Functionalized Carbon Nanotube–Based Sensors for Detecting a Trace Quantity of 2,4-Dinitrotoluene Explosive Vapors, with Selectivity

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ABSTRACT

Stable, surfactant-free semiconducting carbon nanotube (CNT) inks were developed. The inks were functionalized with π-bonder receptor molecules to achieve selectivity toward DNT and TNT molecules. Two types of CNT sensors, interdigitated electrode (IDE) and thin-film transistor (TFT) sensors were printed and were tested with DNT vapor and other analytes. The CNT IDE sensors were able to repeatedly detect DNT vapor levels as low as 0.5 ppb with a response time of less than 10 seconds. These sensors showed a high degree of selectivity toward DNT over nitrobenzene and nicotine. Sensor sensitivity was found to increase with an increase in receptor molecules present in the CNTs. Preliminary results on a CNT TFT sensor showed a response to 300 ppb of DNT, a response similar to that of an IDE sensor prepared with CNTs with the same level of functionalization. Preparation and testing of sensors (especially TFT sensors) made with more functionalized CNT inks are ongoing.

Keywords: carbon nanotubes, 2,4-dinitrotoluene, interdigitated electrode sensor, sensitivity, detection limit

1   INTRODUCTION

Traditional explosive detection technologies such as laser spectroscopy, Fourier transform infrared and THz spectroscopy, mass spectrometry, electromechanical sensors, photoluminescence-based detectors, and Raman spectroscopy [1] suffer from drawbacks such as complex and bulky instrumentation, high cost, poor sensitivity and selectivity, slow response, inability to confirm the detection event in field sites, and lengthy, time-consuming data analysis/computing processes. A simple, low-cost explosive detection system is needed which is highly threat responsive, portable, field-deployable, and able to detect/confirm the threat immediately in the field itself without the need for further data analysis/processing. The carbon nanotube (CNT)–based electrical sensor platform described herein provides those benefits.

Single-walled carbon nanotubes (SWCNTs) have large surface area, extreme sensitivity and fast response to surrounding molecules, good environmental stability, and excellent mechanical and electronic properties [2]. In addition, SWCNTs can provide selectivity to a wide spectrum of analytes simply by modifying SWCNT surfaces with analyte-specific functional groups [3]. Sensors that are based on SWCNTs can offer many advantages over traditional optical spectroscopy–based sensors, including lower cost, device simplicity, portability, energy efficiency, increased sensitivity and selectivity, flexibility, and the capability for remote operation.

In the literature, a report described previous work in which glassy carbon electrodes, coated with triphenylene-functionalized multi-walled CNTs (MWCNTs), were used in an electrochemical cell [4]. The sensing approach was electrochemical, and triphenylene was used to improve response and sensitivity of the electrochemical sensor.

Only a few reports [5, 6] describe using SWCNTs in thin-film transistor (TFT) sensor devices for detecting explosive compounds. These reported efforts used pristine (non-functionalized) SWCNT films as a sensing material, and reported a trinitrotoluene (TNT) sensing detection limit of 2 ppb or 8 ppb. Unfortunately, pristine SWCNTs are sensitive to different chemical environments and lack analyte selectivity, which makes such chemical sensors unreliable to use. Brewer Science has directly attacked these problems by developing a new sensing material and successfully demonstrating functional chemical sensors using this material. These sensors are very sensitive and selective toward explosive molecules. Specifically, these sensors are able to sense a trace level (0.5 ppb) of dinitrotoluene (DNT) vapors, with great selectivity over other analytes, in less than 10 seconds.

2   EXPERIMENTAL

Pure aqueous, surfactant-free, and printable semiconducting SWCNT inks were developed. The CNT inks were functionalized with π-bonder molecules to achieve selectivity toward DNT and TNT molecules when used in explosives sensors. CNT inks with different levels of π-bonder functionalization (1:3 and 1:5 mass equivalents

of π-bonder molecules, where the ratio represents the weight ratio of CNTs to π-bonder agent, respectively) were prepared study the effect of the level of functionalization on the sensor sensitivity. A Raman spectrum of functionalized CNTs is shown in figure 1. The Raman spectrum clearly shows that the CNTs are predominantly semiconducting SWCNTs.
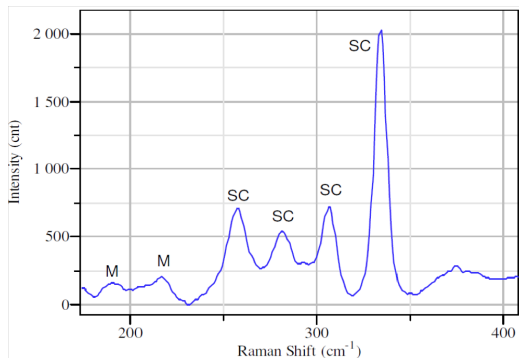

Figure 1. Radial breathing mode (RBM) zone of a Raman spectrum (wavelength = 633 nm) of functionalized semiconducting (SC) CNTs.

Sensor fabrication was done in two steps: i) electrode fabrication and ii) CNT channel printing. For the IDE sensors, arrays of IDEs were made by using an Omnijet 300 ink-jet printer to print DGP-40LT-15C nano-silver ink (Advanced Nano Products) onto a silicon substrate that had a 3000-Å layer of silicon oxide on it. The printed IDE arrays were then cured at 200°C for 30 minutes. For the TFT sensors, arrays of source and drain electrodes were fabricated on a low-resistance silicon substrate (resistivity: < 0.005 ohm-cm) by patterning 100 Å of chrome and 1000 Å of palladium using a standard photolithography process. A 1000-Å-thick SiO_2 layer on silicon served as the dielectric layer of the transistor while the conductive backside of the substrate was used as the back gate electrode. The functionalized semiconducting SWCNT inks were then printed across IDEs (for the IDE platform) and source and drain electrodes (for the TFT platform) using an Aerosol Jet® printer. The SWCNT layer served as the active sensing element in both sensor platforms. The printed CNT IDE and CNT TFT sensors are shown in figure 2.
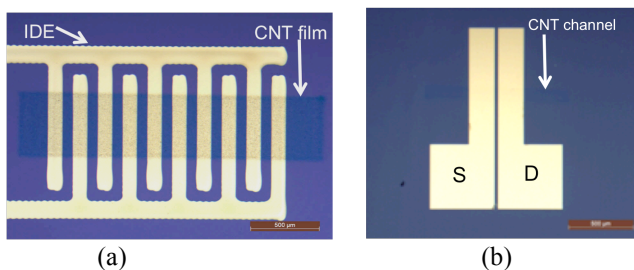

Figure 2. (a) A CNT interdigitated electrode (IDE) sensor, and (b) a CNT thin-film transistor (TFT) sensor.

A sealed chamber with electrical feed-through and gas inlet/outlet was used for sensing experiments. The schematic of the experimental setup is shown figure 3. DNT vapor was generated from its powder, which was kept in a small glass reservoir, by using dry inert nitrogen gas as the carrier gas. The outgoing DNT vapor was diluted with another stream of dry nitrogen gas (dilution gas), in order to obtain a desired DNT concentration. The system was first purged with nitrogen gas and then was exposed to nitrogen gas having a flow rate of 2000 sccm until the conductance of the sensor was relatively stable. Once the conductance was stable, the DNT vapor was allowed to flow through the sensor surface, which was kept inside the chamber. For the CNT IDE sensors, the change in the conductance of the sensor when exposed to DNT vapor was monitored using a Keithley 4200 SCS semiconductor parametric analyzer that was connected to the sensor using the electrical feed-through. The same IDE sensor was exposed to various concentrations of DNT vapor (3 minutes for each), starting from a lower DNT vapor concentration and with a 3-minute nitrogen purge in between the different DNT vapor concentrations. For sensing tests with nitrobenzene and nicotine, a separate glass reservoir was used to prevent cross-contamination. The IDE sensors were first tested with those analytes and then were tested with DNT vapors, in order to observe the difference in response.
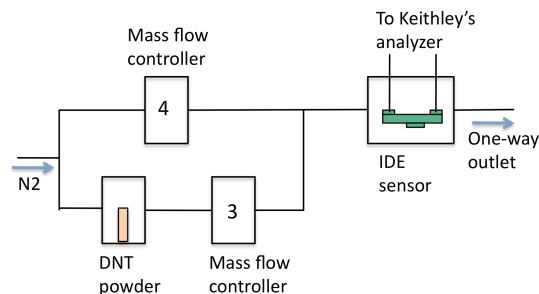

Figure 3. A schematic of the experimental set-up for explosive vapor detection.

For CNT-TFT sensors, a change in drain current at fixed bias and gate voltages when exposed to DNT vapor was monitored.

3   RESULTS AND DISCUSSION

3.1   Detection of DNT Vapor

The reponse to various concentrations of DNT vapor of an IDE sensor that was fabricated using SWCNTs with 1:5 mass equivalent ratio of CNTs to π-bonder molecules is shown in figure 4. As observed in the figure, as soon as the DNT vapor in concentrations as low as 0.5 ppb was introduced, a distinct drop in IDE sensor conductance was observed, indicating the detection of 0.5 ppb of DNT vapor. Each IDE sensor was able to respond to 0.5 ppb of DNT in less than 10 seconds (experimental data time interval).

Although the response to DNT vapor increased when DNT vapor concentration was increased from 0.5 ppb to 3 ppb, the response did not increase linearly with DNT vapor concentration. We attribute this to the effect of residual DNT vapor present in the sensor system from the previous DNT vapor exposure.
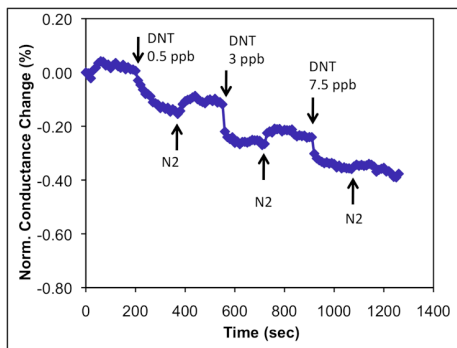

Figure 4. DNT sensing by an IDE sensor that used 1:5 mass equivalents of π-bonder functional groups.

In an earlier test with an IDE sensor that was fabricated using SWCNTs with 1:3 mass equivalent ratio of CNTs to π-bonder molecules, the sensor showed only slight response to 300 ppb of DNT vapor, suggesting the response's dependence on the level of CNT functionalization with π-bonder molecules.

3.2 DNT Selectivity over Nitrobenzene

An IDE sensor was exposed to vapor containing 300 ppb of nitrobenzene in nitrogen, and the change in conductance was monitored. Except for a continuation of a very small, gradual drop in conductance that occurred even before introducing nitrobenzene, the sensor did not show any sharp change in conductance after introducing nitrobenzene (figure 5).
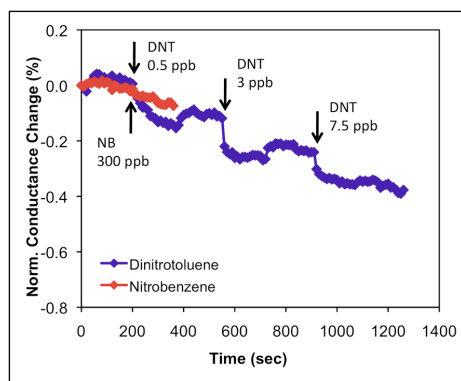

Figure 5. Selectivity tests of an IDE sensor exposed to nitrobenzene vapor and various concentrations of DNT vapor.

After exposure to 300 ppb of nitrobenzene, the testing chamber was cleaned thoroughly by baking it at 150°C for 2 hours and was then purged with compressed nitrogen for 30 minutes. The same sensor was then exposed to a vapor containing ≥ 0.5 ppb of DNT in nitrogen gas. The sensor clearly showed a response to 0.5 ppb of DNT, indicating the sensor's selectivity toward DNT over nitrobenzene.

3.3 DNT Selectivity over Nicotine

An IDE sensor was exposed to vapors containing 70 ppb and 280 ppb of nicotine in nitrogen, with a nitrogen purge in between, and the change in conductance was observed. As shown in figure 6, no substantial change occurred in the conductance of the sensor. However, the conductance curve was not as smooth as with nitrobenzene, which may be due to some nicotine absorption by the CNT surface. After exposure to nicotine, the system was cleaned as described in the previous section. The same sensor was exposed to a vapor containing ≥ 0.5 ppb of DNT in nitrogen. The sensor clearly showed a response to 0.5 ppb DNT, indicating the sensor's selectivity toward DNT over nicotine.
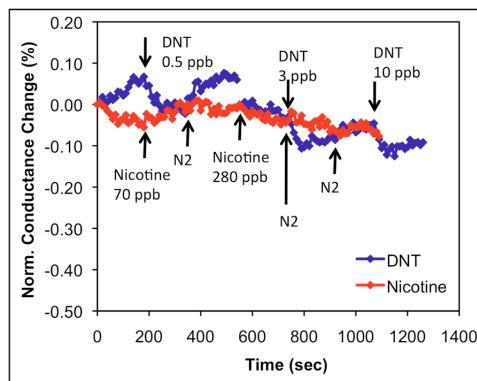

Figure 6. Selectivity tests of an IDE sensor exposed to nicotine and DNT.

3.4 DNT Vapor Detection Using a CNT TFT Sensor

The output and transfer characteristics of a CNT TFT sensor that used a 1:3 mass equivalent ratio of CNTs to π-bonder molecules is shown in figure 7. The output curve clearly showed the p-type semiconducting nature of the CNT material, and the TFT showed an ON/OFF ratio of >10^3. The TFT sensor was able to show a response to DNT in a concentration of 300 ppb by exhibiting a noticeable decrease in conductance (figure 8). CNT TFT sensor testing using CNTs functionalized with higher mass equivalents of π-bonder molecules is ongoing.
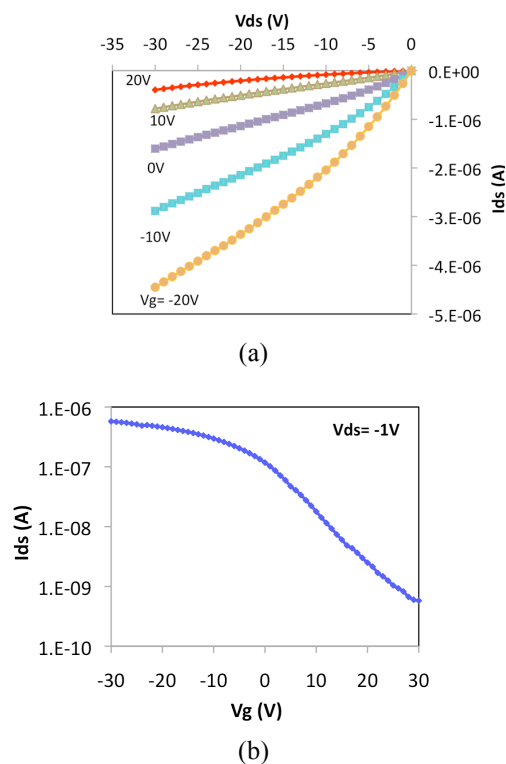
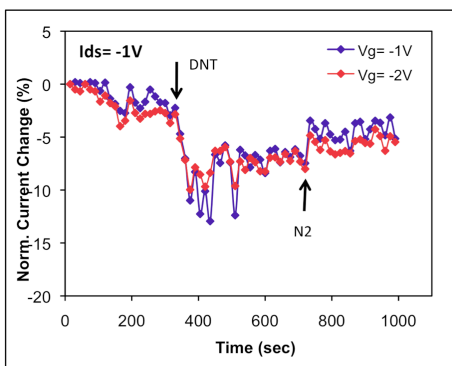Figure 7. (a) An output curve and (b) a transfer curve of a CNT TFT sensor.

Figure 8. DNT sensing using a CNT TFT sensor. The sensor showed a clear response to 300 ppb of DNT vapor.

4   SUMMARY

Pure aqueous, surfactant-free SWCNT inks were prepared and were functionalized with π-bonder molecules to achieve selectivity to DNT and TNT vapor derivatives. CNT IDE and TFT sensors were printed on silicon wafers using the prepared CNT inks and were tested for DNT vapor sensing and selectivity. The IDE sensors are able to sense a trace level (0.5 ppb) of DNT vapors with great selectivity over nitrobenzene and nicotine, with a response time of less than 10 seconds.

5   ACKNOWLEDGEMENTS

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