Robust Cyclohexanone Selective Chemiresistors Based on Single-Walled Carbon Nanotubes

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Robust Cyclohexanone Selective Chemiresistors based on Single-Walled Carbon Nanotubes

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Abstract

Functionalized SWCNT-based Chemiresistors are reported for highly robust and sensitive gas sensor to selectively detect cyclohexanone, a target analyte for explosive detection. The trifunctional selector has three important properties: it non-covalently functionalizes SWCNTs with cofacial π- π interactions, it binds to cyclohexanone via hydrogen bond (mechanistic studies were investigated), and it improves the overall robustness of SWCNT-based chemiresistors (e.g. humidity and heat). Our sensors produced reversible and reproducible responses in less than 30 sec to 10 ppm of cyclohexanone and displayed an

average theoretical limit of detection (LOD) of 5 ppm.

Introduction

Detection of explosives, chemical and biological agents at trace levels as well as at stand off distances, has the potential to thwart terrorist activities. **(*1*)** Cyclotrimethylene trinitramine (RDX) was the second most produced explosive during World War II and is still widely used today. **(*1*)** However, vapors of RDX are difficult to detect due to its extremely low equilibrium vapor pressure of 6 parts-per-trillion (ppt) at 25 °C. **(*2*)** Current methods for detecting RDX such as mass spectroscopy and gas chromatography have high sensitivity and selectivity but are expensive, bulky and require highly trained personnel for operation and data analysis. **(*1*)** An alternative approach to direct detection of RDX, is the detection of cyclohexanone, a chemical used to recrystallize RDX. **(*3*, *4*)** Cyclohexanone has a significantly higher equilibrium vapor pressure of 5000 parts-per-million (ppm) at 25 °C in comparison to RDX. **(*5*)** Previous studies have shown that cyclohexanone has a flux rate from land mines ranging from 1.1 to 98 g/(cm^2 sec x 10^{13}) with varying soil type (soil and clay). **(*6*)**

Herein we describe a method that uses chemically functionalized single-walled carbon nanotubes (SWCNTs) to detect cyclohexanone with a theoretical detection limit of 5 ppm. This method uses highly conductive SWCNTs that experience resistive changes upon exposure to the analyte to yield a small, low power, and simple sensor. **(*7*, *8*)** Although SWCNTs are promising materials for vapor sensing, they currently have limitations. Pristine (unfunctionalized) SWCNTs-based sensors lack selectivity towards analytes that display low adsorbance affinity to the nanotube's graphene surfaces. **(*7*)** Additionally, the often weak adhesion of the SWCNT to the sensor's substrate can lead to structural changes during a sensor's lifecycle that affect performance. (***7*, *9***) To impart selectivity, SWCNTs are often covalently or non-covalently functionalized. **(*8*, *10–19*)** Covalent functionalization creates a robust structure, but reduces the electrical conductivity (lowers carrier mobility) of SWCNTs as a result of the introduction of defects in the π-system. Previous research in our lab has also developed covalently functionalized SWCNT-based sensors to detect cyclohexanone and investigated a number of related receptors. (***20***) Considering that most sensing schemes involve analyte/π-system interactions and therefore increase the resistance of the SWCNTs, beginning with a low resistance generally provides for higher sensitivity sensors. Alternatively, non-covalent functionalization can provide for minimal changes in the SWCNTs electronic properties, but during a sensor's lifecycle these compositions can undergo structural changes with multiple thermal and chemical treatments that change the sensory performance. As a result, there is a need for SWCNT-based sensors wherein the nanotube-receptor structure is fixed in place without the need for covalent functionalization of the sidewalls.

In this study, we non-covalently functionalize SWCNTs by dispersing the nanotubes in a medium of selectors (Figure 1a). The selectors are designed to recognize significant aspects of the analytes chemical structure/properties and we find that trifunctional selector **1a** produces that best overall sensory properties. In addition to hydrogen bonding element selector **1a** employs bis(trifluoromethyl) aryl group, which has been found to π -π stack with aromatic molecules (***21***), and thereby provides a non-covalent interaction with SWCNTs. Selector **2a** uses pyrene, which is well known to interact with graphene surface of SWCNTs (***8***, ***17***, ***22***). Additionally, the SWCNT network presented in this study is immobilized (fixed) through the polymerization of the alkoxyl silyl groups attached to the selectors to create materials suited for demanding solution sensing in high sheer flows.

Results and Discussion

To address the current limitations of SWCNT-based sensors we have designed and synthesized trifunctional selectors that enhance the selectivity, sensitivity, and robustness of the resultant devices. Figure 1b shows the conceptual hypothesis behind the trifunctional selector. The preferred selector identified in this study has three important units: the first component is a bis(trifluoromethyl) aryl group, which promotes non-covalent functionalization of the SWCNTs with cofacial π- π interactions. The second component is a thiourea receptor that is known to bind to ketones via two point hydrogen bonding and has been used to detect cyclohexanone previously. (***20*, *23***) The third component is a triethoxysilane (TES) group that reacts to creates a polymer network structure and also reacts with hydroxyl groups on the surface of glass (***24***) thereby immobilizing both the SWCNT and receptors to produce a highly stable device.

Sensory devices are produced by dispersing SWCNTs and a selector (Figure 1a) with ultra-sonication in tetrahydrofuran (THF) and then dropcasting the solution between two gold electrodes separated by 300 μm. The hydrolysis/polymerization of the TES groups appears to occur under ambient conditions (***25***) and to demonstrate the simplicity of the method we did not introduce any special conditions to enhance this process. Our rationale is that only small amounts of TES are present and the high surface area of the composite structures promotes the hydrolytic reactions. Studies demonstrating insensitivity to humidity (*vide infra*) also suggest that the structures are fixed quickly upon fabrication. Sensing studies are performed by applying a small constant bias voltage (50 mV) using a potentiostat between the electrodes and the amount of material deposited was determined by reaching a target resistance between 26 kΩ-250 kΩ. For controlled vapor delivery the sensor is inserted into a Teflon enclosure and analyte vapors in a nitrogen carrier gas are flowed over the sample while the current is monitored.

Upon exposure to cyclohexanone, there is an instant increase in resistance for both pristine SWCNTs-based sensors and our functionalized SWCNTs-based sensors. For pristine

SWCNTs-based sensors the sensor response is likely the result of the cyclohexanone’s dipole interacting with the cationic carriers (holes) that are present as a result of oxidative (air oxidation) doping. The reduction in the intra-SWCNT conductance is consistent with the pinning and/or scattering of the holes by the carbonyl dipole. It is also possible that absorption of the cyclohexanone increases the resistance between SWCNTs either by swelling the network to give wider tunneling barriers or through dipolar induced changes the energetics of key intertube conduction pathways that are possibly associated with defect sites. Considering the intrinsic sensitivity of SWCNTs to a wide range of molecules, it is important that a selector enhance the sensitivity to a select analyte or analyte class. In the simplest mechanism the selector enhances the response by simply binding the analyte and effectively concentrating it in the SWCNT network. Alternatively the selector can have a more active role in modifying carrier transport. Specifically the sulfur of the thiourea displays dipolar interactions with the nanotubes and binding of these groups to the SWCNTs networks increases the resistance. However, the hydrogen-bonded complex with cylohexanone will give an enhanced collective dipole (Scheme 1) that will further pin or scatter carriers for increased sensitivity.

Scheme 1

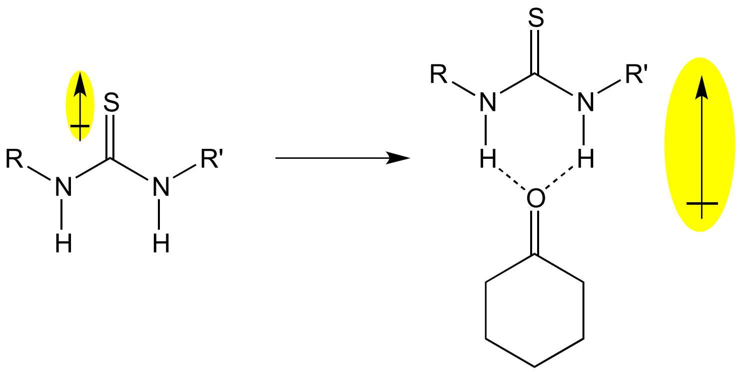

Figure 1c shows a plot of normalized conductance ($-\Delta G/G_0$) responses of SWCNT-based sensors with trifunctional selector **1a** to various concentrations of cyclohexanone. We applied minor base-line-correction to all the data collected in this study to account for the linear current drift of the sensor. As shown, our sensors display real-time detection of cyclohexanone with reversible responses and fast recovery rates. The inset figure displayed a linear concentration-dependent change in resistance. Six sensors were capable of reproducible detection of cyclohexanone 10 ppm and displayed an average theoretical limit of detection (LOD) of 5 ppm. The LOD calculations were based on established procedures described in the Supporting Information (SI). (***26***)

Other trifunctional selectors and control compounds investigated make use of pyrene moieties (**2a** and **2b**) that are well known in the non-covalent functionalization of the SWCNTs by π- π interactions. (***8***, ***17***, ***22***) These trifunctional selectors allow for stable dispersions of SWCNTs to be prepared in THF. As a result of the strong association of the pyrene to the SWCNTs, these sensors were subjected to aggressive treatments to determine the robustness. Three sensors were fabricated from 0.02 mg/mL of **2a** and SWCNTs (2:1 wt ratio) were subjected to overnight treatments to best hydrolyze/polymerize the TES group (ambient conditions, ambient conditions after exposing to HCl vapor from the headspace of 12 M HCl solution, and heating at 80 °C under reduced pressure). These sensors were then sonicated (20 min) in methanol and we found that only the heat treated sensors survived. Most importantly we found that the 80° C pretreatment does not affect the device sensitivity (**Figure S-3a**). The pyrene anchors in **2a** were highly effective in immobilizing the SWCNTs on the surface of the substrate such that it can withstand harsh conditions (e.g. ultra-sonication) without detaching from the substrate (**Figure S-3b**). Although the device stability with these trifunctional selectors **2a** is exceptional, the sensitivity and selectivity was poor and the resultant devices displayed ketone responses that are equivalent to pristine SWCNTs. Therefore, we have focused on **1a** with the bis(trifluoromethyl) aryl group for the non-covalent attachment of the receptors to the SWCNTs. The role of (trifluoromethyl) aryls goes beyond promoting associations with the SWCNTs and also extends to the recognition process. Specifically, the inductive effects of the CF_3 groups cause the thiourea's protons to be more acidic, thereby rendering a more sensitive and selective device towards cyclohexanone. **(*27*)** The interactions between cyclohexanone and the thiourea moiety are shown in **Figure 2b**. Each sensor was placed in a sensor array and simultaneously exposed to 1% cyclohexanone. Both selectors **1a** and **1b** (a homolog without a TES group) showed over 2-fold increases in sensitivity to cyclohexanone in comparison to pristine SWCNTs. Note that selector **1a** also exhibits approximately the same response as selector **1b**, therefore, suggesting that cyclohexanone does not interact strongly with TES. Selector **1a**'s slight decrease in response could be the result of the polymeric/surface chemistry limiting the interactions with the SWCNTs and this can result in fewer selectors residing on or directly proximate to the π-surface of the SWCNTs. To prove that the primary interaction of cyclohexanone is through the hydrogen bonding with the thiourea receptor, we prepared methylated thiourea receptors. Monomethylated selector (**1c**) showed 39% decrease in the response, with respect to selector **1b**. Selector **1d**, in which both hydrogens of the thiourea are replaced with methyl groups, displays an additional 21% decrease in response and effectively produces a response that is equivalent to pristine SWCNTs. Based upon these structure activity relationships it appears that cyclohexanone interacts with the thiourea receptor via hydrogen bonding. This binding in turn causes an increase in the resistance of the functionalized SWCNTs network.

Our investigations of the selectivity of sensors formed from SWCNTs with and without selector **1a** are summarized in Figure 3a. Each sensor was placed in an array and was exposed to 1% vapor concentration of various analytes (acetone, ethyl acetate, hexane, toluene, benzene, ethanol, and acetonitrile). We chose to test these particular interfering analytes because they can be commonly found in tobacco smoke, nail polish, alcoholic beverages, gasoline, lotion, perfume, etc. The pristine SWCNTs exhibited low sensitivity and selectivity to various analytes compared to functionalized SWCNTs. Functionalizing the SWCNTs selectively enhanced their sensitivity toward the analytes that are capable of hydrogen bonding interactions with the thiourea receptor. In accord with our expectations, the sensor exhibited the highest sensitivity enhancement towards cyclohexanone. Note that cyclohexanone displays the lowest vapor concentration, but produces the highest resistive change in comparison to other analytes. We find that sensors produced from **1a** and SWCNTS are particularly sensitive towards cyclohexanone.

We have also investigated the stability and sensitivity of our devices towards mechanical damage by sonication, heat and humidity, because we anticipate that useful sensors will need to withstand extreme conditions (e.g. deserts, sweltering delivery trucks containers, etc.). To evaluate the mechanical robustness of the devices, we submerged sensors into methanol and exposed them to prolonged ultra-sonication (20 min). As mentioned earlier, the pyrene groups provided a strong anchor and survived these harsh conditions with pretreatment of heat. However, devices using selector **1a** did not withstand ultra-sonication conditions even after catalytic efforts to hydrolyze/polymerize TES group by heating devices overnight at 80°C under reduced pressure. To assess the device's thermal resistance each sensor was placed in an array and simultaneously exposed to a 1% vapor concentration of cyclohexanone. The sensors were then heated at 80°C for 11 hrs under reduced pressure, allowed to cool, and re-exposed to 1% vapor concentration of cyclohexanone. We observed enhanced robustness with respect to heat from the SWCNT devices functionalized with TES (**Figure 3b**). After the long duration of heating, sensors with selector **1b** showed 60% decrease in sensitivity whereas sensors with selector devices **1a** showed a 27% decrease in sensitivity, and a response still at least 2-fold better than pristine SWCNTs. The surface linkages and networks formed from TES oligomerization likely prevent selector **1a** from phase separating from the SWCNT's surface or decomposing under high temperature conditions. To examine the sensor's stability under humid conditions, the devices experienced prolonged exposure to relative humidity ranging from 0% to 80% (**Figure S-4a**). At 80% relative humidity, six sensors with selector **1a** had an average resistive change of 20% ± 4% while six pristine SWCNTs sensors had an average resistive change of 47% ± 8%. The trifunctional selector **1a** provides a longstanding SWCNT network that is less probable of SWCNT moving disrupting the SWCNT contacts thus increasing the SWCNT network's resistance. The sensors using selector **1a** that experienced a small change in resistance upon prolonged high humidity conditions showed no significant decrease in sensitivity towards cyclohexanone average conductive changes after devices were exposed to 1% vapor concentration of cyclohexanone with relative humidity ranging from 0% to 80% (**Figure S-4b**).

Conclusion

In summary, we have shown through experimentation that trifunctional selectors can be used to create robust SWCNT chemiresistors with useful response to the explosives signature cyclohexanone. Sensors using selector **1a** displayed the best responses and structure property relationships suggest that the ability of these materials to detect cyclohexanone is the result of selective hydrogen bonding. The resultant robust sensors were able to withstand high temperature and humidity and displayed reversible, reproducible, responses in less than 30 sec to 10 ppm of cyclohexanone. The design strategies of the trifunctional selectors described establish the foundation for the design and fabrication of selective SWCNT-based gas and liquid sensors with exceptional stability and robustness.

Experimental Section

Glass slides were sonicated in acetone (30 min) and treated with an oxygen plasma (5 min) from Harrick Plasma. The glass slides were then placed into the thermal deposition (Angstrom Engineering) with a home-made stainless steal mask on top. Chromium adhesive layers (10 nm) and gold electrodes (75 nm) were deposited onto the surface of the glass with a gap (300 μm) between the metal electrodes. SWCNTs were purchased from Sigma- Aldrich (≥70% purity and 0.7-1.3nm diameter). Before using SWCNTs, they were treated with concentrated hydrochloric acid and washed with deionized water. The SWCNTs were then dried (200 °C) under reduced pressure and stored in dry atmosphere. Solutions (0.02 mg/mL SWCNT and 0.4 mg/mL selector) of selector/SWCNT (20:1 wt ratio) in THF were produced by ultra-sonication (5 min). Approximately 0.1 μL of the solution was dropcast between the gold electrodes until a resistance range (26 kΩ-250 kΩ) was achieved. The sensor chips were allowed to dry (30 min at 40 °C) under reduced pressure before any sensing measurements. After drying, the devices were placed in a small Teflon enclosure and a small voltage (50 mV) was applied from a potentiostat (PalmSens:EMStatMUX16). The current passing through the sensors was monitored while exposing it to various analytes (with dry nitrogen as the carrier gas) four consecutive times for 30 sec with a recovery time of 1 min and the sensors were examined in triplicate. The gas mixtures were produced by KIN-TEK gas generator system. In the sonication study, the devices were placed in a beaker full of methanol and experienced ultra-sonication (20 min). Synthesis of selectors can be found in the SI. The selectors were confirmed using Bruker 400 MHz and 401 MHz nuclear magnetic resonance (NMR) and high-resolution mass spectrometer.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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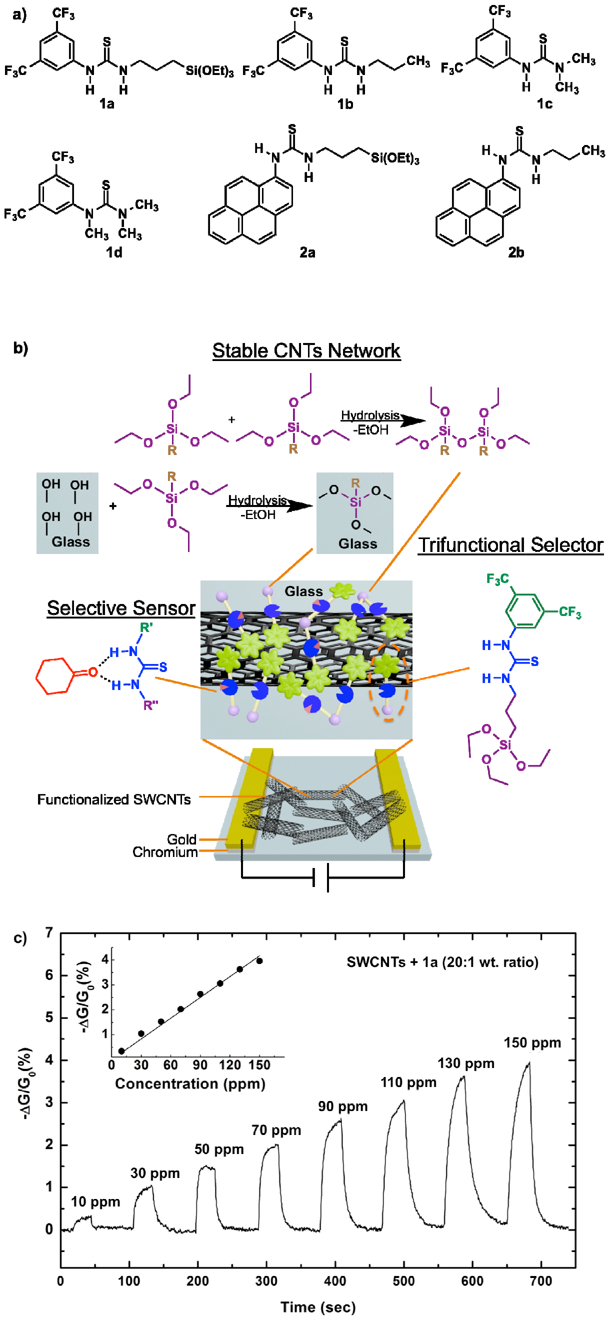

Figure 1. a) Diagram of selectors' chemical structure presented in this study. b) Schematic diagram of sensing mechanism. c) Normalized conductive change ($-\Delta G/G_0$ (%)) of SWCNT-based sensor with trifunctional selector **1a** towards cyclohexanone at varying concentrations. The inset figure shows the magnitude of the normalized conductive change as a function of concentration of cyclohexanone.

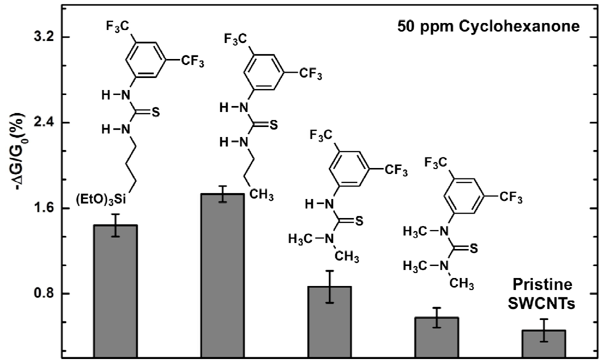

Figure 2. The normalized average conductive change (-ΔG/G$_0$ (%)) of SWCNT-based sensors with different selectors to 50ppm cyclohexanone. The vertical error bars represent the standard deviation from the average based on three sensors exposed to 50 ppm cyclohexanone 4 times for 30 seconds.

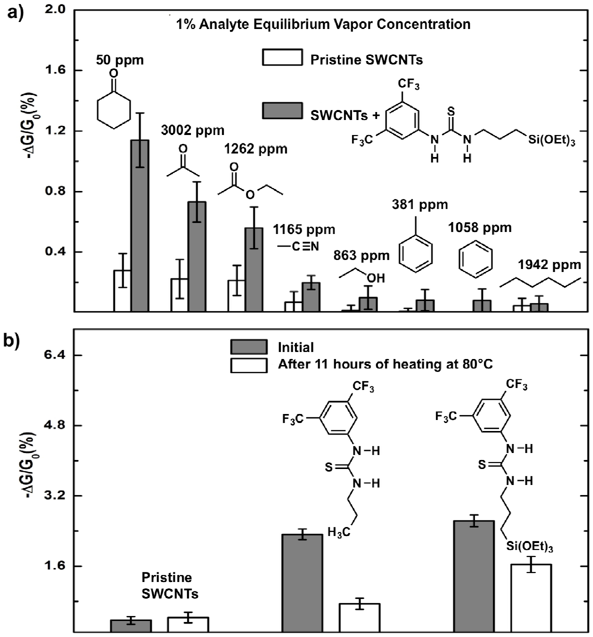

Figure 3. a) The plot of normalized average conductive changes (-ΔG/G$_0$ (%)) of SWCNT-based sensors with or without trifunctional selector **1a**. The sensors were exposed to various analytes at 1% equilibrium vapor concentration. b) The plot of normalized average conductive

change ($-\Delta G/G_0$ (%)) of SWNCT-based sensors with different selectors to 50 ppm cyclohexanone before and after 11 hours of heating at 80°C under reduced vapor pressure.

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References

(1) Moore, D. S. Instrumentation for trace detection of high explosives. *Review of Scientific Instruments* **2004**, *75*, 2499–2512.

(2) Kolla, P. The Application of Analytical Methods to the Detection of Hidden Explosives and Explosive Devices. *Angewandte Chemie International Edition in English* **1997**, *36*, 800–811.

(3) Lai, H.; Leung, A.; Magee, M.; Almirall, J. R. Identification of volatile chemical signatures from plastic explosives by SPME-GC/MS and detection by ion mobility spectrometry. *Anal Bioanal Chem* **2010**, *396*, 2997–3007.

(4) O'Reilly, W. F.; Jenkins, T. F.; Murrmann, R. P.; Leggett, D. C.; Barrierra, R.; COLD REGIONS RESEARCH AND ENGINEERING LAB HANOVER NH *Exploratory Analysis of Vapor Impurities from TNT, RDX and Composition B.*; Defense Technical Information Center: Ft. Belvoir, 1973.

(5) Yaws C. L. *The Yaws handbook of vapor pressure: Antoine coefficients*; Gulf Pub., 2007.

(6) Jenkins, T. F.; U.S. Army Mobility Equipment Research and Development Center *Detection of cyclohexanone in the atmosphere above emplaced antitank mines*; Corps of Engineers, U.S. Army Cold Regions Research and Engineering Laboratory: Hanover, N.H., 1974.

(7) Zhang, T.; Mubeen, S.; Myung, N. V.; Deshusses, M. A. Recent progress in carbon

nanotube-based gas sensors. *Nanotechnology* **2008**, *19*, 332001.

(8) Schnorr, J. M.; Swager, T. M. Emerging Applications of Carbon Nanotubes†. *Chem. Mater.* **2011**, *23*, 646–657.

(9) Su, H.-C.; Chen, C.-H.; Chen, Y.-C.; Yao, D.-J.; Chen, H.; Chang, Y.-C.; Yew, T.-R. Improving the adhesion of carbon nanotubes to a substrate using microwave treatment. *Carbon* **2010**, *48*, 805–812.

(10) Cui, S.; Pu, H.; Lu, G.; Wen, Z.; Mattson, E. C.; Hirschmugl, C.; Gajdardziska-Josifovska, M.; Weinert, M.; Chen, J. Fast and Selective Room-Temperature Ammonia Sensors Using Silver Nanocrystal-Functionalized Carbon Nanotubes. *ACS Appl. Mater. Interfaces* **2012**, *4*, 4898–4904.

(11) Shi, D.; Wei, L.; Wang, J.; Zhao, J.; Chen, C.; Xu, D.; Geng, H.; Zhang, Y. Solid organic acid tetrafluorohydroquinone functionalized single-walled carbon nanotube chemiresistive sensors for highly sensitive and selective formaldehyde detection. *Sensors and Actuators B: Chemical* **2013**, *177*, 370–375.

(12) Qi, P.; Vermesh, O.; Grecu, M.; Javey, A.; Wang, Q.; Dai, H.; Peng, S.; Cho, K. J. Toward Large Arrays of Multiplex Functionalized Carbon Nanotube Sensors for Highly Sensitive and Selective Molecular Detection. *Nano Lett.* **2003**, *3*, 347–351.

(13) Staii, C.; Johnson, A. T.; Chen, M.; Gelperin, A. DNA-Decorated Carbon Nanotubes for Chemical Sensing. *Nano Lett.* **2005**, *5*, 1774–1778.

(14) Chen, L.; Xie, H.; Yu, W. Functionalization Methods of Carbon Nanotubes and Its Applications. In *Carbon Nanotubes Applications on Electron Devices*; Marulanda, J. M., Ed.; InTech, 2011.

(15) Bekyarova, E.; Davis, M.; Burch, T.; Itkis, M. E.; Zhao, B.; Sunshine, S.; Haddon, R. C. Chemically Functionalized Single-Walled Carbon Nanotubes as Ammonia Sensors†. *J. Phys. Chem. B* **2004**, *108*, 19717–19720.

(16) Kong, L.; Wang, J.; Luo, T.; Meng, F.; Chen, X.; Li, M.; Liu, J. Novel pyrenehexafluoroisopropanol derivative-decorated single-walled carbon nanotubes for detection of nerve agents by strong hydrogen-bonding interaction. *Analyst* **2010**, *135*, 368–374.

(17) Karousis, N.; Tagmatarchis, N.; Tasis, D. Current Progress on the Chemical Modification of Carbon Nanotubes. *Chem. Rev.* **2010**, *110*, 5366–5397.

(18) Dionisio, M.; Schnorr, J. M.; Michaelis, V. K.; Griffin, R. G.; Swager, T. M.; Dalcanale, E. Cavitand-Functionalized SWCNTs for N-Methylammonium Detection. *J. Am. Chem. Soc.* **2012**, *134*, 6540–6543.

(19) Wang, F.; Swager, T. M. Diverse Chemiresistors Based upon Covalently Modified Multiwalled Carbon Nanotubes. *J. Am. Chem. Soc.* **2011**, *133*, 11181–11193.

(20) Schnorr, J. M.; van der Zwaag, D.; Walish, J. J.; Weizmann, Y.; Swager, T. M. Sensory Arrays of Covalently Functionalized Single-Walled Carbon Nanotubes for Explosive Detection. *Advanced Functional Materials* **2013**.

(21) Liu, J.; Wendt, N. L.; Boarman, K. J. Trifluoromethyl Groups in Crystal Design of 1,4-Diphenyl-1,3-butadienes for Topochemical [2 + 2] Photodimerization. *Org. Lett.* **2005**, *7*, 1007–1010.

(22) Lerner, M. B.; Resczenski, J. M.; Amin, A.; Johnson, R. R.; Goldsmith, J. I.; Johnson, A. T. C. Toward Quantifying the Electrostatic Transduction Mechanism in Carbon Nanotube Molecular Sensors. *J. Am. Chem. Soc.* **2012**, *134*, 14318–14321.

(23) Cox, J. R.; Mu□ller, P.; Swager, T. M. Interrupted Energy Transfer: Highly Selective Detection of Cyclic Ketones in the Vapor Phase. *Journal of the American Chemical Society* **2011**, *133*, 12910–12913.

(24) Haensch, C.; Hoeppener, S.; Schubert, U. S. Chemical modification of self-assembled silane based monolayers by surface reactions. *Chemical Society Reviews* **2010**, *39*, 2323.

(25) Yang, Y.; Bittner, A. M.; Baldelli, S.; Kern, K. Study of self-assembled triethoxysilane thin films made by casting neat reagents in ambient atmosphere. *Thin Solid Films* **2008**, *516*, 3948–3956.

(26) 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.

(27) Pihko, P. M. *Hydrogen Bonding in Organic Synthesis*; John Wiley & Sons, 2009.

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