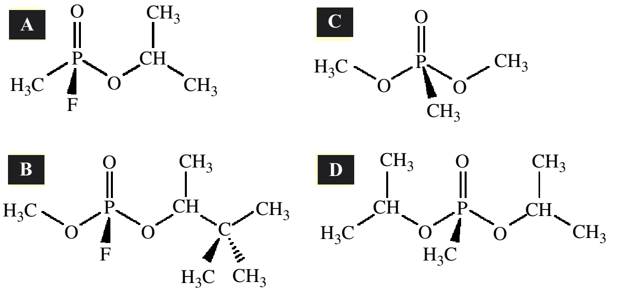

Figure 1. Chemical structures of the nerve agents (A) Sarin and (B) Soman, and their simulants: (C) dimethyl methylphosphonate (DMMP) and (D) diisopropyl methylphosphonate (DIMP).

to include a larger diversity of organic vapours, including nerve agent simulants [8]. In a recent study, network films of *individual SWNTs*, grown by chemical vapour deposition (CVD) on a silicon substrate, were shown to function simultaneously as a chemiresistor and a chemicapacitor, in which the conductance/capacitance ratio could be used as a new analytical vector to aid in molecular identification [9]. In contrast, we have recently described a chemiresistor using network films of *bundles of SWNTs* (20–30 nm diameter) on flexible PET substrates for organic vapour sensing, in which the magnitude of the sensor response was found to correlate to a specific solvent polarity scale (E_T30 scale) of the vapours used [1]. In this study, we extend the use of these network films to detect DIMP and DMMP. These SWNT/PET films can be readily synthesized using line patterning, which is a simple and rapid room temperature method (involving no lithography or printing), to obtain any desired pattern of SWNT films from aqueous surfactant supported dispersions of SWNTs on flexible substrates like plastic, paper, cloth, etc [10]. While the method has many advantages, it is important to point out that device resolution is limited to what can be achieved using a conventional commercial laser printer (20 μm). This study, therefore, is an attempt to demonstrate the generality of the phenomenon of simulant sensing using these flexible SWNT-based sensors, and not an attempt to optimize device fabrication to drive down detection limits (ppb levels).

2. Experimental details

2.1. Materials

Diisopropyl methylphosphonate (DIMP) was purchased from Alfa-Aesar and dimethyl methylphosphonate (DMMP) from Sigma-Aldrich, and used without further purification. Chemically purified HiPco SWNT bundles (Bucky Pearls) were purchased from Carbon Nanotechnologies Inc. Polymer-free carbon nanotube fibres are spun from aqueous dispersions using a flocculation-based process described previously [11]. These fibres are 1–2 inches long and 10–50 μm in diameter, composed of well resolved 10–20 nm diameter SWNT bundles.

2.2. Instruments and electrical measurements

Surfactant-supported dispersions of 20–30 nm diameter bundles of HiPco SWNT were used to obtain films on PET substrates in 'four-probe patterns' using our previously described line patterning method [1]. Electrical contacts were made by inserting four-pin SIP sockets at the top of the four-probe patterned SWNT/PET sensor and soldering copper wire to them. Prior to vapour sensing, all sensors were checked for I/V linearity in the current range -10 to $+10$ μA. A Keithley 2000 multimeter, interfaced with LabView 6.0 software, was employed to measure the percentage change in resistance ($\%\Delta R/R$) upon exposure to simulant vapours and also during the pump down cycle. A Keithley 4200 SCS system was also used to source a current through the outer leads (consistent with the resistance range of the sensor), while simultaneously measuring the voltage across the inner leads. For Raman spectroscopy, a Jobin Yvon LabRam HR800 Raman microscope equipped with a He:Ne laser ($\lambda = 632.8$ nm) was used.

2.3. Experimental procedure

All experiments were carried out at room temperature, with five sensors being tested simultaneously. Additional details on the construction of the sensor chamber are described in our previous study. Prior to the injection of DIMP or DMMP, the sensor chamber was evacuated for 10 min using a vacuum pump (10^{-5} Torr). Under vigorous magnetic stirring, a known amount of liquid DIMP or DMMP was then injected into the chamber and the % $\Delta R/R$ monitored continuously with time for 20 min, followed by a 10 min pump down cycle. For each simulant, resistance changes for a minimum of three vapour exposure/evacuation cycles were monitored, and the average % $\Delta R/R$ values employed in all subsequent analyses. Resistance measurements on polymer-free SWNT fibres were carried out by placing an individual fibre across a four-pin SIP socket and silver paste to ensure connectivity.

In situ Raman spectra on an SWNT fibre were obtained by first attaching the fibre to the underside of a plastic dish with epoxy resin and placing the fibre in the path of the laser beam. A drop of DMMP was placed on top of the fibre and the Raman spectrum was obtained.

3. Results and discussion

The chemical formula of the simulants DIMP and DMMP, and their corresponding nerve agents Soman (methylphosphonofluoridic acid) and Sarin (1,2,2-trimethylpropyl ester), respectively, are shown in figure 1. When 87 μl DIMP, equivalent to 10 000 ppm, is injected into the chamber, the resistance of the SWNT/PET sensor increases significantly over a period of 20 min, corresponding to a 172% change in $\Delta R/R$ (figure 2). The corresponding change in the $\Delta R/R$ value for DMMP is 66%. The sensor response is reversible, with resistance falling sharply when the simulants are evacuated from the chamber over a period of 10 min. A robust, reproducible sensor response is also observed at lower vapour concentrations with detection limit in the 25–50 ppm range, corresponding to a 5–8% change in $\Delta R/R$ values (figure 2, insets). The sensor response is reproducible over multiple vapour exposure/evacuation cycles, and individual sensors can be used interchangeably between DIMP and DMMP. Although simulants were injected at a concentration of 10 000 ppm in order to compare the sensor response with organic vapours tested previously [1], it is

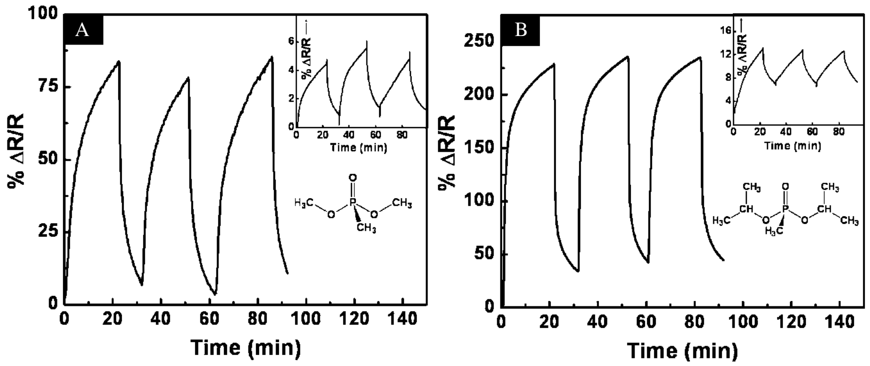

Figure 2. SWNT/PET sensor response to simulants at saturated vapour pressure (injection volume 10 000 ppm): (A) DMMP at 1620 ppm; (B) DIMP at 299 ppm. Insets: injection volume at 10 ppm.

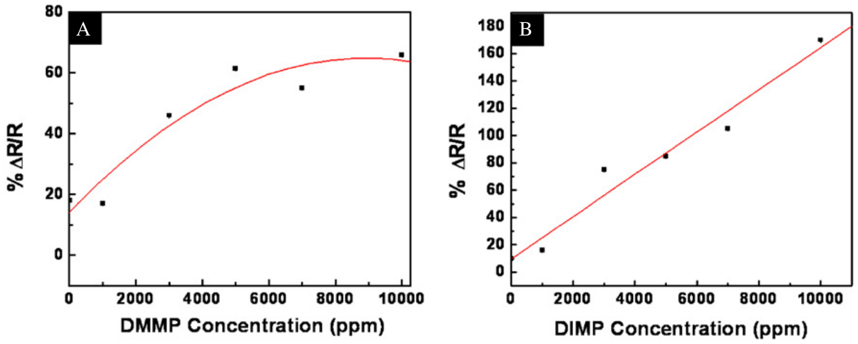

Figure 3. Response of SWNT/PET sensors to (A) DMMP and (B) DIMP at different concentration volumes.

important to point out that both DIMP and DMMP have low vapour pressures, and vapour concentration in the chamber is significantly below 10 000 ppm, e.g., 299 ppm for DIMP, and 1620 ppm for DMMP (at 25 °C) [9]. Although excess simulant in the chamber would be present in liquid form and is not expected to contribute to sensor response, an anomalous concentration response is observed for both DMMP and DIMP.

For example, the profile of sensor response as a function of injection concentration for DMMP plateaus at 5000 ppm, which is significantly higher than its saturated vapour concentration of 1620 ppm. For DIMP, the effect is even more pronounced, with no observable plateau even at 10 000 ppm (figure 3). The vapour concentration of DIMP in the chamber cannot exceed 299 ppm, and yet the sensor response is proportional to the volume of liquid DIMP injected into the chamber. A pseudo-linear concentration profile emerges, with higher injection concentrations yielding plots having a higher slope and larger magnitude of % $\Delta R/R$ values. These results are consistent with non-equilibrium conditions present in the chamber, where sensor response is under kinetic control. For example, vapour exposure time is limited to 20 min, which is not sufficient to ensure vapour–tube equilibrium, and response is driven by the kinetics of vapour sorption on the SWNT surface. A similar anomalously high response for DMMP has been observed in a carbon-based sensor, which is attributed to the higher partition coefficient of DMMP in the carbon film [4]. While both simulants display enhanced physisorption on the walls of the SWNTs compared to common organic vapours, the larger sensor response for DIMP is consistent with strong hydrophobic interactions between the isopropyl group and the SWNT surface. When sensor response to DMMP was carried out under equilibrium conditions, e.g. by extending the vapour exposure time to ~6 h, the $\Delta R/R$ values approach a plateau value of ~110%, regardless of the initial injection volume (see the supporting information available at stacks.iop.org/Nano/17/4123).

Sensor function is robust even when the SWNT/PET sensor is bent all the way to a crease (figure 4), which is consistent with results observed previously for common organic vapours [1]. For example, while there was only an 8% loss in % $\Delta R/R$ for DIMP when the sensor was bent to a crease, there was almost no change in the case of DMMP. The larger magnitude of loss of % $\Delta R/R$ in the case of DIMP could be related to its higher affinity to interbundle sites, which might be expected to be more sensitive to mechanical stresses associated with creasing. The precise mechanisms associated with strong electrical continuity across a crease in SWNT/PET coatings are still unclear, although we postulate that there could be an underlying layer of smaller diameter SWNTs, or individual SWNTs (debundled during the sonication step), between the PET substrate and the SWNT bundles that could help prevent discontinuities in the SWNT film from forming when the device is bent.

The recovery of the resistance values to pre-exposure baseline levels during the pump-down cycle is consistent with facile simulant desorption from the SWNT walls (physisorption) and the absence of strong chemical bond formation between simulant vapours and SWNTs (chemisorption). In

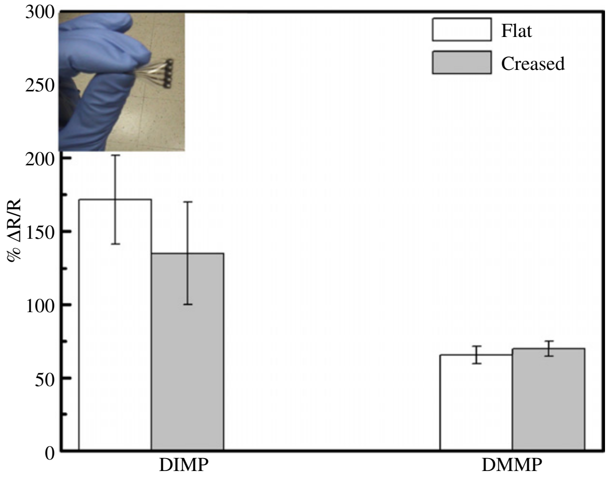

Figure 4. Sensor response of flat (bending angle 180°) and creased (clasped with a paper clip with a bending angle ∼5°) SWNT/PET device when exposed to simulant vapours at saturated vapour concentrations. Inset: optical image of sensor when bent to a crease.

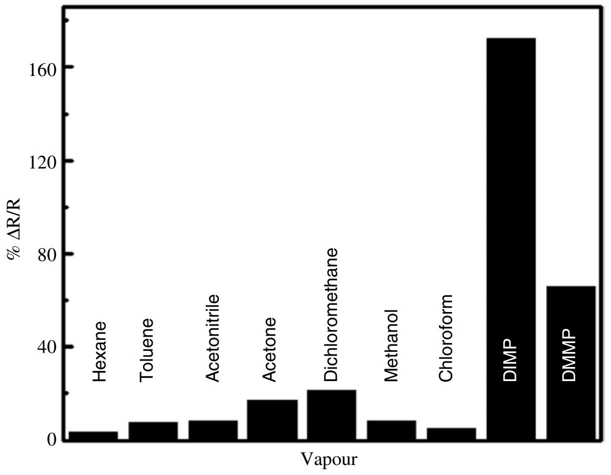

Figure 5. Sensor response of SWNT/PET device to common organic solvent vapours and DIMP and DMMP under saturated vapour conditions.

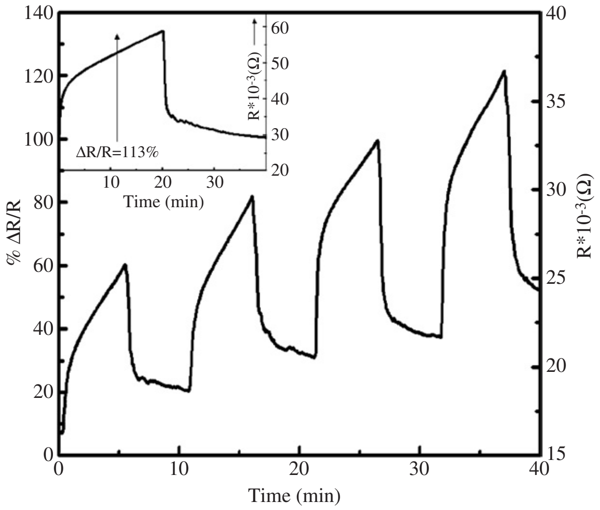

Figure 6. Sensor response of SWNT/PET device to DMMP saturated vapour (1620 ppm at 21°C) under ambient laboratory conditions. Exposure and evacuation cycles 5 min. Inset: exposure and evacuation cycles 20 min.

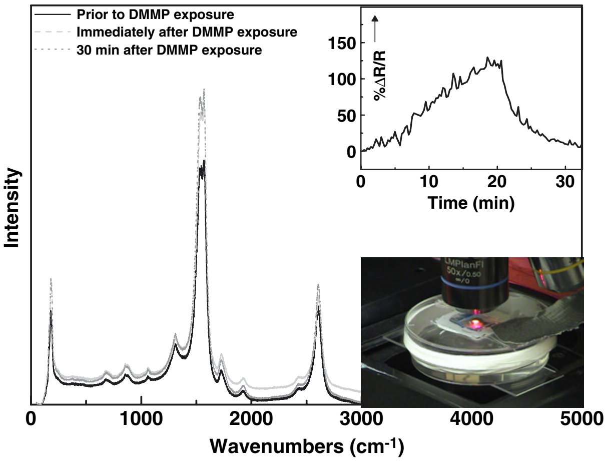

Figure 7. *In situ* Raman spectra of single SWNT native fibre (dark line), fibre immediately after exposure to DMMP (dashed line), and after 30 min exposure to DMMP (dotted line). Insets: sensor response of single fibre (top), and optical image of Raman set-up (bottom).

addition, the magnitude of the response is significantly larger in these films composed of a network of SWNT bundles, individual SWNTs, or even films composed of a network of individual SWNTs [9]. The heightened sensor response to DIMP and DMMP vapours (80–150%) indicates that simulant sorption is fundamentally different from common organic vapours tested previously (figure 5) [1]. In addition, the previously observed correlation between sensor response and solvent polarity (E_T30 scale) for common organic vapours does not hold true in the case of DIMP or DMMP. Among a wide variety of sites available for vapour sorption, such as tube surface, tube ends, interstitial sites, defect sites, etc, we believe that low vapour pressure analytes such as DIMP and DMMP could preferentially adsorb at sites whose microenvironment significantly affects electron transport through the SWNT film [12]. Our working hypothesis is that these sites are regions where SWNT bundles cross one another (interbundle sites), and physisorption of simulant vapours directly at these sites, or migration to these sites from other sites, can increase interbundle distance, and consequently the resistance of the film. Since electron transport through a network film is extremely sensitive to the density of interbundle contacts (network percolation), adsorption of DIMP and DMMP at these sites is expected to have a significant effect.

Network films of SWNT/PET can also sense DIMP and DMMP in the presence of other interferent vapours. For example, figure 6 shows the sensor response to a saturated vapour concentration of DMMP in air under ambient conditions. A glass jar containing excess DMMP (10 ml) at the bottom was raised and lowered to a fixed SWNT/PET sensor to simulate a vapour exposure/removal effect. Unlike the previous experiments, the sensor chamber was not pumped

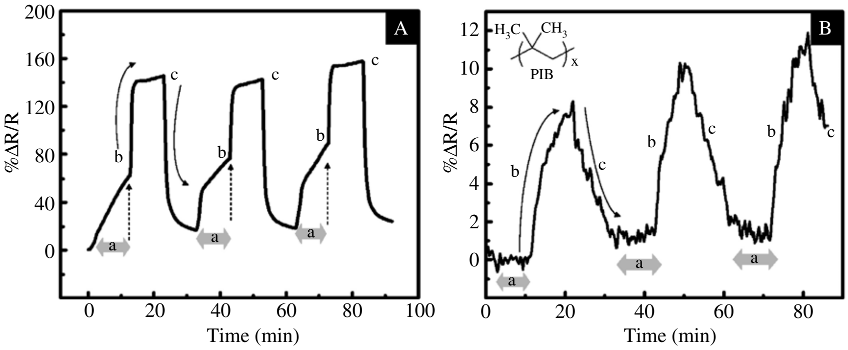

Figure 8. Mixed interferent sensor response of SWNT/PET device to DIMP in the presence of 10 000 ppm each of water, hexane and xylene introduced at 'a'. DIMP introduced at 'b', and chamber evacuated at 'c'. (A) Uncoated sensor, and (B) sensor coated with a 2 μm film of polyisobutylene.

down to evacuate the DMMP. The strong sensor response observed ($\Delta R/R$ 65%) shows that laboratory air, humidity, etc, do not interfere significantly with sensor function. The upward sloping baseline could be due to slow desorption of the DMMP from the SWNT film when the glass jar is lowered (chamber not evacuated). The relative humidity under ambient laboratory conditions could also be playing a role in the response drift. When the glass jar is lowered for a sufficient amount of time to ensure complete desorption, however, the resistance falls to the original baseline value (figure 6, inset).

In order to rule out contributions to sensor response from reversible swelling of the PET substrate upon exposure to organic vapours [1], we exposed a single fibre composed of SWNT bundles (no substrate) to DIMP, and observed a large increase in resistance ($\Delta R/R = 200\%$). In addition, there is no significant change in the radial breathing mode or the G-line of the Raman spectrum of the single fibre [13] upon exposure to DIMP, which suggests that sensor response is not influenced by vapour-tube electronic effects, such as vapour-induced doping/dedoping effects on SWNTs (figure 7).

In addition to air, humidity, etc, network films of SWNT/PET can detect simulant vapours in the presence of large quantities of interferent vapours commonly found in field applications, such as hexanes and xylenes, constituents of gasoline and diesel fuel, respectively. In a sequential interferent vapour experiment, SWNT/PET films were first exposed to 10 000 ppm each of water, hexane and xylene followed by DIMP under saturated vapour conditions (299 ppm). A robust sensor response was observed in spite of 30 000 ppm of total interferent vapours. Importantly, in a mixed interferent experiment, SWNT/PET was first exposed to a mixture of 10 000 ppm each of water, hexane and xylene, and then to DIMP. The resistance increases initially by 45% when exposed to a mixture of water, hexane and xylene, followed by a sharp increase to 200% upon exposure to DIMP (figure 8(a)). The results show that DIMP–tube interactions are strong enough to even displace interferent vapours from the SWNT surface, which could be leveraged to advantage in field applications.

In an effort to improve the selectivity of SWNT/PET films to simulants in the presence of large amounts of interferent vapours, a wide range of polymer coatings were screened for chemoselectivity. A 2 μm thick film of polyisobutylene (PIB) spin-coated on the SWNT sensor provided an effective barrier coating. For example, in the mixed interferent experiment mentioned above, the PIB-coated sensor could completely screen out 30 000 ppm of interferent vapours, while still being able to detect DIMP (at 299 ppm). Although the magnitude of the sensor response is significantly lowered in the PIB-coated sensor, to 11% (from 200% for the uncoated sensor), reproducible resistance changes are observed even under these severely stressed conditions (figure 8(b)). The response drift could be due, in part, to relative humidity under ambient conditions (similar to DMMP described in figure 6).

In summary, we demonstrate for the first time (i) the extension of our recent study on organic vapour detection using flexible SWNT films on plastics to detect organophosphorus-based chemical warfare agent simulants, (ii) an unusually strong resistance change in SWNT bundles when exposed to CWA simulant vapours, even under ambient conditions, (iii) a robust sensor response to CWA simulants in the presence of large amounts (30 000 ppm) of interferent vapours commonly found in battle-space and urban air environments, and (iv) the use of polyisobutylene as a barrier coating polymer that can screen out high concentrations of interferent vapour signatures. While significant challenges remain in optimizing sensor performance with regard to tunability, stability, detection limit, elimination of false positives, etc, these findings open new opportunities in the design of real-time CWA sensors with independent response signatures.

Acknowledgments

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