Supporting information for

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

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Experimental Section

Materials: Carbon nanotubes (SG65i, single walled, >95% semiconducting species) were purchased from SouthWest NanoTechnologies. Carbazolylethynylene oligomer (Tg-Car) with triethylene glycol monomethyl ether (Tg) side chains was synthesized following steps reported previously.[1] 4-nitrotoluene (NT, 99%) and 2,4-dinitrotoluene (DNT, analytical standard) were purchased from Aldrich. 2,4,6-trinitrotoluene (TNT) was obtained from Dyno Nobel. Other chemicals were purchased from Aldrich or Fisher at the reagent grade and used as received.

Dispersing carbon nanotubes with oligomer: 1.0 mg carbon nanotubes and 5.6 mg Tg-Car oligomer were added to 9.0 ml of chloroform and sonicated in a water bath (Fisher Scientific FS30H model) at room temperature for 90 min. Then the suspension was set aside for 30 min. Then suspension was transferred to a centrifugation tube and centrifuged (IEC Centra CL2) at 4200 rpm (~ 3000 g) for 20 min. The supernatant was transferred into another centrifugation tube

and the centrifugation process was repeated two more times. The final supernatant is very stable with no precipitate observed after three years.

Interdigitated electrodes: The interdigitated electrodes (IDE) were patterned onto a silicon wafer with a 300 nm thermal oxide layer (purchased from Silicon Quest) using a standard photolithography procedure. The gap between fingers in the IDE is 80 μm. The width of the channel is 2100 μm and the length is 20 μm. There are 10 finger pairs in total. The 20 nm adhesive titanium layer and the 50 nm gold layer were sputtered on the wafer.

Tg-Car/CNT sensors fabrication: The IDE chips were cleaned by sonication in acetone, methanol and isopropanol successively. Then the devices were made by drop-casting 2-6 μL (2 μL at a time) of the diluted Tg-Car/CNT suspension (diluted 40 times from the original Tg-Car/CNT suspension, the supernatant after three times of centrifugation above) until the resistances of the sensor devices were within the range of 50 kΩ to 200 kΩ. The devices were heated at 80 °C for 5 minutes under ambient environment to remove chloroform residue.

Uncoated CNT sensors fabrication: 1.0 mg CNTs was placed in 50 ml dimethylformamide (DMF) and sonicated for 2 hours. Then the suspension was diluted 50 times. To fabricate the sensor devices, 2-6 μL (2 μL at a time) of the CNT suspension was drop-cast on the pre-cleaned IDE chips until the resistances of the devices were within the range of 50 kΩ to 200 kΩ. Then, the sensor devices were heated at an elevated temperature (~ 120 °C) for 5 min under ambient environment to get rid of extra DMF on the surface of the IDE chips.

Characterization Methods: Atomic force microscopy (Veeco MultiMode V scanning probe) operating in tapping mode was used to characterize the surface morphology of Tg-Car/CNT film deposited on IDEs. Optical images were obtained using a CCD camera in the microscope.

Sensor testing system: The sensor devices were wire-bonded into a ceramic chip carrier and connected to an Agilent 4156C Precision Semiconductor Parameter Analyzer. A custom designed Teflon enclosure was used to cover the ceramic chip carrier. A DC voltage (1.0 V) was applied to the electrode and the current was monitored.

Vapor generation system: Different concentrations of vapor were obtained by mixing the saturated analyte vapor[2] at room temperature with delivery gas (fixed at 100 sccm by a mass flow controller). Either 250 mg of a solid analyte or 0.5 mL of a liquid analyte was placed in a 60 ml glass syringe for two hours for saturation (shown in Figure S1). The saturated analyte vapor at room temperature was infused by the syringe pump (NE-4000 New Era Pump System, Inc.) with different pumping rates. Table S1 shows vapor concentrations diluted from a certain flow rate of saturated vapor. The diluted concentration is calculated from the saturated concentration multiplied by the percentage of the analyte flow rate over the total flow rate.

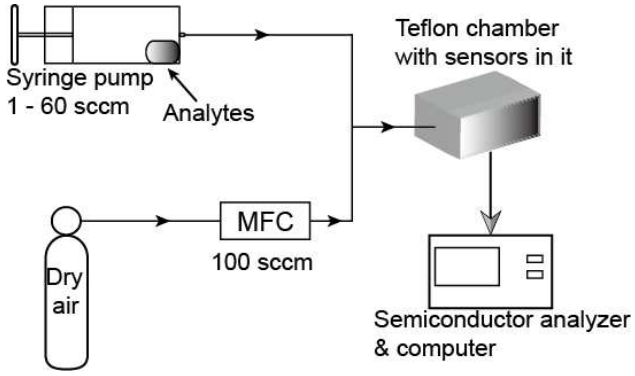

Figure S1. Vapor generation and delivery system.

Table S1. Vapor concentrations for Figure 2 and Figure S3.

	Vapor Pressure 23 °C (Torr)	Estimated Concentration	Analyte flow rate: 2 sccm	3 sccm	4 sccm	6 sccm	8 sccm
NT	4.02e-2	52.9 ppm	1.0 ppm	1.5 ppm	2.0 ppm	3.0 ppm	3.9 ppm

Table S2: Vapor concentrations for Figure 4.

	Vapor Pressure 23 °C (Torr)	Estimated Concentration	Analyte flow rate: 9 sccm	Analyte flow rate: 15 sccm	Analyte flow rate: 30 sccm
NT	4.02e-2	52.9 ppm	4 ppm	7 ppm	12 ppm
DNT	2.08e-4	274 ppb	23 ppb	36 ppb	63 ppb
TNT	4.12e-6	5.42 ppb	0.4 ppb	0.7 ppb	1.3 ppb

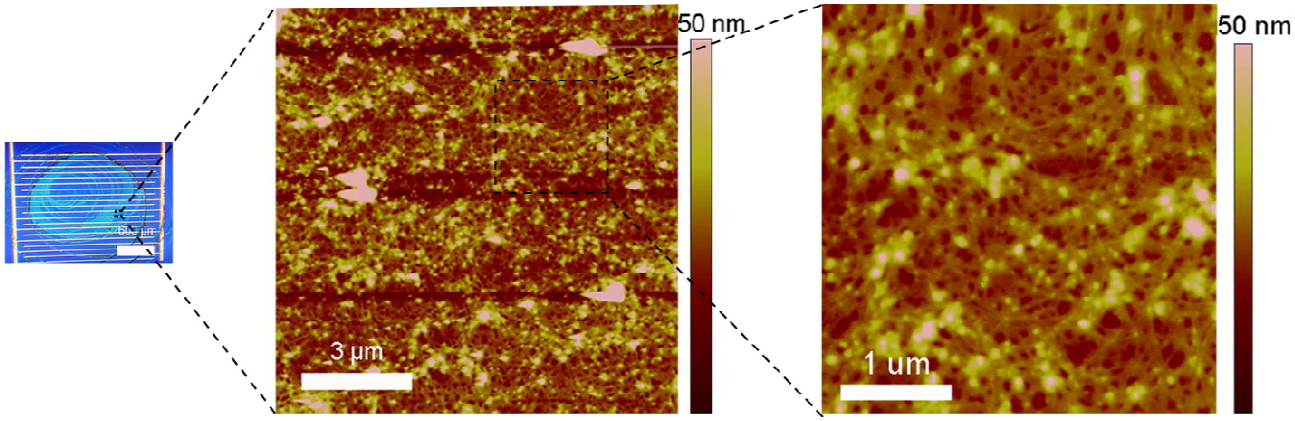

Figure S2. Optical microscope image (scale bar: 600 µm) and AFM images of the Tg-Car/CNT thin film drop-cast on IDEs.

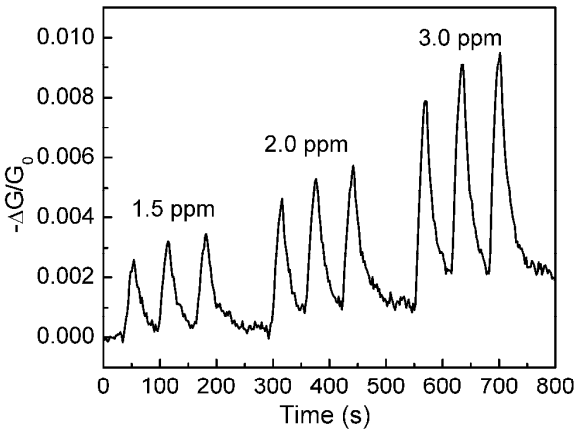

Figure S3. The real-time sensory response (without baseline correction, compared to the corrected data presented in Figure 2a) to NT at concentration of 1.5 ppm, 2.0 ppm, and 3.0 ppm (Table S1). Exposures to each concentration were repeated three times.

Calculation of the Limit of Detection:

A limit of detection (LOD) of 95 ppb for NT is calculated based on the following equation:

LOD = 3* rms_noise/slope.[3]

The slope is 0.0026, which is from the linear fitting the five points in the Figure 2b. The noise level (rms_noise) is 0.000082, which is calculated from the root-mean-square deviation of 15 data points from the baseline.

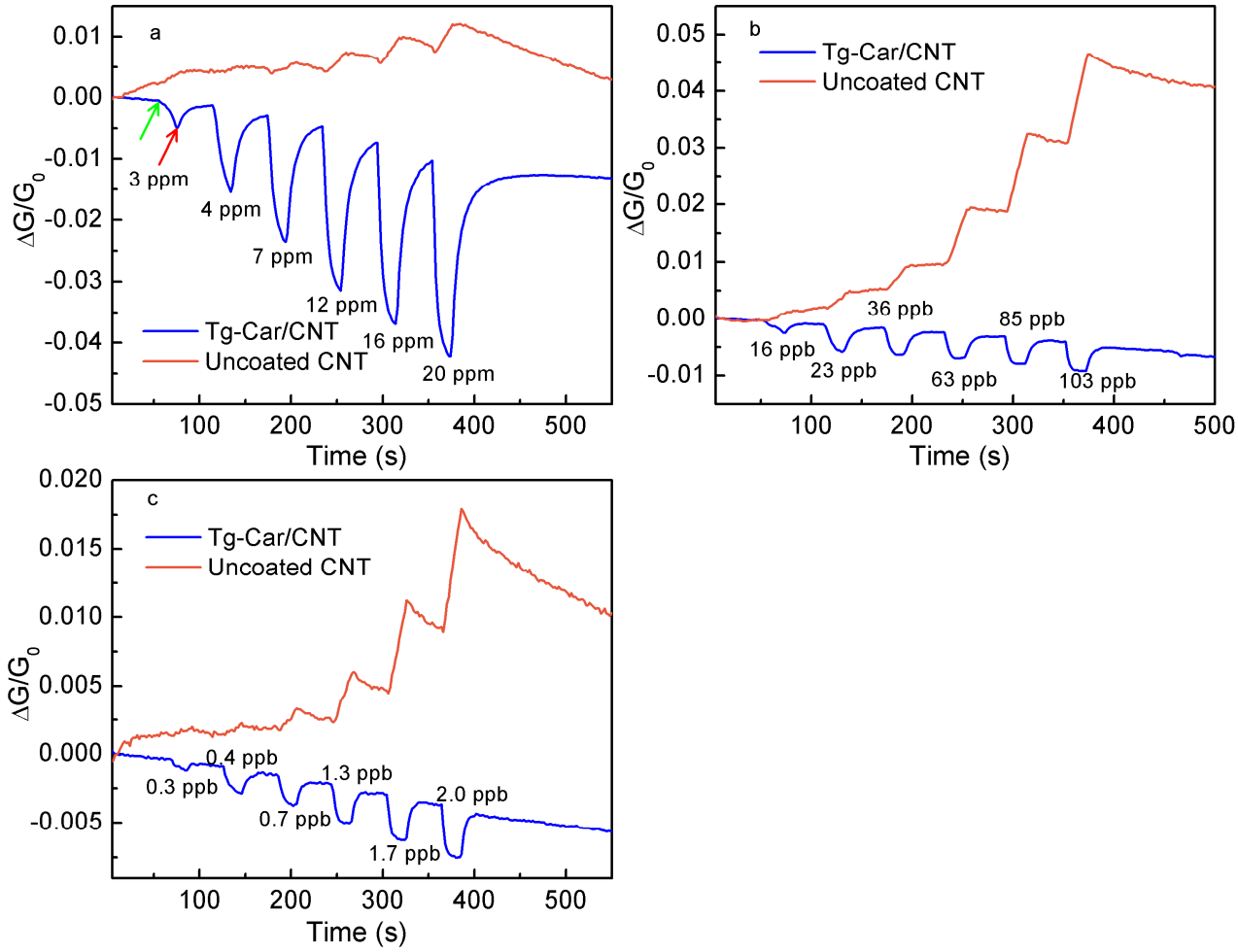

Figure S4. The sensory response of the Tg-Car/CNT sensors and the uncoated CNT sensors to (a) NT, (b) DNT and (c) TNT vapor at different concentrations diluted from 6 sccm, 9 sccm, 15 sccm, 30 sccm, 45 sccm, and 60 sccm of corresponding saturated vapor at room temperature. The green arrow represents the beginning of the exposure to an analyte and the red arrow represents the end of the exposure to an analyte. The time for the exposure to an analyte is 20 seconds and the recovery time is 40 seconds for each test.

Reference:

(1) Gross, D. E.; Moore, J. S. Arylene–Ethynylene Macrocycles via Depolymerization–Macrocyclization. Macromolecules **2011**, *44*, 3685-3687.
(2) Östmark, H.; Wallin, S.; Ang, H. G. Vapor Pressure of Explosives: A Critical Review. Propellants, Explos., Pyrotech. **2012**, *37*, 12-23.
(3) Li, J.; Lu, Y.; Ye, Q.; Cinke, M.; Han, J.; Meyyappan, M. Carbon Nanotube Sensors for Gas and Organic Vapor Detection. Nano Lett. **2003**, *3*, 929-933.