



Chemical diversity in electrochemically deposited conducting polymer-based sensor arrays



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ABSTRACT

The mammalian olfactory system is highly complex, with more than 1000 non-specific binding receptors. The chemical diversity among these receptors yields differential responses resulting in a ‘fingerprint’ response pattern characteristic of a particular gas phase odorant or mixture. It is through these response-patterns that our brain perceives its chemical environment. While the concept of an electronic nose has been explored over the past several decades, the emergence of integrated circuits analogous to charge-coupled device (CCD) devices with this kind of chemical sensitivity have yet to emerge. One of the main stumbling blocks is the ability to deposit large numbers of chemically diverse sensing layers within large-scale integrated circuits. The use of electronically conducting polymers (ECP) as sensing layers are attractive since they can be electrodeposited on existing fabricated structures without the need for additional lithographic steps, however they are limited by the number of chemically different monomer units available. In this study, we demonstrate the ability to significantly increase the level of diversity through the control of the dopant and the oxidation level of the deposited polymer layers. By using two polymers, several dopants and different oxidation states determined by applied electrochemical potential, fifty-five chemically diverse sensing elements are produced. These results suggest that by using these orthogonal variables, a chemically diverse integrated sensor array chip can be generated through a combinatorial approach of deposition conditions.

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1. Introduction

Chemical sensors continue to increase in importance due to the information they provide about the physical, chemical and biological nature of environment in which we live [1]. Electronically conducting polymers (ECPs) have been developed extensively for use as gas sensors in recent years since they overcome many of the disadvantages of metal–oxide semiconductor (MOS) based sensors including, lower sensitivity toward numerous toxic vapors, elevated operating temperature (~300 °C) and lack of specificity [2,3]. In contrast, ECPs typically provide rapid and reversible responses at room temperature by altering their base-resistance

upon portioning of vapor analytes into the polymer [4]. While selectivity can be achieved using a lock-and-key design for a particular analyte of interest [5]. ECPs are generally sensitive to a range of vapors, resulting in lower selectivity [6]. An alternative approach utilizing ECPs has been to assemble chemically different, broadly responsive sensors into arrays that mimic the olfactory system of mammals. This approach is inspired by mammalian genomes which contain approximately 1000 different non-specific receptor genes, resulting in receptor arrays that generate response patterns that can be used by the brain to discriminate various odors [7]. In the case of ECPs, chemical diversity has been achieved by varying the identity of the ECP [8] or by changing the nature of composites formed with a single ECP [9]. Sensor arrays using this approach for generating response patterns have been used successfully to classify various gases and gas mixtures [10–16].

Chemical sensing behavior of many ECPs including polypyrrole (PPy) upon exposure to a vapor is due to their interaction with the absorbed gas molecules [17]. Different vapors produce distinct responses through several possible interactions including [18]: (i) either oxidation or reduction of the polymer effectively changing

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charge carrier concentration; (ii) interaction with the charge carriers of polymer affecting their mobility; (iii) interaction between the dopant and vapor; (iv) altering the potential barrier for the hopping of carriers between chains; and (v) causing morphological changes due to swelling. In some cases, a vapor analyte can act as a solvate for the ECPs counter ions. For example, the presence of moisture dedopes poly(3,4-ethylenedioxythiophene) (PEDOT) by removing the counter ions while a positive gate bias is applied to PEDOT based field-effect transistor. When the gate bias was removed, the polymer redoped slowly [19].

The integration of chemical sensor arrays into electronic devices (machine olfaction) has the potential to follow in the footsteps of the CCD chip, which has revolutionized many technological areas and has enabled the evolution of machine vision [20]. The creation of an integrated circuit device that can perceive the chemistry of its environment poses numerous challenges, the most important of which is the integration of chemically diverse sensing materials with complementary metal-oxide-semiconductor (CMOS) technologies. Current approaches involving spraying of composites are limited to relatively large area sensors [21]. In order to increase the chemical diversity of chemiresistor based vapor detectors, Lewis et al. have added different weight percentage of plasticizers (including diethylene glycol dibenzoate and chloroparaffin) with few conducting composite materials (PVA, PMMA and PVC containing 20% carbon black) [22]. An additional challenge of using organic materials is their ability to survive steps involved in CMOS fabrication, requiring post-processing deposition of responsive materials [21].

The electrochemical polymerization of conducting polymers provides a unique opportunity to overcome spatial limitations of other deposition methods by allowing the controlled deposition on conducting substrates of virtually any size. In addition, this approach allows the production of chemically and structurally diverse polymers through the control of deposition conditions (monomer, dopant and morphology) and the final doping (oxidation) state. By adjusting all of these parameters it should be possible to build up large numbers of chemically diverse materials without the need for additional lithographic processing.

It has been demonstrated that the nature of the dopant in conducting polymers can play an important role in the structure of the polymer backbone as well as the morphology of deposited films, and that these changes can impact their response to vapors [6,23–28]. In addition, it has been shown that the oxidation state of the polymer (doped vs. dedoped) can also impact its gas sensing properties [17,29,30]. For example, the undoped emeraldine base form of polyaniline (PAni) is more suitable for detecting acidic vapors since exposure to strong acids such as HCl, results in protonation of the backbone and doping with Cl^- , thereby increasing conductivity. On the other hand, the conducting emeraldine salt form of PAni is more suitable for basic vapors such as ammonia which deprotonate the conducting PAni and increase its resistance [31,32]. Sadek et al. [29] used both emeraldine base and doped acidic forms of PAni as sensing materials for H_2 (which increases their conductivity), and found that doped PAni is more sensitive toward all concentrations of H_2 though the emeraldine base provided faster response and better reproducibility. Conductivity increases in both cases because H_2 reportedly forms a bridge between two adjacent polymer chains through their nitrogen atoms (or) the presence of H_2 may lead to partial protonation of imine nitrogen, thus creating more delocalized charge carriers along its backbone.

In this work, we explore the use of PPy [6,27,33–35] and PAni [17,29–32,36–38] in order to investigate the impact of all of the above described conditions on response and the ability to use this approach to create chemically diverse sensor arrays. This was explored by electrodeposition of polymers on pairs of interdigitated

electrode arrays (IDA) on custom printed circuit boards under varying conditions. The IDA electrodes (Fig. S1) were designed in collaboration with Iders Inc., Winnipeg, and were fabricated by Dynamic & Proto Circuits Inc., ON, Canada. Resistance changes upon partitioning of various analytes were used to generate response patterns, which were then processed using unsupervised pattern recognition in order to demonstrate chemical diversity and in turn differentiation through the creation of response patterns.

2. Materials and methods

2.1. Materials

Pyrrole monomer (Sigma–Aldrich, USA) was distilled under low pressure and stored in a dark freezer before further use. The other monomer, aniline was purchased from Sigma–Aldrich, stored in refrigerator at 5 °C, and used as such. Ultrapure water (Milli-Q, 18.2 M Ω cm at 25 °C) was used to prepare all aqueous solutions and to produce water vapor in sensor experiments. The dopants, sulfuric acid, nitric acid, oxalic acid (all three from Fisher Scientific Inc.), 10-camphor sulfonic acid, 1-naphthalene sulfonic acid, sodium dodecyl sulfate, *p*-toluene sulfonic acid, copper(II) phthalocyanine-tetrasulfonic acid tetrasodium salt and sodium dodecyl benzene sulfonate (all from Sigma–Aldrich) were used as received to make their respective solutions. For sensor experiments, analytical grade solvents of toluene (Fisher Scientific Inc.), dichloromethane (Fisher Scientific Inc.), acetonitrile (EMD Chemicals) and methanol (Fisher Scientific Inc.) were used as received. Indium tin oxide (ITO) coated glass slides (R_s : 4–8 Ω) were purchased from Delta Technologies, and cleaned thoroughly by performing several cycles of sonication with soap water, ultrapure water, acetone, ethanol and isopropanol before using them for deposition. The carrier gas of commercial nitrogen (purity > 90%) was purchased from Praxair Canada and used as such.

2.2. Deposition solutions

Pyrrole and aniline solutions were prepared by adding 0.1 M of monomer and 0.1 M–0.3 M dopant to water unless otherwise indicated. The dopants used for electrodeposition of PPy were sulfuric acid, nitric acid, oxalic acid, 10-camphor sulfonic acid, 1-naphthalene sulfonic acid, sodium dodecyl sulfate (SDS), *p*-toluene sulfonic acid (*p*-TSA) and copper(II) phthalocyanine-tetrasulfonic acid tetrasodium salt (CuPcTs). The dopants used for the deposition of PAni films were sulfuric acid, *p*-TSA acid and dodecyl benzene sulfonate (DBS).

2.3. Polymerization procedure

All polymer films were deposited electrochemically on IDAs using potentiostatic methods. A single printed circuit board (Fig. S1a) contains seven IDA sensor elements, in which each element consists of a pair of gold-coated micro bands separated by thin insulating spacing (100 μm). The design and dimensions of the microbands in a sensor element are shown in Fig. S1b. A conventional three-electrode electrochemical set up was used for the electrochemical deposition processes. Platinum, IDA sensor element and Ag/AgCl were used as counter, working and reference electrodes respectively. Polymers were grown under constant potential using CHI 760C potentiostat on each sensor element electrode pair to same charge density. Therefore once grown, all seven electrode-pairs on the printed circuit board were identical and should behave in a similar manner before performing any further modification (e.g., changing oxidation state).

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