Highly Sensitive Detection and Discrimination of Biogenic Amines Utilizing Arrays of Polyaniline/Carbon Black Composite Vapor Detectors

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We have previously reported the construction of an "electronic nose" consisting of an array of chemically sensitive resistors in which each resistor is composed of a conductor (typically carbon black, CB) dispersed into an insulating organic polymer.[1] In this architecture, sorption of an odorant into the insulating polymeric phase of the composite swells the material and produces a characteristic increase in the direct current (dc) electrical resistance response of the detector. These types of conducting polymer composite vapor detectors have been shown to exhibit trends in odor detection thresholds that generally parallel the human nose.[2] This thermodynamically based relationship holds for vapors of alkanes, alcohols, esters, carboxylic acids, and ketones, which all exhibit detection threshold behavior in human olfactory tests similar to that observed for the conducting polymer composite-based electronic noses.[2,3]

A striking exception to this trend is the behavior of biogenic amine odorants such as putrescine, cadaverine, and spermine. Although the average equilibrium sorption behavior, and thus the detection thresholds, of these odorants in the carbon black/insulating organic polymer composite detectors are close to those of analogous alkanes and alcohols, humans can detect biogenic amines at concentrations that are 10^3−10^4 lower than the corresponding chain length alkanes, alcohols, or ketones.[4] Without a mechanism to obtain increased sensitivity to these classes of compounds, it will not be possible for the conducting polymer composite-based electronic nose to reproduce faithfully the general odor classification or intensity perception characteristics of the human olfactory system. In addition, biogenic amines have been related to the freshness of foodstuffs such as meats,[5−9] cheeses,[10] alcoholic beverages,[11,12] and other fermented foods.[13−15] Additionally, aniline and *o*-toluidine have been reported to be biomarkers for patients having lung cancer,[16] whereas dimethylamine and trimethylamine have been reported to be the cause of the "fishy" uremic breath odor experienced by patients with renal failure.[17] We report herein sensor film chemistry that has allowed us to obtain a *million-fold* enhancement in sensitivity toward these biogenic amines, such that chemiresistor-based electronic noses can now significantly outperform the detection capabilities of human olfaction and other ambient-pressure detection methods for this important class of analytes.

Instead of using an insulating organic polymer in the composite chemiresistor films, we sought to exploit the possibility of the amines interacting with, and manipulating chemically, the electrical properties of a conducting organic polymer used in a composite material. In this fashion, a small degree of sorption could induce a significant change in the conductivity of the organic conducting regions of the composite. To explore this possibility, we used polyaniline, a proton-dopable conducting polymer, as the polymeric phase of a carbon black/polyaniline composite. Polyaniline was chosen because its half-oxidized form, the emeraldine base ($y = 0.5$), is rendered electrically conductive upon reaction with a strong acid. The conductive form of polyaniline, commonly referred to as the emeraldine salt (ES), has been reported to deprotonate to the emeraldine base and become insulating in alkaline environments.[18−20] Because of this unique doping/undoping behavior, polyaniline is particularly sensitive to both acids and bases and has been used as a gas sensor for ammonia and HCl vapors as well as for a solution pH detector.[21−24] We report the preparation and unique properties of five types of polyaniline/carbon black chemiresistive detectors in this work.

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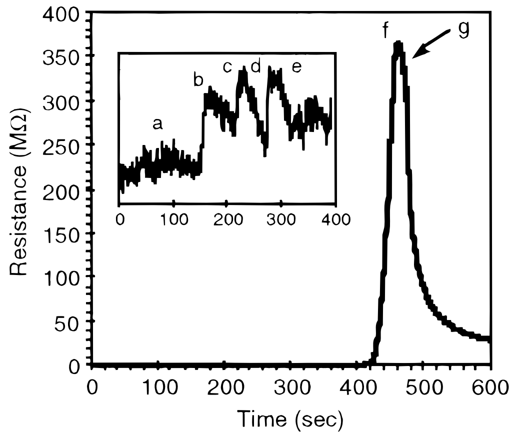

Figure 1. Resistance response of an EM−DBSA(1:0.5)/CB (80:20) detector exposed to water (a), acetone (b), methanol (c), ethyl acetate (d), butanol (e), and butylamine (f), all at 0.05% of their saturated vapor pressure. The ordinate on the inset was multiplied by a factor of $\approx 1 \times 10^6$ from the ordinate on the main plot of the figure. The value at the low end of the ordinate of the insert is 0.1682 MΩ, and the value at the high end of the ordinate is 0.1687 MΩ. The baseline value of R in the inset is 0.1683 MΩ. At point g, the sensor was removed from the chamber.

Emeraldine salt/carbon black suspensions were prepared by first dissolving the emeraldine base (Polysciences, Inc.) into hexafluoro-2-propanol. Sulfonic acid (reported as the mole ratio of polyaniline repeat to sulfonic acid) was then added,[25,26] and sufficient carbon black was introduced to produce a suspension that was 20 wt % carbon black and 80 wt % polymer, excluding the weight of the solvent. The solution was then sonicated for 20 min to disperse the carbon black. Substrate properties and other measurement methods have been described previously.[27]

Figure 1 depicts a series of headspace exposures (performed by injecting 1 mL of analyte-saturated air into a 2000 mL sealed glass container that contained a magnetically controlled fan to mix the headspace air in the vessel) of an ES−dodecylbenzenesulfonic acid (DBSA) (1:0.5)/CB detector to water (14.7 ppm), acetone (145 ppm), methanol (79 ppm), ethyl acetate (59 ppm), butanol (4 ppm) and butylamine (58 ppm). Each analyte was present at the same activity, corresponding to 0.05% of its vapor pressure. The steady-state relative differential resistance responses, defined as $\Delta R/R_b$, where R_b is the baseline resistance before exposure to the solvent vapor and ΔR is the change in resistance upon exposure to the solvent, were calculated to be 0, 0.0018, 0.0012, 0.0015, 0, and 2.25×10^3, respectively. Thus, the response of the detector is approximately 6 orders of magnitude greater to butylamine than to the five nonamine analytes. Composite detectors made from carbon black and insulating organic polymers, which can only respond by analyte-induced swelling effects on the insulating organic polymeric phase of the composite film, showed responses for all six analytes that were similar in magnitude to the responses displayed in the inset of Figure 1 of the polyaniline/carbon black composite detectors to nonamine vapors.

Detection thresholds, defined as the response required to obtain a signal-to-noise ratio of 3, were experimentally determined via headspace exposures to be 10 parts per trillion (ppt) for butylamine and 1 ppt for cadaverine on an ES−DBSA (1:0.5)/CB composite film. For comparative purposes, the human detection threshold for butylamine has been reported to be between 0.1 and 1 ppm,[28−30] and pristine emeraldine salt chemiresistive detectors have been reported to have detection thresholds of 1 ppm to ammonia.[23,31] Despite the pseudoreversibility of the ES−DBSA (1:0.5)/CB responses (see Figure 1) at high (between 50 parts per million and 1 part per thousand) concentrations of butylamine, the responses were reversible to exposures of butylamine at vapor phase concentrations between 10 ppt and 700 ppb. Exposure times under 30 s were generally sufficient to produce 90% of the limiting value of the electrical resistivity response. The variation in magnitude of the signals observed for a set of nominally identical detectors during exposures to a given vapor concentration of amine was less than 10% of the mean response of the detectors in such trials, with measurements typically performed on >5 detectors and for >10 exposures to each analyte.

The reversibility of the amine detectors can be explained in terms of the equilibrium established between the polyaniline emeraldine salt, and the amine analyte. At low concentrations of amine vapor, i.e., below 700 ppb for ES−DBSA (1:0.5)/CB, the polymer is not expected to undergo large changes in its secondary structure as a result of amine sorption. However, at concentrations above this limit, the secondary structure could undergo significant changes (i.e., breakup of crystallinity) that may not be restored on a rapid time scale and that may account for the quasireversibility of the signals at the higher amine concentrations.

To quantify the sorption behavior of these composites, a quartz crystal microbalance (QCM) with a 10 MHz resonant frequency was used to assess the mass uptake characteristics of butylamine, butanol, and acetone onto an ES−DBSA (1:0.5)/CB composite film. The response to both butanol and acetone was rapid (2 s to achieve 100% of the response) and reversible, whereas the response to butylamine was slower (10 s to achieve 80% of the response) and was only pseudoreversible. By using the Saurbrey equation and by assuming that modulus changes in the film are minimal, the mass uptakes for acetone, butanol, and butylamine were calculated to be 17.1, 23.2, and 272 ng cm^{-2}, respectively. Thus, although the sorption equilbria favor the amine relative to acetone or butanol, the sorption effect can only account for a factor of $\approx 10^1$ out of the $\approx 10^6$ enhancement in dc resistance sensitivity of these composites to amine vapors.

Evidence supporting an amine-induced change in the conductivity of the conducting organic polymer compo-

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nent of the chemiresistors was obtained through the use of UV−visible spectrophotometry. The spectrum for an ES−DBSA (1:0.5)/CB detector in air was identical to that previously reported for the emeraldine salt.[25] In contrast, after the injection of 1 μL of saturated butylamine vapor into a sealed 4.5 cm^3 quartz cuvette, the ES/CB film displayed absorption maxima at 340 and 660 nm. These two maxima have been observed previously for the emeraldine base and have been attributed to the $\pi-\pi^*$ transition (340 nm) and the polaron/bipolaron transition, respectively, in such materials.[25,32]

Classification and differentiation between amines was achieved by using an array of ES/CB detectors, each of which contained a chemically different polyaniline material to produce a diversity in response properties over the detector array. The $\Delta R/R_b$ values in response to aniline and butylamine, respectively, were as follows: ES−methanesulfonic acid (1:1)/CB, 0.389 ± 0.037 and 17.27± 2.6; ES−ethanesulfonic acid (1:1)/CB, 0.441± 0.0048 and 8.6 ± 0.9; ES−*p*-toluenesulfonic acid (1:0.5)/CB, 0.892 ± 0.067 and 8.6 ± 0.9; ES−*p*-dodecylbenzenesulfonic acid (1:0.5)/CB, 1.61± 0.081 and $(6.7 \pm 0.7) \times 10^4$; and ES−*p*-dodecylbenzenesulfonic acid (1:1)/CB, 16.31 ± 1.33 and 215 ± 52. Normalization of the $\Delta R/R_b$ values was performed to remove the concentration dependence of the data so that only changes in pattern type, as opposed to pattern height, contribute to the differences between the signatures of the different amines on the detector array. For these two amines, the Fisher linear discriminant method[27,33] yielded an resolution factor of 5300, where a resolution factor of 3 corresponds to a 98% probability of correctly identifying one analyte from the other. Thus, in this test case, the analytes were essentially perfectly separated from each other based on their distinctive patterns on the detector array.

The enhanced sensitivity obtained to this class of compounds from the ES/CB detectors indicates the flexibility in detector design that is made possible by using organic conductors with inorganic conductors to form composite chemiresistors as elements of vapor sensor arrays. Obtaining analogous sensitivity improvements for these classes of compounds using polymer-coated surface acoustic wave resonators[34,35] would require the introduction of amine-selective binding sites into the polymer film or the establishment of very large amplification effects due to extreme changes in the acoustic modulus of the polymer film upon analyte sorption. Mass-based detectors, such as QCMs[36] or micromachined cantilevers,[37] coated with these same polymer films could not display the enhanced sensitivity to amines reported here, given the small increase in sorption properties exhibited by these types of films for amine vapors relative to other classes of compounds. The superior dc electrical resistance sensitivity of these materials to biogenic amines now means that it is possible to exceed the sensitivities of organoleptic panels to these chemically important components of a variety of odors. Applications of these detectors in a variety of analytical scenarios, as well as exploitation of the chemiresistor-based approach described herein to obtain enhanced sensitivity toward other classes of biomedically important odorants, are currently in progress in our laboratories.

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Supporting Information Available: Frequency shift of an ES-DBSA-coated crystal, UV-vis spectrum of EM-DBSA, and pattern of relative differential resistance signals. This material is available free of charge via the Internet at http://pubs.acs.org.

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