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Oligomer-Coated Carbon Nanotube Chemiresistive Sensors for Selective Detection of Nitroaromatic Explosives

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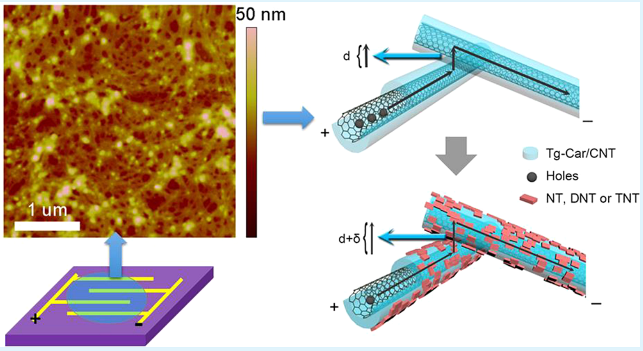
Supporting Information

ABSTRACT: High-performance chemiresistive sensors were made using a porous thin film of single-walled carbon nanotubes (CNTs) coated with a carbazolylethynylene (Tg-Car) oligomer for trace vapor detection of nitroaromatic explosives. The sensors detect low concentrations of 4-nitrotoluene (NT), 2,4,6-trinitrotoluene (TNT), and 2,4-dinitrotoluene (DNT) vapors at ppb to ppt levels. The sensors also show high selectivity to NT from other common organic reagents at significantly higher vapor concentrations. Furthermore, by using Tg-Car/CNT sensors and uncoated CNT sensors in parallel, differential sensing of NT, TNT, and DNT vapors was achieved. This work provides a methodology to create selective CNT-based sensors and sensor arrays.



KEYWORDS: *carbazole oligomer, carbon nanotube, thin film, chemiresistive vapor sensor, nitroaromatic explosive, differential sensing*

A low-cost, portable, and sensitive sensor for explosive compounds can provide great benefits to homeland security, military operations, and environmental safety.[1−4] Nitroaromatic (NA) explosive compounds, such as 2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (DNT), are among the most common explosives in the world. Several detection technologies have been developed. Although traditional analytical methods like gas chromatography−mass spectrometry[5] and ion mobility spectrometry[6] afford accurate measurements, they require sophisticated and expensive instruments, which limits their usage. NA explosive sensors based on fluorescence materials,[7−9] especially carbazole-based polymers[10] or oligomers,[11−14] provide easy, sensitive detection of NA explosives. Yet, fluorescence-based sensors involve optical excitation and monitoring, which require precise alignment and calibration. Chemical sensors based on field-effect transistors using functionalized one-dimensional semiconducting materials[3,15] (e.g., metal oxide nanowires, silicon nanowires, and carbon nanotubes) have attracted much attention because of their high sensitivity and simple integration with circuits. However, their applications have been limited by complicated fabrication processes arising from factors including a lack of solubility of the nanomaterials. Moreover, metal oxides and other inorganic sensor materials demonstrate significant responses to water vapor (humidity), causing false positives.

Chemiresistive sensor systems based on carbon nanotubes (CNTs) are easy to fabricate, small in size, and highly sensitive.[16,17] However, their use has been limited to the lab scale because of difficulties in dispersing CNTs and poor sensor selectivity. Researchers have explored both covalent[18] and noncovalent[19,20] modifications to solve these problems. Although covalent modifications are robust, they usually alter the electric properties of the CNT significantly and require complicated organic synthesis.[21] Noncovalent modifications provide a wide range of materials to choose from without changing the CNT's band structure.[22] We report herein the demonstration of a NA explosive sensor using single-walled CNTs noncovalently functionalized with a carbazolylethynylene oligomer (Tg-Car, see Figure 1a for the structure). There are three key features of our design. (1) The Tg-Car oligomer greatly enhances the dispersion of CNTs in organic solvents and thus facilitates the fabrication of an unbundled, uniform, and porous thin film using a very simple drop-casting method. The porous surface of Tg-Car/CNT composite also aids in vapor diffusion, which enhances the vapor detection efficiency. (2) The noncovalent modification not only maintains the electron transport properties of CNTs, but also improves the

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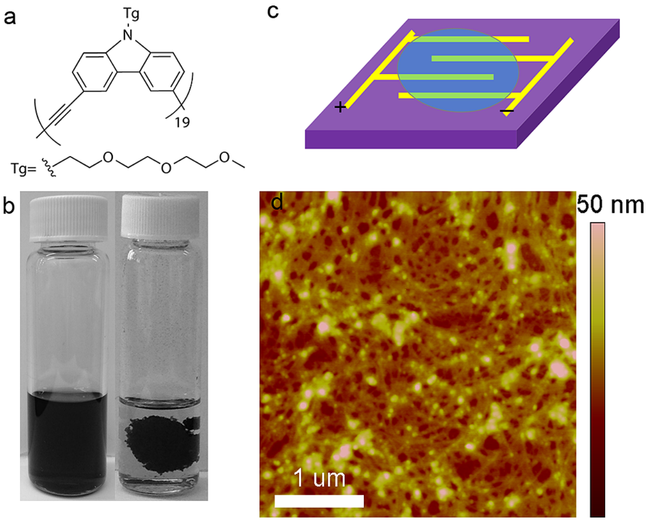


Figure 1. (a) Molecular structure of the Tg-Car oligomer. (b) CNT suspensions in chloroform with (left vial) and without Tg-Car oligomer (right vial). (c) Schematic view of the sensor device with the Tg-Car/CNT thin film. (d) AFM image of the Tg-Car/CNT thin film drop-cast on an IDEs chip.

selectivity of the sensors to NA explosive compounds. Moreover, by adding a separate channel of the uncoated CNT sensors as a reference, we can both distinguish NAs from potential interferences and differentiate three different NAs compounds from each other. (3) The insulating oligomer coating creates charge carrier tunnel barriers at the junctions of the CNT network. Swelling of the oligomer due to exposure to an analyte decreases the conductivity of the CNT network by increasing the tunneling distance. Meanwhile, the carbazole building block of the Tg-Car oligomer is very similar to previously reported fluorescence sensing materials,[11−14] which were also based on the carbazole structure and demonstrated strong binding affinity and selectivity for NA explosives.

The CNTs were dispersed following a process previously developed in our lab[22,23] (see the Supporting Information). Briefly, CNTs were added into a chloroform solution containing an excess amount of Tg-Car oligomer, followed by sonication. The synthetic details of the Tg-Car oligomer can be found in our previous work.[24] Aggregates were removed by three iterations of centrifugation. Finally, a uniform and stable Tg-Car/CNT suspension in chloroform was obtained (shown in the left vial in Figure 1b). The suspension was stable for over three years without precipitation while the uncoated CNTs in chloroform aggregated within minutes after sonication (shown in the right vial Figure 1b). This demonstrates an improvement in solubility, which makes the device fabrication process facile and reproducible. Then, 2−6 μL (2 μL at a time) of the diluted Tg-Car/CNT suspension was drop-cast on a chip with prepatterned interdigitated electrode pairs (IDEs) until the resistance was within the range of 50 kΩ to 200 kΩ. The device was heated to 80 °C for 5 min in an ambient environment to remove the remaining chloroform. Figure 1c shows the schematic view of the sensor. The morphology of the thin film was studied by atomic force microscopy (AFM) (Figure 1d) directly after fabrication. The AFM image indicates that a porous, bundle-free thin film was formed. The fibril materials in the thin film are individually separated CNTs coated with a layer of Tg-Car oligomer (see the black arrows in Figure 1d). An AFM image showing the surface morphology of a larger area is provided in the Supporting Information (see Figure S2). This continuous, porous surface of these devices allows diffusion of analyte molecules into the thin film, which facilitates vapor detection.

To evaluate of the sensory performance of the Tg-Car/CNT devices, we first tested the vapor of 4-nitrotoluene (NT), which is commonly used as a taggant in NA explosive materials. It is relatively easy to accurately dilute and deliver NT vapor with our vapor generation system (see the Supporting Information, Figure S1, for details) because its saturated vapor pressure at room temperature is much higher than TNT and DNT (Table S2 in the Supporting Information). The vapor generation system consists of a diluting stream of dry air at a constant flow rate of 100 sccm (standard cubic centimeter per minute). To this stream of dry air, a known volume of saturated vapor was infused by a programmable syringe pump. The saturated vapor of each analyte was generated in a 60 mL glass syringe and allowed to equilibrate for 2 h at room temperature. The diluted vapor was then delivered into a custom PTFE enclosure, in which the sensors were contained. The sensory response to the exposure of an analyte is defined as the relative conductivity change of the sensor before and after the exposure. The sensors were operated at a constant bias voltage of 1.0 V. Figure 2a shows the baseline-corrected response of the Tg-Car/CNT sensor to 1.5, 2.0, and 3.0 ppm of NT vapor, which were diluted from 3, 4, and 6 sccm streams of the saturated vapor of NT.[25] The original data plot without baseline correction is shown in the Supporting Information (Figure S3). Overall, the sensor's response is fast and recoverable. A limit of detection (LOD) of

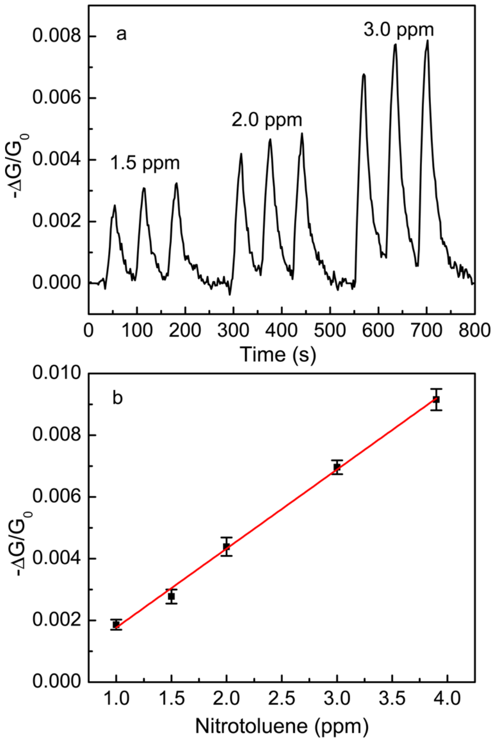


Figure 2. (a) Real-time sensory response to NT vapor at concentrations of 1.5, 2.0, and 3.0 ppm. The exposure at each concentration was repeated three times. The analyte exposure time is 20 s and the recovery time is 40 s for each test. (b) Calibration curve of the sensor's response at different vapor concentrations of NT, 1.0, 1.5, 2.0, 3.0, and 3.9 ppm.

95 ppb is calculated based on a linear fitting of the data following a method reported in literature (see the Supporting Information).[26]

The sensor's ability to discriminate between NT and common reagents, such as acetone, ethanol, hexane, methanol, toluene, and water, was investigated. These common reagents were diluted to about 1% of the saturated vapor at room temperature (1 sccm of saturated vapor diluted with 100 sccm of dry air) and delivery to the sensor. Figure 3 shows the conductance change of the Tg-Car/CNT sensor in response to the vapors of these common reagents. The selectivity of the sensor to NT is good considering that the other vapors are at concentrations 2−3 orders of magnitude higher than that of NT while the sensory response to NT is significantly lower. Moreover, the sensor shows a minimal response to water vapor, which indicates robustness against humidity.

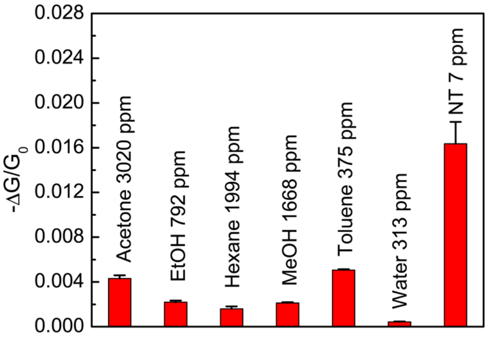


Figure 3. Response of the Tg-Car/CNT sensor to NT (15 sccm of saturated vapor diluted with 100 sccm of dry air, about 13% of saturated vapor at room temperature) and other common chemical reagents (1% of saturated vapor at room temperature).

Next, we compared the vapor detection performance of the Tg-Car/CNT sensors with uncoated CNT sensors, similar to those reported previously.[15,17] The uncoated CNT sensors were fabricated from a CNT/dimethylformamide (DMF) suspension (see the Supporting Information for fabrication details). Figure 4a shows the results from both sensors in response to NT (7 ppm), DNT (36 ppb), and TNT (0.7 ppb) diluted from 15 sccm of saturated vapors at room temperature. The sensory response of the Tg-Car/CNT sensors and uncoated CNT sensors were monitored simultaneously and the real-time results are provided in the Supporting Information (Figure S4). The uncoated CNT sensor shows an increase of conductance to all the analytes while the Tg-Car/CNT sensor shows an opposite response trend. This is reasonable because uncoated CNTs are p-type materials with holes as the major charge carriers and the conductivity is expected increase when exposed to electron-withdrawing analytes such as NA explosive compounds. For instance, even though the concentration of DNT is about 200 times lower than the concentration of NT, the sensory response is higher for DNT. This is mainly because the electron-withdrawing ability of DNT is higher than that of NT. For the Tg-Car/CNT sensor, the conductivity decreases upon exposure. To account for this decrease, we propose a sensing mechanism based on the swelling of the Tg-Car oligomer between adjacent CNTs, rather than charge transfer. This mechanism will be discussed in detail later.

There are significant research interests regarding the differential detection of NT, DNT, and TNT, as the chemical structures and properties of these compounds are so similar. One possible solution is to use sensor arrays[27] that incorporate multiple sensors in one detection system. We built a simple array using the Tg-Car/CNT sensors and uncoated CNT sensors. Figure 4b shows a scatter plot of the sensory response from the Tg-Car/CNT sensor and the uncoated CNT sensor to vapors of NT (4, 7, and 12 ppm), DNT (23, 36, and 63 ppb), and TNT (0.4, 0.7, and 1.3 ppb). As it is clearly shown, the cluster of data points for NT is far away from the clusters of data points for DNT and TNT, which means it can be distinguished from the other NA compounds. The clusters of DNT and TNT are closer but still separate. This result demonstrates that by using a simple array of just two sensor components, DNT and TNT can be selectively detected in this range of concentrations. The sensory response of Tg-Car/CNT is nearly saturated at higher concentrations of DNT and TNT (see Figure 4b). This may be due to the strong electron donor−acceptor interaction between these compounds and the carbazole units in Tg-Car oligomer. The noncovalent modification of CNTs not only simplifies the device fabrication, but also demonstrates a practical way to improve the selectivity of the CNT sensors through the choice of monomer building blocks.

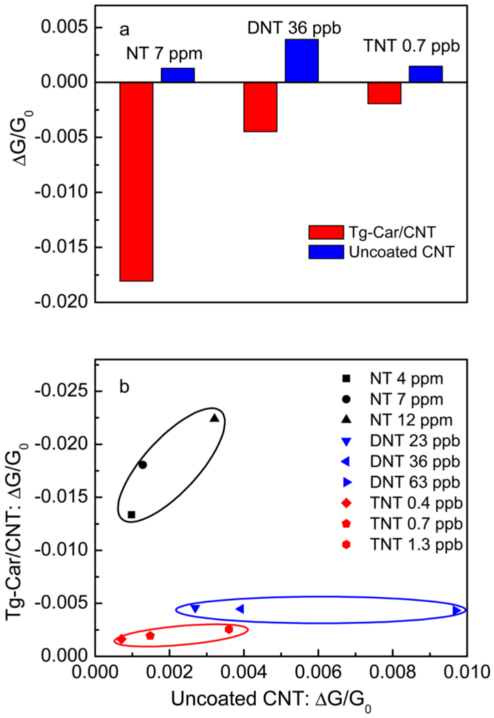
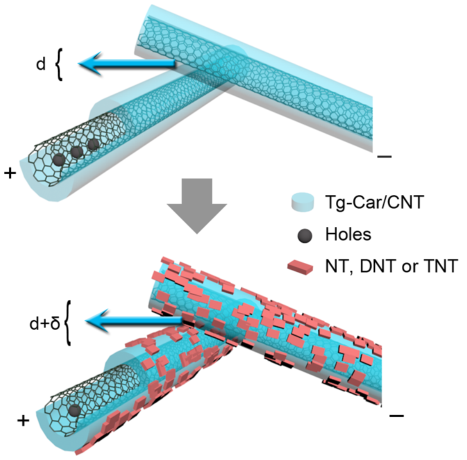


Figure 4. (a) Conductance changes of the Tg-Car/CNT sensor and the uncoated CNT sensor in response to NT at 7 ppm, DNT at 36 ppb, and TNT at 0.7 ppb (15 sccm diluted in 100 sccm of dry air). (b) Scatter plot of the conductance changes of the Tg-Car/CNT sensor and uncoated CNT sensor to three different vapor concentrations of NT, DNT, and TNT.

The mechanism of the Tg-Car/CNT sensors is different from the charge-transfer mechanism mentioned in previous reports[28] and in the uncoated CNT sensors used in this work. We propose that the mechanism of the Tg-Car/CNT sensors is due to the swelling of the Tg-Car/CNT thin film (shown in Scheme 1), which is similar to previously reported carbon-black/polymer[29] or carbon-black/small-molecule[29,30] chemical sensors. In the Tg-Car/CNT sensors, the conductivity of the thin film is from the CNT network. However, the junctions

Scheme 1. Schematic of the Charge Carriers (holes) Moving in the CNT and Tunneling through the Tg-Car Oligomer before and after the Exposure to NA Explosive Compounds



between CNTs are separated by the insulating Tg-Car oligomer. When voltage is applied between source and drain, the charge carriers (holes) in the CNT network tunnel through the interfaces formed by the Tg-Car oligomer. When the sensor is exposed to an analyte, the Tg-Car oligomer swells and the distance separated by the oligomer increases; thus, the tunnel barrier in the CNT network increases. As a result, the conductivity of the sensor decreases. However, the sensing performance from our Tg-Car/CNT sensors to the NA explosive compounds is significantly enhanced compared to the previous carbon-black swelling-based NA sensors[30] because of the following reasons. First, the porosity in our sensors is high. This is important for vapor sensors because it greatly enhances the surface area available for interaction with the analyte. Meanwhile, we can disperse CNTs using a relatively small amount of Tg-Car oligomer. For most of the previous carbon-black swelling-based sensors,[29,30] carbon-black was immersed in a large volume of polymer or small molecule with limited open surface area, which decreases the sensitivity. Second, the Tg-Car oligomer provides a strong affinity to NA explosive compounds, which helps the sensor respond at low concentrations and improves the selectivity of the sensor from other common chemical reagents (as shown by the results in Figures 3 and 4).

In summary, we have fabricated a Tg-Car/CNT composite sensor using a very simple drop-casting method. The sensor shows high sensitivity to NA explosive compounds and also shows high selectivity among other common organic reagents. The combination of uncoated CNT sensor with the Tg-Car/CNT sensor provides differential sensing between the three NA explosive compounds. The work demonstrates the use of a carbazole oligomer and CNT composite materials for a simple chemiresistive sensor with high sensitivity, which can be easily integrated into sensor arrays to achieve differential sensing.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental method, vapor generation system, optical and AFM images, original real-time sensory response data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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