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.

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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 electrophilic 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.
Figure 2. A) Sensing responses of p-dihalobenzene–SWCNT composites to varying concentrations of pyridine in N₂ carrier gas at room temperature. Each type of sensor was examined in triplicate. The three traces for each type of sensor are overlaid to display reproducibility. For clarity, each series is displayed with a 20% offset. B) Magnitudes of sensing responses shown in (A). The vertical error bars represent the standard deviation from the mean based on three devices.

To further investigate consistency with the effect of halogen bonding, sensing experiments were performed with bromodurene and iododurene, as shown in Figure 3 and Figure S2. In addition to their decreased volatility compared to the p-dihalobenzenes for higher device stability, we observed that the composites containing durene derivatives behaved more like waxes, enabling them to be drawn onto devices more easily, analogous to "Crayons." A composite material with unsubstituted durene and the pristine CNT pellet were used as controls. These controls exhibited similar behavior with $\Delta G/G_0 = 0.7 \pm 0.2 \%$ at 4 ppm whereas the bromodurene and iododurene composites produced responses of 2.2 ± 0.1% and 3.2 ± 0.1%, respectively.

Sensing measurements were also carried out using 4-picoline (4-methylpyridine) as an analyte, as shown in Figure 3 and Figure S2. As a result of the electron-rich character relative to pyridine, an enhanced sensing response is predicted by previous solution phase studies on halogen bonding. Indeed, the sensing responses are significantly enhanced upon exposure to 25 ppm 4-picoline in comparison to 25 ppm pyridine; however, the pristine CNT and durene composite controls also exhibited an increase in the sensing response. Because the pristine carbon nanotube control lacks a swelling composite matrix, a greater propensity of 4-picoline to dedope the carbon nanotubes relative to pyridine is likely the operative mechanism that contributes most to the attenuated conductance. Signals for the iododurene composite 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.

Figure 3. Sensing response of halodurene series to varying concentrations of pyridine (left) and picoline (right). A composite with unsubstituted durene and pristine CNTs were used as controls. Each type of sensor was examined in triplicate. The sensing traces for each data point can be found in Figure S2.

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-diiodo-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. The N···I interaction of 4,4′-dipyridyl and 1,4-diodobenzene 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. Conversely, the introduction of electron-donating groups results in a worse XB donor. As expected, the methoxy-bearing selector resulted in an attenuated signal relative to p-diodobenzene, 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. 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 com-
ply 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 be-
tween 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.\textsuperscript{4,5} Using 1,4-didodecyl-2,5-diiodobenzene 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 in-
creased sensing response. An additional benefit of the longer
alkyl chain is the mechanical behavior of the composite pel-
let when depositing on paper. The pellet is robust enough to
be easily manipulated by hand and abrades similar to a Cray-
on when abraded on the weighing paper. The ease with
which uniform films are deposited likely explain the excel-
lent reproducibility of this particular CNT composite sensor.

After assessing the trends associated with halogen bonding
and carbon nanotube interactions, we investigated the re-
sponse of our top selectors, 3-iododurene and 1,4-didodecyl-
2,5-diiodobenzene, to elevated concentrations (> 1000 ppm)
of hexanes, benzene, isopropanol, and acetonitrile in addi-
tion 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. In-
terestingly, 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. Expos-
ure 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 nitro-
gen’s \textit{sp} hybridization.

Figure 4. Screening for XB-specific signal enhancement. Pyr-
idine was tested as an analyte in comparison to hexanes,
benzene, isopropanol, and acetonitrile at significantly higher
concentrations. The sensing traces for these bars can be
found in Figure S5.

In conclusion, we utilized halogen bonding in carbon
nanotube-based chemiresistive sensors to selectively en-
hance the response to the Lewis base pyridine. The chemire-
sitors were prepared by ball milling of SWCNTs and selec-
tors, compression into a pellet, and mechanical abrasion
between gold electrodes onto paper. p-Dihalobenzene and 3-
halodurene derivatives were investigated and exhibited sens-
ing responses consistent with halogen bonding. The funda-
mental 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 avail-
able 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

(1) Sparkman, O. D.; Penton, Z. E.; Kitson, F. G. Gas
Chromatography and Mass Spectroscopy: A Practical Guide;
(2) Zhou, X.; Lee, S.; Xu, Z.; Yoon, J. Recent Progress on the
8000.
(3) Kong, J.; Franklin, N. R.; Zhou, C.; Chapline, M. G.; Peng,
S.; Cho, K.; Dai, H. Nanotube Molecular Wires as Chemical Sensors.
(4) Fam, D. W. H.; Palaniappan, A.; Tok, A. I. Y.; Liedberg, B.;
Moochhala, S. M. A Review on Technological Aspects Influencing
Commercialization of Carbon Nanotube Sensors. \textit{Sensors Actuators
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