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Detection of a nerve agent simulant using single-walled carbon nanotube networks: dimethyl-methyl-phosphonate

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Abstract
Single-walled carbon nanotube (SWNT) networks were used to detect hazardous dimethyl-methyl-phosphonate (DMMP) gas in real time, employing two different metals as electrodes. Random networks of SWNTs were simply obtained by drop-casting a SWNT-containing solution onto a surface-oxidized Si substrate. Although the electrical responses to DMMP at room temperature were reversible for both metals, the Pd-contacting SWNT network sensors exhibited a higher response and a shorter response time than those of the Au-contacting SWNT network sensors at the same DMMP concentration, due to the stronger interactions between the SWNTs and Pd surface atoms. In Pd-contacting SWNT network sensors, the response increased linearly with increasing DMMP concentration and reproducible response curves were obtained for DMMP levels as low as 1 ppm. These results indicate that SWNT networks in contact with Pd electrodes can function as good DMMP sensors at room temperature with scalable and fast response and excellent recovery.

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

1. Introduction

Dimethyl-methyl-phosphonate (DMMP) is a stimulant for the nerve agent sarin, which is an extremely toxic chemical warfare agent that belongs to the chemical group of organophosphorus compounds [1, 2]. Due to its rapid action and lethality, there is an urgent demand to develop rapid and reliable methods to detect and identify DMMP [3, 4]. Until now, a number of approaches to detect the chemical warfare agent have been reported, using various types of sensors such as semiconducting metal oxide (SMO) sensors [5, 6], microcantilever sensors [7, 8], and surface acoustic wave (SAW) sensors [9–13]. Although these sensors have advantages such as their rapid response and high sensitivity, their operational temperatures are generally high, which limits their wide-spread use.

Carbon nanotubes (CNTs), in particular, single-walled carbon nanotubes (SWNTs) have been intensively investigated as a sensing element for various gases due to their high electrical conductivity, adaptability to surface modulation, interactivity with exterior matters, and the exquisite changeability of their physical properties [14–18]. However, most SWNT-based DMMP sensors have exhibited slow response and long recovery times at room temperature, demonstrating that reproducible, room-temperature sensing of DMMP based on SWNTs is challenging. In this work, we successfully fabricated DMMP sensors using SWNT networks with a proper electrode metal. The sensors operated reversibly and reproducibly at room temperature, and were able to detect infinitesimal amounts of DMMP when Pd electrodes were incorporated. The electrode-dependent DMMP sensing properties of the SWNT network sensors are discussed with regard to the nature of the interactions between SWNTs and electrode surfaces.

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Figure 1. A schematic picture of a SWNT network sensor with Pd electrodes on the oxidized Si substrate. The inset shows a SEM image of the dispersed SWNT networks on the substrate.

2. Experimental details

2.1. Device fabrication

First, we patterned metal electrodes and subsequently dispersed SWNTs on them to avoid the physical damage commonly caused by plasma in conventional post-patterning processes. To fabricate the electrodes, two metals, Pd and Ti/Au, both with thicknesses of 100 nm, were deposited on thermally oxidized Si(100) substrates using ultra-high vacuum (UHV, base pressure: 5 \times 10^{-6} \text{Torr}) DC magnetron sputtering. Subsequently, a combination of photolithography and a lift-off process was used to pattern the micron-scale metal electrodes. Then, SWNTs were dispersed between the electrodes by a drop-casting method to produce the SWNT network sensors, as schematically drawn in figure 1. The inset of figure 1 shows a scanning electron microscopy (SEM) image of the dispersed SWNT networks. To improve the dispersion quality of the SWNTs, they underwent a sonication process before drop-casting, as described below.

2.2. Pretreatment of the SWNTs

Purified SWNTs were immersed in a de-ionized water solution containing 0.2 wt% sodium dodecyl sulfate (SDS). The SWNT-containing solution was sonicated for 4 h to ensure good dispersion, followed by vacuum filtration using Teflon filters (pore size: 20 \mu m). After filtration, the filtered film was rinsed, usually for several minutes, with de-ionized water to remove the SDS surfactant until no bubbles were observed.

To evaluate the quality of prepared SWNTs, we employed Raman scattering, which is one of the most widely used and powerful techniques to characterize CNT samples. Figure 2 shows a Raman spectrum characteristic of our SWNTs. The radial breathing mode of all Raman modes is specifically assigned to the SWNTs, which appears in the high energy region around 1600 cm$^{-1}$ as shown in the figure. Furthermore, a separate examination of the SWNTs by Raman spectroscopy verified a very strong peak at \( \sim 1600 \text{ cm}^{-1} \) along with a negligible peak at \( \sim 1300 \text{ cm}^{-1} \), indicating that our SWNTs were of high quality [19].

2.3. Electrical measurements

The measurement system used to evaluate the DMMP sensing properties of the SWNT network sensors consisted of a 180 cc sealed chamber with an inlet and outlet, mass
The response properties of the SWNT network sensors to DMMP were electrically measured at room temperature employing Pd and Au as electrodes. When a SWNT network sensor is exposed to DMMP, DMMP molecules are adsorbed, transferring electrons to the CNT networks, as shown in figure 1. The injected electrons modulate the carrier density and Fermi level of the semiconducting SWNT networks. The adsorbed DMMP molecules may also deform the local structure of the SWNTs due to their large molecular size, interrupting the free motion of charge carriers. These variations of physical properties result in increases in resistance, as demonstrated in figure 3. Figure 3(a) shows real-time responses of the SWNT network sensors incorporating Pd and Au electrodes, respectively, to 10 ppm DMMP. Here, the response of a SWNT network sensor to DMMP is defined as:

\[
\text{Response}(\%) = \frac{\Delta R}{R_O} \times 100(\%) = \frac{R_{DMMP} - R_{Air}}{R_{Air}} \times 100(\%)
\]

where \( R_{DMMP} \) is the steady state resistance after exposure to DMMP and \( R_{Air} \) is the initial resistance before exposure to DMMP. The onsets of the DMMP gas flow and ventilation are indicated by arrows. For both sensors, the response is reversible undergoing DMMP absorption and desorption processes, in the sense that the resistance rapidly decreases when the DMMP is evacuated from the chamber. Comparing the sensors with different electrodes, the Pd-contacting SWNT networks show a cleaner resistance change with a larger response than the Au-contacting networks. For instance, the measured responses are 2.1 and 0.8% at 10 ppm DMMP.

3. Results and discussion

The response properties of the SWNT network sensors to DMMP were electrically measured at room temperature employing Pd and Au as electrodes. When a SWNT network sensor is exposed to DMMP, DMMP molecules are adsorbed, transferring electrons to the CNT networks, as shown in figure 1. The injected electrons modulate the carrier density and Fermi level of the semiconducting SWNT networks. The adsorbed DMMP molecules may also deform the local structure of the SWNTs due to their large molecular size, interrupting the free motion of charge carriers. These variations of physical properties result in increases in resistance, as demonstrated in figure 3. Figure 3(a) shows real-time responses of the SWNT network sensors incorporating Pd and Au electrodes, respectively, to 10 ppm DMMP. Here, the response of a SWNT network sensor to DMMP is defined as:

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with the Pd-contacting and Au-contacting SWNT networks, respectively. Despite its larger response, the response and recovery times (15 s) of the Pd-contacting SWNT networks are shorter than those (20 s) of the Au-contacting SWNT networks. Here, the response time is defined as the time required to reach 90% of the total resistance change at a given DMMP gas concentration.

Taking into account that the geometries and constituents are the same for the two sensors except for the electrode materials, the contrast in the response behaviors is expected to originate from the different natures of the SWNT/electrode contacts, as schematically illustrated in figure 3(b). However, it is an oversimplification if the difference is attributed to the different Schottky barrier heights at the two contacts, because Au and Pd have nearly identical work functions (~5.1 eV). Based on a previous simulation study using the density functional theory (DFT), the atomistic spacing (2.1 Å) between the SWNTs and the Pd surface is shorter than that (3.1 Å) between the SWNTs and the Au surface, due to the stronger interactions of the SWNTs with the Pd surface [20]. Moreover, the stronger interactions of the SWNTs with Pd lead to the more than seven-fold larger binding energy between the carbon (C) atoms and Pd surface atoms, as compared to Au. It is inferred that the larger binding energy between the SWNT and Pd surface is mediated by a hybridization change of Pd-contacting C atoms from sp$^2$ to sp$^3$, which involves the breakdown of a weak π bond between two C cores and the formation of another σ-like bond consisting of a lone pair electron of the C atom and an itinerant electron of a Pd surface atom (see figure 4 for schematic illustration). The strong interactions of the SWNTs with Pd and the consequent interfacial bond formation are supported by another simulation study that used first-principles calculations. The simulation revealed that there is no energy barrier to charge transfer between the SWNTs and Pd surface due to the high density of interface states in the original band gap of the SWNTs, resulting from the strong interaction between the nearest C and Pd atoms [21]. The absence of an energy barrier at the SWNTs and Pd contact enables the DMMP-modulated carrier density and mobility to be quickly monitored by measuring the resistance change externally without intensity degradation at the interface, generating a large response and a short response time. This is in contrast to the Au case, where a certain amount of energy barrier should be overcome for carriers to move across the SWNT/Au interface [22].

Owing to the better contact properties, we focused on the Pd-contacting SWNT network sensors for examination of the concentration-dependent electrical responses. Figure 5 shows the real-time responses of the sensor at room temperature and the response curves converted from the data shown in (a) for a Pd-contacting SWNT network sensor. (c) Response versus DMMP concentration plot demonstrating a linear relationship.
density along with more scattering chances at higher DMPP concentrations. It is noteworthy that the response curve is still clean and reproducible at 1 ppm DMPP (response ≈ 0.8). To our knowledge, this is the lowest detection level of DMPP in air ever reported, using pure CNTs without any chemical pretreatment. The small slope (0.160) of the response versus DMPP concentration in figure 5(c) suggests the possibility of detecting even lower concentrations of DMPP, which was partly verified from another experiment in association with this study. This is possible because the high density semiconducting CNT networks are incorporated into the sensor and the CNT/Pd contacts are almost perfect.

4. Conclusions

In summary, we investigated the response behaviors of SWNT network sensors to DMPP gas at room temperature. Two different materials (Pd and Au) were incorporated as electrodes. Although all SWNT network sensors with the different electrodes worked reversibly, the Pd-contacting sensors showed a larger response and a shorter response time at a given DMPP concentration, as compared to the Au-contacting sensors. This was attributed to the barrier-free almost perfect SWNT/Pd contacts originating from the strong interactions between the SWNTs and Pd surface atoms. The Pd-contacting SWNT network sensors exhibited a linear relationship between the response and DMPP concentration as well as a very low detection limit of 1 ppm, making them suitable for DMPP gas sensing. Our results indicate that CNTs with the proper choice of electrode materials can be practically utilized as efficient gas sensing materials.

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References