Nerve agent detection using networks of single-walled carbon nanotubes

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We report the use of carbon nanotubes as a sensor for chemical nerve agents. Thin-film transistors constructed from random networks of single-walled carbon nanotubes were used to detect dimethyl methylphosphonate (DMMP), a simulant for the nerve agent sarin. These sensors are reversible and capable of detecting DMMP at sub-ppb concentration levels, and they are intrinsically selective against interferent signals from hydrocarbon vapors and humidity. We provide additional chemical specificity by the use of filters coated with chemoselective polymer films. These results indicate that the electronic detection of sub-ppb concentrations of nerve agents and potentially other chemical warfare agents is possible with simple-to-fabricate carbon nanotube devices.   © *2003 American Institute of Physics.*   [DOI: 10.1063/1.1626265]

Semiconducting single-walled carbon nanotubes (SWCNTs) are unique structures in that they are composed entirely of surface atoms, while exhibiting transport properties superior to single-crystalline Si.[1,2] These features make SWCNTs an ideal candidate material for a new class of molecular sensors. Researchers have demonstrated that individual semiconducting SWCNT devices produce a large resistance change in response to certain types of gaseous analytes.[3–5] In such sensors, the adsorption of an analyte molecule with strong electron donor or acceptor properties results in a partial charge transfer between the analyte and the nanotube that changes its electrical resistance. Such sensors have detected 0.1 ppb of NO_2, which is superior to current state-of-the-art NO_2 sensors by several orders of magnitude.[4] Because chemical nerve agents and other chemical warfare agents also have strong electron donor (i.e., high Lewis basicity) properties, CNT-based devices are excellent candidates for highly sensitive chemical agent detectors provided that chemical specificity and simple fabrication procedures are established.

In this letter, we report simple-to-fabricate SWCNT-based chemical sensors that are chemically specific and capable of detecting sub-ppb concentrations of dimethyl methylphosphonate (DMMP), a simulant for the nerve agent sarin. We fabricated thin-film transistors and flow-through chemiresistors from semiconducting random networks of SWCNTs.[6] Previously, we have shown that dilute networks of interconnected SWCNTs behave like a *p*-type semiconducting thin film[6] and can be fabricated into devices using conventional microfabrication technology. The use of SWCNT networks eliminates the problems of individual nanotube assembly and conductivity variations, while maintaining the sensitivity observed in individual semiconducting nanotubes.

We find that the electronic properties of the nanotube networks are strongly affected by the presence of DMMP. DMMP readily adsorbs on the SWCNTs, resulting in an ef-fective transfer of negative charge that manifests itself as a shift of the transistor threshold voltage. The molecular adsorption is fully reversible by applying a small positive gate bias that releases the DMMP from the nanotube surface. The SWCNT-based sensors are capable of detecting DMMP at sub-ppb concentration levels, and they are intrinsically selective against common interferents. In addition, we demonstrate an approach to achieving chemical specificity that uses filters composed of chemiselective polymers. These results indicate that the electronic detection of sub-ppb concentrations of nerve agents and potentially other chemical warfare agents is possible with simple-to-fabricate CNT devices.

The thin-film transistors were fabricated from SWCNT networks using a previously described method.[6] The devices consist of a lithographically-patterned SWCNT network that bridges Ti source and drain contacts. The network is grown on the surface of a thermal SiO_2 layer, and the Si substrate serves as a common gate electrode. Figure 1(a) shows an optical image of a completed device. Also shown is a composite atomic force microscope (AFM) image [Fig. 1(b)] of the SWCNT network that composes a 10-μm-long by 35-μm-wide transport channel. Such networks are easily patterned into devices of arbitrary size and geometry with high yield.

Chemiresistor flow cells were fabricated on to the inner surface of 1/8 in. inner diameter by 2 in. long quartz tubing. The inner surface of the tubing was coated with SWCNTs by sealing one end with laboratory film and filling with liquid catalyst (ferric nitrate nonahydrate, 1.5 mg/l in 2-propanol). The catalyst was then removed, rinsed with hexanes, and dried under a N_2 stream. Nanotubes were grown in a tube furnace, as described in Ref. 6. The ends of the quartz tube were then coated with silver paint to provide electrical contacts. End-to-end resistance of the flow cell is typically around 1 to 10 MΩ. An optical image of a chemiresistive flow cell is shown in Fig. 1(b).

The sensors were exposed to vapors of DMMP, NH_3, water, xylene, and hexane, with air used as the carried gas. Calibrated doses of DMMP were delivered using a permeation tube and mass flow controllers. Upon exposure to a saturated vapor of DMMP, the transistor threshold voltage

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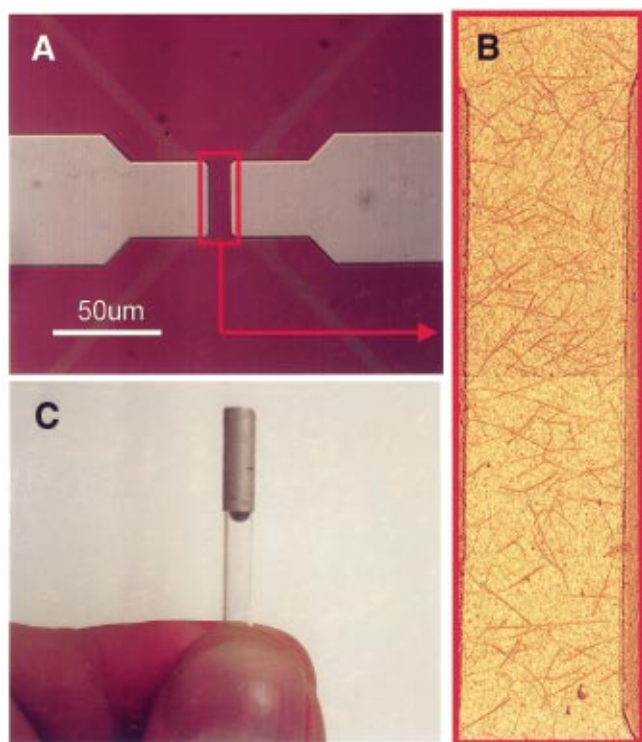[b]Electronic mail: snow@bloch.nrl.navy.mil

FIG. 1. (Color) (a) Optical micrograph of a SWCNT device. Ti contacts were evaporated on top of a SWCNT film grown on thermal SiO_2. The source/drain channel dimensions are 10×30 μm^2. The Si substrate serves as a back gate. (b) Representative AFM image of a SWCNT network that shows multiple conduction pathways via interconnected CNTs. (c) Optical micrograph of a SWCNT flow-cell chemiresistor sensor made from 1/8 in. outer diameter quartz tubing.

shifts by approximately -2 V relative to its pre-exposure value. Such a voltage shift has been observed in other SWCNT devices and is caused by an effective charge transfer between the adsorbed molecules and the nanotube.[3,7,8] The shift to negative voltage indicates that the adsorption of DMMP vapor affects a negative charge on the nanotubes; that is, additional positive charge from the gate bias is required to offset the negative charge resulting from the DMMP adsorption. The electron transfer is consistent with the fact that DMMP is a strong electron donor. Although details of the binding of DMMP molecules to SWCNTs are not known, the observed transfer of negative charge is attributed to an interaction of the SWCNTs with the partial negative charge on the terminal phosphonate oxygen.

Figure 2 displays the time dependence of the resistance of a SWCNT transistor (0 V gate bias) in response to a 10 s exposure of a concentrated dose of DMMP. The resistance rises rapidly as the DMMP adsorbs onto the surface of the nanotubes. After the removal of the DMMP vapor the resistance of the device initially decreases, but does not fully recover. The initial rapid recovery is only observed at high dose levels and is likely caused by secondary interactions between DMMP molecules that lower the desorption energy. Following this initial partial recovery, the remaining DMMP desorbs very slowly and can remain on the nanotubes for many hours. Previous nanotube sensors have required exposure to ultraviolet light or heat to desorb the analyte molecules from the surface.[3,4]
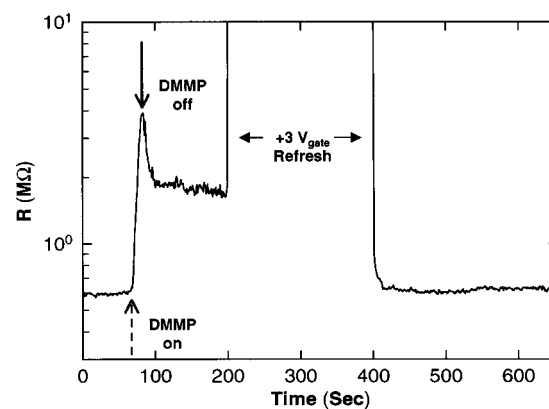
We have found that rapid recovery of the sensor can be

FIG. 2. Device resistance versus time in response to a 10 s exposure to DMMP. The device recovery is facilitated by using a $+3$ V gate bias.

achieved by applying a positive bias to the Si gate. In Fig. 2, a 3 V gate bias is applied between $t=200$ and 400 s. After the gate bias is removed the resistance returns to its pre-exposure value, indicating the removal of the DMMP. This exposure and refresh process can be repeated many times without degrading the performance of the device. We postulate that the Coulomb interaction between the DMMP and the negative charge induced by the gate bias lowers the desorption barrier sufficiently to refresh the sensor at room temperature.

The low desorption rate at 0 V gate bias combined with the large charging effect yields a high sensitivity to low concentrations of DMMP. Figure 3 plots the time dependence of the relative change in resistance $\Delta R/R$ in a chemiresistor flow cell for an exposure to 1 ppb DMMP that was delivered for 3000 s. The 1 ppb exposure results in a $\Delta R/R=1.5$. This large value of $\Delta R/R$ relative to the background noise ($R_{noise}/R \sim 0.01$) indicates that sub-ppb concentrations are easily detectable.

Defining the sensitivity of the response as $S = (\Delta R/R)/(P/P_o)$, where P_o is the equilibrium vapor pressure at 20 °C ($P_o = 2.6$ parts per thousand for DMMP),[9] we obtain $S = 3.9 \times 10^6$. For comparison, the measured sensitivity to DMMP of carbon black/polymer composite chemiresistors is $S = 0.6$,[9] a difference of more than six orders of magnitude. Another metric of performance is EC_{50}, the airborne concentration of a chemical agent that is sufficient to induce effects of interest in 50% of those exposed for 30

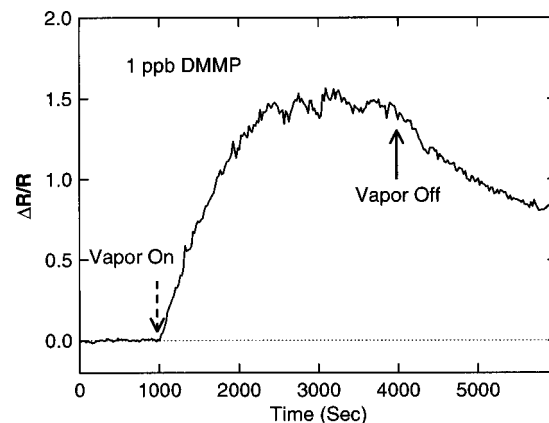FIG. 3. Relative change in resistance versus time for a chemiresistive flow-cell exposed to a 1 ppb concentration of DMMP for 3000 s.
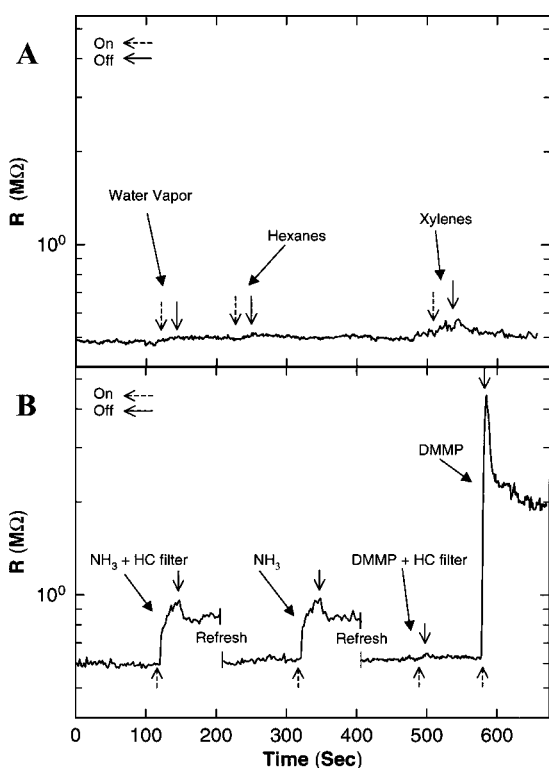
FIG. 4. (a) Resistance versus time curves for a sensor exposed to saturated vapors of water, hexanes, and xylenes. These potential interferents produce little or no sensor response. (b) Sensor specificity is demonstrated by using a chemiselective polymer to distinguish between two electron-donating molecules: NH_3 and DMMP. The HC-coated filter does not affect the dose of NH_3 vapor, while it greatly reduces the dose of DMMP.

min. For a resting exposure to sarin, $EC_{50} = 450$ ppb.[10]

From the previous discussion it is clear that SWCNT-based sensors offer an intrinsically high level of sensitivity to chemical nerve agents. However, in order to serve as an effective chemical detector, such devices must be insensitive to potential interferents. Two of the most common interferents are water and fuel vapors. Figure 4(a) shows the response of a sensor to 1-min exposures of saturated vapors of water, xylene, and hexane. Hexanes (aliphatic hydrocarbon) and xylenes (aromatic hydrocarbon) were used as simulants for gasoline and diesel fuel, respectively. These saturated vapors produce little or no resistance change, indicating that SWCNTs are intrinsically insensitive to some of the most common interferents present in field applications.

In order to obtain further chemical specificity, we used chemoselective polymers to filter vapors from the air flowing to our sensors. Chemoselective polymers have been designed to concentrate the vapors of many organic analytes and can thus be used to provide additional chemical specificity to the SWCNT-based sensors.[9,11–13] Such polymers have been applied to SWCNTs to distinguish between the adsorption of an electron-donating (NH_3) and an electron-withdrawing (NO_2) molecule.[4]

Here, we demonstrate the use of a chemoselective polymer to distinguish between two electron donors: NH_3 and DMMP. We constructed a filter composed of glass wool coated with an acidic, strong hydrogen-bonding polymer: HC.[14] The HC-coated glass wool, as well as an uncoated filter, were placed in-line with the flow of air to our sensors. In this case, the chemical selectivity is derived from two

mechanisms. One mechanism is the degree of hydrogen bonding between the polymer and the two analytes. In addition, the adsorption coefficient of permanent gases into a polymer film is typically much smaller than the coefficient for organic vapors. We use the relative response of the coated and uncoated filters to distinguish between the two electron-donating molecules.

In Fig. 4(b), we show the response of a sensor to NH_3 that is filtered with an HC-coated and an uncoated filter. The coated and uncoated responses are nearly identical, indicating that the two filters equally affect the concentration of NH_3. When this same experiment is performed with DMMP vapor, we observe a large difference in response [Fig. 4(b)] that indicates that the HC-coated filter is selectively removing the DMMP from the vapor stream. This simple example illustrates how chemoselective polymers can be combined with SWCNT-based sensors to provide additional chemical specificity.

Our results indicate that sensors fabricated from random networks of SWCNTs offer potential for a new class of chemical nerve agent detector. Such agents are strong electron donors and cause a reduction of the hole density in SWCNTs that increases their electrical resistance. Such a transduction mechanism is highly sensitive, easily detecting sub-ppb levels of DMMP, a simulant for nerve agents. In addition to this high sensitivity, SWCNT-based sensors are intrinsically selectivity against potential interferents such as hydrocarbons and humidity that do not possess charge transfer properties. We have also demonstrated that we can attain chemical specificity for such sensors using chemoselective polymers. Thus, with further development SWCNT sensors have the potential to provide chemical agent detection with performance far superior to current electronic transducers.

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[14] HC is a hydrogen-bonding acidic polycarbosilane. The details of its synthesis will be published elsewhere: E. J. Houser, J. L. Stepnowski, and R. A. McGill (unpublished).