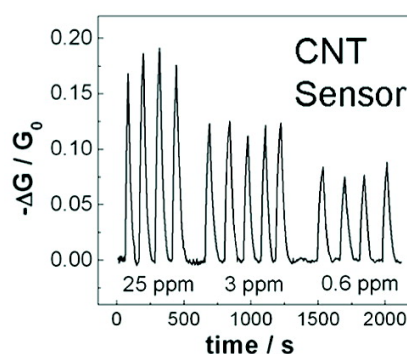
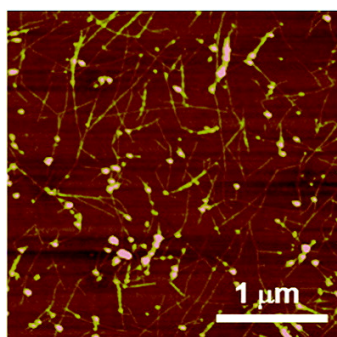


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Carbon Nanotube/Polythiophene Chemiresistive Sensors for Chemical Warfare Agents

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New generations of low power, low cost, and portable sensing devices are needed for homeland security and monitoring of agriculture, medical, and manufacturing environments. A leading candidate is the chemiresistor: a chemical sensor based on the simple change in resistance in response to the binding of analytes. Advantages of chemiresistors include low power consumption and the ease of high precision resistance measurements. Several materials have been utilized as gas sensors, including metal oxides, organic semiconductors, and carbon nanotubes. Metal oxides are the most widely used materials for chemiresistors.¹ Despite their sensitivity, the applications of these materials have been limited by high power consumption and poor selectivity. Organic semiconductors, especially conjugated polymers, have long been considered as chemiresistor materials.² The integration of molecular recognition into their structures is attractive; however, these materials are limited by electrostatic/dielectric interferences and fragile organic metal interfaces.

Carbon nanotube (CNT) field effect transistors have been studied as chemical³ and biological⁴ sensors. They are sensitive because their resistance can change drastically in the presence of analytes via charge transfer (doping), carrier pinning, and/or modification of the Schottky barrier at the nanotube/metal contact. However, their applications have largely been limited by the complexity associated with device fabrication. Recently, chemiresistors based on polymer/CNT systems have been reported.^{3c,d,5} In these cases, polymers are deposited onto single CNT devices^{5b} or prepatterned CNT networks.^{3c,d,5a} The polymer coatings generally provide increased selectivity but have not simplified the fabrication process. We report herein that CNTs dispersed with a hexafluoroisopropanol functionalized polythiophene produce highly sensitive and selective chemiresistor sensors using a greatly simplified fabrication process.

Figure 1a shows the schematic of our simple sensor structure. Stable dispersions of single-walled CNTs (SWCNTs) were prepared by sonication in the presence 50 wt % of a hexafluoroisopropanol substituted polythiophene (HFIP-PT) or poly(3-hexylthiophene) (P3HT). Polymer/SWCNT films (50 nm thick) were spin-coated from 0.2 wt % solutions (THF for HFIP-PT and CHCl₃ for P3HT) on to a glass substrate, and two gold strip electrodes (50 nm thick) were then sputter-coated on to the film. The resistance of HFIP-PT/SWCNT devices ranges from 0.5 to 1.5 MΩ. The quality of the dispersions is very important and ensures that the CNTs form a percolative network of largely individual tubes. The AFM image in Figure 1b shows that the CNTs are well debundled and dispersed by HFIP-PT. The relative low intensity of the (10, 2) radial breathing mode (RBM) at 264 cm⁻¹ of HFIP-PT/SWCNT (red) compared with that of bare SWCNT (black) in Figure 1c further demonstrates the decrease of the SWCNT bundles when dispersed by HFIP-PT.⁶

We choose to attach the HFIP group to polythiophene because of its H-binding with phosphate esters that are common to a

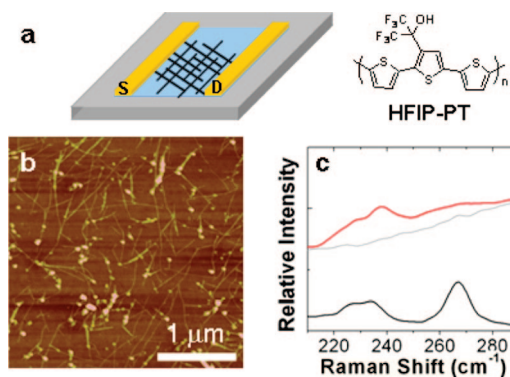


Figure 1. (a) Schematic view of the device consisting of a percolative network of carbon nanotubes between two gold electrodes deposited by casting a HFIP-PT stabilized dispersion. Source-drain dimension is 5 mm × 5 mm. (b) AFM image of a SWCNT network drop cast from 0.02 wt % solutions (CNT $d = 1.5 \pm 0.4$ nm). (c) Raman spectra of RBMs of SWCNTs from THF suspensions sonicated for 2 h with (red curve) and without (black curve) HFIP-PT. The gray curve is a HFIP-PT solution in THF without SWCNTs. Excitation wavelength = 785 nm.

number of chemical warfare agents, including sarin gas.^{3d,7} As a result of the similar hydrogen bonding characteristics and vapor pressure (160 Pa at 25 °C) of dimethyl methylphosphonate (DMMP) to chemical warfare agents, we have focused our present measurements on this less toxic simulant.

The sensory response investigated is a conductance measurement between the two electrodes at a constant bias voltage (0.1 V). Chemiresistors based on an HFIP-PT/SWCNT hybrid system were shown to be highly sensitive and selective for DMMP. As shown in Figure 2a, the sensor response is fast and reproducible even at low analyte concentrations. For instance, it gives an 8% conductance change upon exposure to 0.6 ppm of DMMP. A conductance change of 1% was observed in response to 0.05 ppm DMMP, which qualifies the sensor a parts per billion level sensing. Moreover, the sensor displays a linear logarithmic response to analyte concentration over 2 decades of concentration (Figure 2b). Figure 2c shows a comparison of the selectivity and sensitivity for SWCNTs deposited from HFIP-PT, P3HT stabilized dispersions, and nonstabilized dispersions. The selectivity is excellent considering that the equilibrium vapor pressure of methanol (167 000 ppm) is more than 100 times that of DMMP (1600 ppm). Moreover, the H-binding ability of HFIP-PT/SWCNTs has greatly increased the response and selectivity for DMMP, as compared to P3HT/SWCNTs and bare SWCNTs. The enhancement due to the HFIP-PT is most impressive at low analyte concentrations. At equilibrium vapor pressures of DMMP, the HFIP-PT/SWCNT sensor has only ~40% larger response than the P3HT/SWCNT, whereas at 1 ppm of DMMP HFIP/SWCNT is 9 times more sensitive.

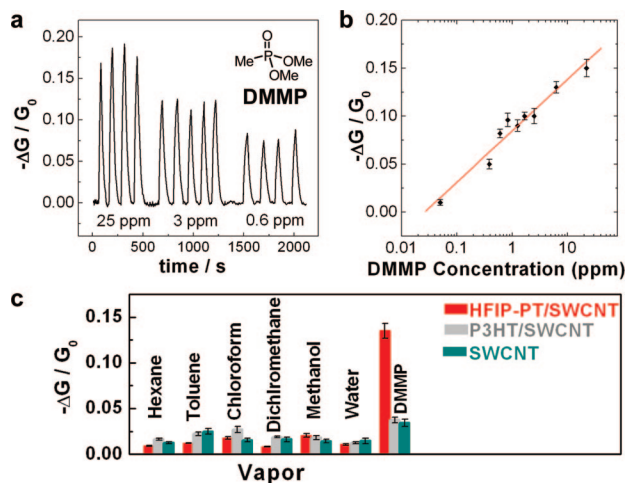


Figure 2. (a) Conductance change ($-\Delta G/G_0$) of the sensor upon exposure to varying concentrations of DMMP. The bias voltage is fixed at 0.1 V, and the temperature is 70 °C. (b) Calibration curve of the sensor at DMMP concentration of 0.05–25 ppm. (c) Conductance change of the SWCNT sensors in response to common organic solvents and DMMP diluted to 1% of saturated vapor conditions at room temperature, with a bias voltage fixed at 0.1 V.

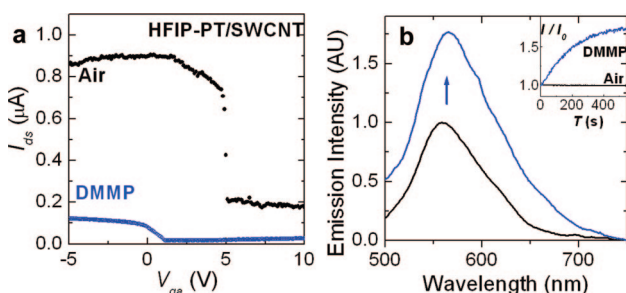


Figure 3. (a) The source-drain current versus gate voltage of the sensor under air and saturated DMMP vapors ($V_{SD} = 1$ mV). The gate voltage was scanned from 10 to -5 V. (b) Emission intensity ($\lambda_{ex} = 450$ nm) of HFIP-PT/SWCNT film in air (black) and after 10 min exposure to saturated DMMP vapors (blue).

To explore the mechanism of the DMMP response in our HFIP-PT/SWCNT sensors, we first performed sensory studies in a field effect transistor architecture (see Supporting Information for device structure). As shown in Figure 3a, the source-drain current I_{ds} increases with more negative gate voltages saturating at ~ 5 V V_g , indicating a p-type behavior, although the outputs do not resemble a standard field effect transistor due to the contribution of the metallic SWCNTs. We also noted a negative shift of threshold voltage and a decrease in transconductance with exposure to saturated DMMP vapor. Such behaviors have been found in other SWCNT devices, and the shift of threshold voltage^{3a,4a} and the decrease in transconductance^{4a,5b} have been, respectively, attributed to a charge transfer process associated with the analyte and introduction of scattering sites. Another possible source of the resistance changes is that DMMP changes the nature of the Schottky barrier of HFIP-PT/SWCNT–Au contact. This effect has been eliminated from consideration by passivating the electrode interfaces. Specifically, we observed similar results to DMMP when the electrodes' interfaces were coated with a 50 μm thick film of polymethylmethacrylate (PMMA). The effectiveness of PMMA to block the diffusion of DMMP to the sensor was demonstrated by passivating the entire device, and under these conditions, no response is observed with exposure to DMMP for 60 s.

The presence of the HFIP group was intended to promote strong interactions between the DMMP and HFIP-PT. To probe this interaction, we have monitored changes in the fluorescence

intensity in response to DMMP.⁸ HFIP-PT is an emissive polymer with a quantum yield of 28% in THF and absorption and emission maxima of 435 and 546 nm, respectively. The dispersions with SWCNTs have a quenched HFIP-PT fluorescence with a decreased quantum yield (corrected for the optical absorptions of the SWCNTs) of 11%. Spin-coated films containing only HFIP-PT prepared in the same fashion as the sensory devices display absorption and emission maxima at 447 and 570 nm, respectively. From comparative studies with thin films of HFIP-PT/SWCNTs, we estimate that 60% of the emission is quenched by the SWCNTs, thereby indicating that most of the polymer is closely associated with the SWCNTs. The thin film of HFIP-PT exhibits some self-quenching due to interchain interactions and the extended conformation of the PT, and extended exposure to DMMP increased this emission at 570 nm by 55%. In the case of HFIP-PT/SWCNT films (Figure 3b), the emission at 570 nm was very constant in air without DMMP, showing this polymer is rather stable against photobleaching. Upon exposure to DMMP vapor, the fluorescence is enhanced by 76%. This increase indicates that the polymer bound to the SWCNT is still capable of interacting with the DMMP and that quenching by the SWCNT is attenuated. These observations together suggest a DMMP induced conformational change of the polymer backbone. Hence a working model for our sensory mechanism is a combination of charge transfer, introduction of scattering sites, and an increased physical separation of the SWCNTs caused by the interaction of the HFIP-PT and DMMP.

In conclusion, we have fabricated a high-performance polymer/SWCNT chemical sensor using very simple spin-casting technique. The dispersing polymer provides increased sensitivity due to strong H-bonding interactions with the analyte. The effectiveness of this approach suggests that carbon nanotubes dispersed with receptor containing polymers are a promising approach for the production of low cost chemiresistive sensors.

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Supporting Information Available: Synthetic procedures, device details, and Raman spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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