Employing Halogen Bonding Interactions in Chemiresistive Gas Sensors

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Employing Halogen Bonding Interactions in Chemiresistive Gas Sensors

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Supporting Information Placeholder

ABSTRACT: This paper reports the use of halogen bonding interactions for gas-phase detection of pyridine in SWCNT-based chemiresistive sensors with sub-ppm theoretical detection limits. The chemiresistors are prepared by solvent-free ball-milling of single-walled carbon nanotubes (SWCNTs) and aryl halide-based selectors, compression into a pellet, and subsequent mechanical abrasion between gold electrodes on paper. The sensing responses reflect halogen bonding trends, with few exceptions. The predominant signal transduction mechanism is likely attributed to swelling of the insulating haloarene matrix.

KEYWORDS: halogen bonding, carbon nanotubes, gas sensors, chemiresistors, aryl halides

An ideal chemical sensor rapidly communicates small changes in chemical environment with selectivity and predictability. Currently, the most common methods for molecular detection and identification rely on high-performance liquid chromatography-mass spectrometry (HPLC-MS) or gas chromatography-mass spectrometry (GC-MS), both of which demand considerable resources — time, power, money, and physical space. Thus, the development of sensors that are rapid, low-power, inexpensive, robust, simple to use, and portable are highly desired. The resulting technology would have tremendous impact in environmental monitoring, diagnostic medicine, agriculture, food processing, and homeland security.

Carbon nanotubes (CNTs) are promising materials for chemical sensors as a result of an electronic structure that is sensitive to slight changes in local chemical environment. Additional advantages of CNTs for their application in chemical sensors are their nanoscale physical size, high electrical conductivity, remarkable strength, and extraordinary specific surface area. Furthermore, the chemistry for covalently and noncovalently functionalizing CNTs is well established, enabling the facile introduction of selectivity to the sensors.

A number of device architectures are available to exploit the high electronic sensitivity of CNTs, including resistors, field-effect transistors, and capacitors. The simple nature of a direct current measurement with only two electrical contacts (source and drain) makes the chemiresistor an attractive architecture for sensors (Figure 1). The advantages of this simple design include portability, ease of use, low cost, and suitability for operation at room temperature. When located between two electrodes, individual CNTs or networks of CNTs can be considered a variable resistor whose resistance is modulated by changes in the chemical composition of their surrounding environment.

Figure 1. A) Schematic of a chemiresistor based on a randomly oriented network of CNTs deposited between two electrodes. B) Proposed sensing mechanism based on swelling of haloarene matrix upon exposure to pyridine.

The CNT networks can be deposited into a device using several approaches, including direct growth on substrates, deposition of dispersions, Langmuir–Blodgett, dip coating, and electrophoresis. However, there are a number of drawbacks to these methods, including the dependence on expensive, specialized equipment for growing CNTs directly on substrates. For solution-based methods, the main obstacles are the need for solution processing, the poor solubility of CNTs in most solvents, and the limited stability of dispersions of CNTs. Our group has reported the mechanical abrasion of compressed CNT composites on various substrates to overcome these difficulties.
Although highly sensitive, SWCNT-based sensors often suffer from a lack of selectivity. A strategy to address this concern utilizes covalent or noncovalent functionalization of SWCNTs with small molecules or polymers. Hydrogen-bonding motifs are often employed to introduce selective enhancement of signals towards targeted analytes. This approach, however, has limited selectivity, as many potential interferents can compete with target analytes through hydrogen bonding. Thus, expansion of strategies for molecular recognition of analytes with SWCNT-based sensors would enable the improved design of selective and sensitive gas sensors based on cross-reactive arrays.

We introduce halogen bonding moieties into our chemiresistive sensors to complement traditional hydrogen bonding motifs. Halogen bonds (XBs) are generally described as electrostatic interactions between an electronegative halogen atom (XB donor) and a Lewis base (XB acceptor). The nature of halogen bonding is rooted in the σ-hole of the halogen, a positive potential along the R–X bond axis. The σ-hole becomes more positive — and the halogen bonding interaction becomes stronger — as i) X is less electronegative, ii) X is more polarizable, and iii) R is more electron-withdrawing. It is important to note that the σ-hole forces halogen bonding interactions to be highly directional: the R–X···Y bond angle is approximately 180°. This restriction is in stark contrast to traditional hydrogen bonds and halogen--halogen bonds.

Halogen bonding offers an untapped new dimension of selectivity in the creation of cross-reactive sensing arrays. Many years after its discovery, the discovery of XB adducts has led to modern advances in crystal engineering, liquid crystals, and anion sensing. Exploiting these strong N–X halogen bonding interactions, we envisioned the detection of nitrogen-containing heterocycles (e.g., pyridines) using rationally designed CNT-based chemiresistive sensors incorporating aryl iodides as “selectors.”

We fabricated the sensors employed in this study using our previously reported fabrication techniques PENCIL (Process Enhanced NanoCarbon for Integrated Logic) and DRAFT (Deposition of Resistors with Abrasion Fabrication Technique). Briefly, selectors and pristine SWCNTs were combined in a 2:1 mass ratio, respectively, ball-milled for five minutes at 30 Hz, and compressed into a pellet at 10 MPa for one minute. The pellet was then mechanically abraded between thermally evaporated gold electrodes (120 nm thick with a 1 mm gap between the electrodes) on weighing paper (i.e., highly compressed cellulose) to attain resistances between 30 and 100 kΩ. It is important to note that the values of the resistance did not affect the relative sensing response, as long as the measured resistances were within the same order of magnitude.

We chose the aryl halides in this preliminary study based on their relative ambient stability, their commercial availability, and the following hypotheses: 1) the sensing response of the selectors follows Cl < Br < I, consistent with solution-phase studies and corresponding to the polarizability of the XB donor; 2) electron-deficient aryl halides are stronger XB donors than electron-rich aryl halides; and 3) longer alkyl chains increase the interaction between the nanotubes and the selector material, as a result of the geometrical fit between alternating methylene groups on the alkyl chain and the centers of the CNTs’ hexagonal rings.

We first investigated the p-dihalobenzene series, as shown in Figure 2. p-Dichlorobenzene, p-dibromobenzene, and p-diiodobenzene were chosen over the ortho and meta isomers because the para isomers exist as solids at room temperature and exhibit lower volatility compared to their ortho- and meta- substituted counterparts. This property is necessary to produce mechanically robust PENCILs for abrading a film on paper. As predicted, the sensing response intensifies as the polarizability of the halogen increases. This observation is consistent with solution-phase studies. For the p-diiodobenzene composite, a maximum response is obtained upon exposure to only 3 ppm pyridine (ΔG/G = 5.1 ± 0.9%). The response to pyridine for the chloro- and bromoderivatives rises as the concentration of pyridine is increased to 25 ppm. In all cases, the response to pyridine is significantly greater than the control sensors fabricated with pristine CNTs in the absence of a selector (p-CNTs), where the response was only 1.5 ± 0.3 % at 25 ppm. We calculated the theoretical limits of detection for pyridine of p-diiodobenzene–, p-dibromobenzene–, and p-dichlorobenzene-based composites to be 16, 37, and 92 ppb, respectively. These values exceed previously reported detection limits for pyridine by at least 10-fold.

We attribute the significant enhancement of the response with the composites as compared to the pristine CNT control to the swelling of the haloarene matrix. Increased affinity for the vapor leads to increased swelling. The resulting increased intertube distance leads to the attenuation of conductivity that is observed as the sensing response. Such swelling mechanisms have been previously reported in the literature with non-covalently functionalized CNTs. While it is possible that there is some covalent functionalization of the CNTs induced by ball milling with “selectors,” the relatively low resistances that we observe are inconsistent with a substantial degree of covalent functionalization. Furthermore, experiments performed by reacting CNTs with diazonium salts of haloarenes formed in situ failed to result in the enhancements we observe with the non-covalent mixture of aryl halide and CNTs, as described in the Supporting Information.
were 150 and 240% greater than the durene composite and pristine CNT controls in response to 25 ppm pyridine and 110% and 210% greater in response to 25 ppm picoline, respectively. Attempts for gas-phase sensing of other commercially available electron-rich or electron-poor pyridine derivatives were unsuccessful as a result of technical difficulties associated with the controlled generation of vapors from the selected compounds.

To supplement comparisons within the dihalobenzene and halodurene series, we investigated the effect of arenes’ electronics on the sensing response to pyridine, as shown in Figure S3. In addition to p-diodobenzene, 1,4-diiodotetrafluorobenzene and 1,4-diido-2,5-dimethoxybenzene were investigated as electron-deficient and electron-rich analogues, respectively. As the group attached to the halogen atom becomes more electron-withdrawing, the σ-hole of the halogen atom becomes more positive, creating a better XB donor. Indeed, 1,4-diiodotetrafluorobenzene has been used as an ideal XB donor in solution phase assembly.7 The N···I interaction of 4,4′-dipyridyl and 1,4-diiodobenzene in an infinite chain is 13.2 kJ/mol but is strengthened to 24.3 kJ/mol when 1,4-diiodotetrafluorobenzene is used as the XB donor.28,29 Conversely, the introduction of electron-donating groups results in a worse XB donor.30 As expected, the methoxy-bearing selector resulted in an attenuated signal relative to p-diiodobenzene, although the response was significantly greater than that of pristine carbon nanotubes. Surprisingly, the electron-withdrawing tetrafluoro-containing selector behaved similarly to the selector possessing the electron-donating methoxy groups. This unexpected behavior could be ascribed to a number of factors. The perhalogenated XB-donor could produce a coating repulsive to most organic analytes of interest, similar to the interactive orthogonality of the fluorous effect.30 The result would be diminished swelling effects and consequently weakened sensing response in the CNT composite. Alternatively, the introduction of four fluorine atoms changes the quadrupole moment of the benzene ring resulting in a different interaction with the carbon nanotubes. This interaction could alter the susceptibility of the CNTs to changes in local dipole moment or impose geometrical limitations on the halogen bonding interaction near
the nanotubes — i.e., the pyridine analyte is unable to comply with the strongly directional nature inherent to halogen bonding.

We also investigated the effect of alkyl chain length on the sensing response to pyridine, as shown in Figure S4. Longer alkyl chains could increase the interaction parameter between the carbon nanotubes and the selector, as a result of the geometrical fit between alternating methylene groups on the alkyl chain and the centers of the CNTs’ hexagonal rings. Using 1,4-didodecyl-2,5-diodobenzene as a selector produced a slightly greater response to pyridine than the xylene analogue. In addition to the greater interaction with the nanotubes, the dodecyl derivative is likely to exhibit greater swelling effects, which we expect to produce an increased sensing response. An additional benefit of the longer alkyl chain is the mechanical behavior of the composite pellet when depositing on paper. The pellet is robust enough to be easily manipulated by hand and abrades similar to a Crayon when abraded on the weighing paper. The ease with which uniform films are deposited likely explain the excellent reproducibility of this particular CNT composite sensor.

After assessing the trends associated with halogen bonding and carbon nanotube interactions, we investigated the response of our top selectors, 3-iododurene and 1,4-didodecyl-2,5-diodobenzene, to elevated concentrations (> 1000 ppm) of hexanes, benzene, isopropanol, and acetonitrile in addition to varying low concentrations of pyridine (≤ 25 ppm). As displayed in Figure 4, both sensing composites responded more strongly to pyridine at a concentration of 1 ppm than to higher concentrations (> 1000 ppm) of the interferents. Interestingly, the composite with 3-iododurene produced a perceptible signal to hexanes and benzene. This result can almost certainly be attributed to swelling effects rather than local electronic changes near the carbon nanotubes. Exposure to acetonitrile resulted in no response, consistent with its significantly weaker interaction in halogen bonding in comparison to hexanes and pyridine as a result of the nitrogen’s sp hybridization.

In conclusion, we utilized halogen bonding in carbon nanotube-based chemiresistive sensors to selectively enhance the response to the Lewis base pyridine. The chemiresistors were prepared by ball milling of SWCNTs and selectors, compression into a pellet, and mechanical abrasion between gold electrodes onto paper. p-Dihalobenzences and 3-haloiododurene derivatives were investigated and exhibited sensing responses consistent with halogen bonding. The fundamental transduction mechanism of these sensors is likely based on swelling of the CNT composite, which is dictated by the affinity of the insulating selector matrix for the analyte. We believe that these sensors can offer halogen bonding as an additional dimension in CNT-based cross-reactive sensing arrays. The development of more complex selectors — those with multiple halogen bonding sites at calculated spacings — could facilitate the specific detection of biologically relevant N-heterocyclic compounds in solution.

ASSOCIATED CONTENT
Supporting Information
Supporting Information Available: The following file is available free of charge: se-2015-001846_SI.pdf. Details fabrication of sensors, acquisition of sensing data, and additional sensing traces and plots.

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Notes
The authors declare no competing financial interests.

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REFERENCES


