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An Electronic Nose for the Detection of Carbonyl Species

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Conjugated polymers are an important class of materials due to their luminescent and electrical properties which result from electronic charge delocalization. Consequently, these polymers provide a suitable platform for new sensors since electronic and conformational changes that arise from the interaction with analytes translate into measurable changes in electrical conductivity or luminescence. The main advantage of this platform is based on the ability to partially tune the response of the sensor by changing the chemical structure of the polymer. The present work illustrates proof-of-concept chemical sensors that incorporate a molecular recognition site for the detection of common indoor air polluting carbonyl species such as aldehydes and ketones. Emphasis is placed on the detection of formaldehyde which poses major concerns in Indoor Air Quality (IAQ). By taking advantage of the differential response of various polymers towards analytes in question, sensor elements can be implemented in an array format to give an electronic nose

Introduction

Conjugated polymers have been the subject of intense research since the first observation of electrical conductivity in polyacetylene in its oxidized form (1,2,3). More recently, research on conjugated polymers has focused on their luminescent, photovoltaic and sensing properties (4,5). Due to their electrical and luminescent, which result from charge delocalization, this class of polymers presents a suitable platform for sensing applications that may be based on the formation of charge-transfer complexes or on conformational changes that result from the interaction between the polymer and the analyte (6,7). In addition to the above advantages, the chemical structure of these polymers may be designed to include a “molecular recognition” element that can provide a powerful handle in sensing as illustrated in the present work. Sensing applications in practice require the detection of one or more analytes in the presence of a complex matrix of interfering molecules. The artificial nose concept provides a powerful solution for sensing in real world environments. In this configuration, the artificial nose relies on the analysis of the pattern of responses from an array of sensing elements when exposed to a complex mixture of analytes as it is the case for pollutants in air.

Formaldehyde is considered a major pollutant in indoor environments due to its harmful effects that range from severe irritation and asthma-related respiratory symptoms to the possibility of developing cancer as reported by WHO (8). This has led to the well-known “sick building syndrome” (9). This is particularly important in regions of cold climates where energy conservation measures aim at the construction of air-tight buildings.

Health Canada has identified a variety of formaldehyde sources and these include the burning processes of tobacco, automotive fuels and wood, for example from wood stoves and fireplaces. Other sources include a variety of materials such as paints, plastics, carpet cleaners, etc. However, emissions from urea-formaldehyde resins that are widely employed in construction materials such as particleboards presently account for dangerous levels of formaldehyde in indoor environments. There exist other indirect sources of formaldehyde such as the interaction of ozone with building materials. This is an important source since photocopier machines are known to emit significant concentrations of ozone. As a result, Health Canada has issued a new guideline that limits the exposure to formaldehyde in indoor environments to less than $123 \mu\text{g}/\text{m}^3$ (100 ppb) for 1 hour and less than $50 \mu\text{g}/\text{m}^3$ (40 ppb) for 8 hours of exposure (10).

The present work describes a rapid and highly sensitive sensor for formaldehyde based on polyaniline and its derivatives which takes advantage of a molecular recognition element that influences conformational changes in the polymer. Such changes result in measurable resistivity changes that enable the detection of formaldehyde at the ppb level. The concept is being extended as an electronic-nose (e-nose) for the detection of other indoor pollutants.

Experimental

Aniline, 2-methoxyaniline, 3-nitro aniline, pyrrole, 3,4-ethylenedioxythiophene (EDOT), ammonium persulphate, paraformaldehyde, poly(vinyl phosphonic acid) (PVPA), dodecyl benzene sulfonic acid (DBSA), sodium fluoride and phosphoric acid were purchased from Aldrich Chemicals Inc. Polymerization of aniline and its derivatives was accomplished following the IUPAC method using ammonium persulphate as the oxidizing agent and hydrochloric acid as the dopant (11). In the case where the homopolymer could not be obtained, the desired derivative was copolymerized with aniline as it is the case 3-nitroaniline. In all cases, the polymers were isolated, dedoped with sodium hydroxide and purified. Doping of polymers with the desired dopant at a predetermined doping level was accomplished in solution under anhydrous conditions. Electrical resistance measurements were performed with a 4-probe station from Signatone Corp. in conjunction with a 2400 source-meter from Keithley Instruments Inc. Generation of formaldehyde and other analytes was performed in-situ with Dynacal permeation tubes from VICI Metronics Inc. Desired concentrations were achieved by adjusting the temperature and the flow rate of air. Sensing elements were prepared by solution casting the desired polymer at a particular doping level on a glass substrate with or without four gold lines (electrodes) with their respective pads for alignment with the commercial probe head.

Results and Discussion

It is well known that aniline reacts in an efficient manner with aldehydes in a two-step manner and these steps are fully reversible as depicted in Figure 1A. The first step yields the formation of a carbinolamine intermediate which can undergo dehydration to yield a Schiff base. Consequently, it was postulated that polyaniline presents the ideal platform for sensing carbonyl species. In this case, the molecular recognition element is built in the polymer backbone where the nitrogen from polyaniline reacts with a carbonyl group in the analyte to yield the carbinolamine intermediate (Figure 1A). It should be noted that for the case of the polymer, the Schiff base cannot be formed since the nitrogen lacks a second hydrogen. The fully reversible formation of the intermediate leads to a change in conformation where the phenyl rings become less coplanar thereby disrupting their conjugation and leading to an increase in its resistivity. Figure 1B illustrates in a qualitative manner the optimized (ChemDraw 3D Ultra 6.0) structures of diphenylamine and the corresponding carbinolamine intermediate. As expected, it is clear from this qualitative assessment that there is a significant deviation from coplanarity.

Figure 1. A) Basic premise that illustrates the reversible interaction between formaldehyde and polyaniline. B) Conformational changes that occur when formaldehyde reacts with diphenyl amine.

Experimentally, the above expectation has been confirmed with the rapid detection of formaldehyde with polyaniline (emeraldine salt) doped with various doping agents. However, the best results have been obtained with PVPA as doping agent. Figure 2 illustrates proof-of-concept detection of formaldehyde at 60 ppm at various doping levels. In this experiment, the sensor is kept under a constant stream of dry air and formaldehyde at 60 ppm in air is injected as plugs that last for 5 to 60 sec. Best sensitivity is obtained at low doping levels. Sample traces are illustrated at the right hand side of Figure 2.

Figure 2. Characteristic response for polyaniline/PVPA sensor. A) Resistance as a function of fractional doping level and B) representative formaldehyde sensing curves at two different doping levels in response to 60 ppm formaldehyde in dry air. Peaks represent the response at various lengths of time.

In addition to polyaniline, polypyrrole has a nitrogen in the backbone of the polymer. Although this nitrogen in part of the aromatic system and therefore less nucleophilic, it is expected to interact with formaldehyde. Figure 3 illustrates the response of polypyrrole doped with phosphomolybdic acid when exposed to 60 ppm formaldehyde. On the other hand, polythiophenes are expected to be unreactive towards aldehyde since they lack a nucleophilic heteroatom. Indeed, the lack of response of poly(3,4-ethylenedioxythiophene) (PEDOT) doped with phosphomolybdic acid is illustrated in Figure 3. This provides strong evidence for the premise for the sensing mechanism.

Figure 3. Response of polypyrrole/phosphomolybdic acid and PEDOT/ phosphomolybdic acid films to formaldehyde (60 ppm)

As it might be expected from the signal-to-noise ratio, sub-ppm detection should be possible. In fact, we have achieved ppb detection of formaldehyde under a relative humidity of 44% by carefully purifying, optimizing film preparation and electrode geometry.

In addition to sensor sensitivity, it is important to evaluate its selectivity towards other carbonyl species. To this end, its cross-reactivity towards acetaldehyde was evaluated since its chemical structure is most similar to formaldehyde. This represents the most difficult system to resolve. A large number of derivatives at different doping levels and various dopants were examined and selected examples are presented in Table 1 where the selectivity factor is defined as the ratio of the responses from formaldehyde and acetaldehyde. It is interesting to note polyaniline and polyanisidine exhibit similar selectivities whereas the nitro derivatives have a much higher selectivity factor. Since methoxy groups are electron-donating, polyanisidine should be more nucleophilic. Consequently, there appears to be a limiting effect where the strength of the nucleophile has a small effect. On the other hand, the nitro group is known to be an electron-withdrawing group which should decrease the nucleophilicity of the nitrogens. This should allow for the kinetic resolution of formaldehyde and acetaldehyde. Efforts are underway to resolve mixtures of formaldehyde and acetaldehyde with two sensing elements. This concept is being extended to an e-nose format for the detection of other carbonyl species.

TABLE I. Response of polyaniline derivatives towards formaldehyde and acetaldehyde.

Polymer/dopant	Response to Acetaldehyde (0.92ppm)*	Response to Formaldehyde (0.92ppm)	Selectivity factor (Formaldehyde/Acetaldehyde)
PANI/PVPA	0.1%	1.0%	10.0
Polyanisidine/PVPA	0.4%	4.3%	10.8
Poly(3-nitroaniline-co-aniline)/DBSA	2.3%	51.5%	22.4

*Response has been normalized to 0.92 ppm acetaldehyde

Summary

Polyaniline and polypyrrole derivatives are promising materials for the detection of carbonyl species since they possess a built in molecular recognition site that is based on the reaction between the carbonyl group and the nitrogen in the polymer. Such interaction leads to rapid measurable changes in resistivity of the polymer. Control experiments with polythiophene derivatives support this premise. Detection of formaldehyde at 250 ppb level has been demonstrated with a high signal-to-noise ratio at 44% relative humidity which simulate “real environment” sensing. Moreover, cross-reactivity studies indicate that the most difficult system can be resolved with the nitro derivative of polyaniline by

virtue of its selectivity factor of 23. Two sensing elements are currently employed to detect and quantify mixtures of acetaldehyde and formaldehyde. This concept will be extended to the e-nose configuration for the detection of other carbonyl species.

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