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Detection of formaldehyde vapor using conductive polymer films

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ABSTRACT

We have developed conductive elements incorporating thin poly(aniline)/poly(ethyleneimine) composite films prepared by spin casting and report on their characteristics for formaldehyde detection via changes in conductivity. We find significant increases in the resistance, for example greater than 10 kΩ at a concentration of 38 ppm exposed for 1 min, of these films upon exposure to formaldehyde vapor in a laboratory gaseous exposure chamber. The films are less responsive to other volatile organic vapors, such as methanol, acetone and dichloromethane. The morphology of the films was analyzed by scanning electron microscopy, which indicated a porous surface well suited to vapor phase adsorption.

1. Introduction

Formaldehyde has been classified as a likely carcinogen by the U.S. Environmental Protection Agency and workplace exposure is strictly regulated. Exposure is suspected to cause cancers of the lungs, throat and mouth and leukemia [1–3], as well as damage to the reproductive system. Chronic formaldehyde exposure may reduce immunoresponse in otherwise healthy individuals, leading to an increased risk of infection [4]. It has been reported that sensitive individuals are affected by formaldehyde concentrations on the order of several hundred parts per billion [5,6]. This number represents the ultimate goal for our sensor development. The toxicity of formaldehyde argues for the development of a sensing device that is compact, wearable and reporting to the owner in real time. Most commercially available formaldehyde sensing devices employ a two-stage process. That is, the sensor includes a pump to draw air through a solid phase material that traps formaldehyde. The extent of targeted material in the trap is indicated by laboratory analysis for room monitors or a color change for personnel monitoring. A number of other products are described as passive air monitoring badges, which are worn on the lapel and adsorb ambient gases from the user environment. The badges are then delivered to a lab for chromatographic analysis. As such they are not especially useful for real time or site-specific monitoring, but provide a general, time-weighted average of individual exposure.

A number of potential formaldehyde detection methods have been reported in the literature. For example, laser induced fluorescence provides sensitive recording of ambient concentrations [7] and levels in engines and flames [8]. Chemiluminescence via a reaction with myoglobin and luminol detected pmole levels of formaldehyde [9]. A GC–MS method [10] is applicable in a range of circumstances. Formaldehyde dehydrogenase was used to develop a "sniffer chip" capable of detecting formaldehyde emission from timber [11,12]. Electrochemical methods were applied to the task in the form of a fuel cell-like sensor [13] and MEMS technology resulted in a micro-gas sensor based on a SnO_2—NiO polycrystalline composite [14]. More recently, SnO_2 nanowires and a quartz crystal microbalance coated with an amine functionalized SBA-15 material were described [15,16]. Finally, a poly(aniline)/fluoral-p indirect chemical sensor based on the generation of ammonia from formaldehyde was reported [17]. Some of the more recent efforts have produced schemes capable of real time monitoring of the target formaldehyde, however, we seek a *direct* procedure that is sensitive, specific and relatively inexpensive. The current effort is directed toward development of such a personal device using a resistive sensor based on a conductive polymer and a formaldehyde-targeting polymer additive.

Conductive polymers such as poly(aniline), PANi see Fig. 1, are of interest as components of electrochemical devices [18–20] and as active materials for a variety of sensing applications [21–23]. In sensors, the key feature of doped, electrically conductive PANi is the presence of protonated nitrogen atoms that give up the proton to an adsorbed vapor molecule, decreasing the conductance of the polymer. Thin films optimize the density and availability of protonated receptor sites by minimizing the diffusion distance necessary for the adsorbant to travel during binding events. Thin films also increase the responsivity, if the reporting electrode lies beneath the polymer film as in the current research. There are various

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techniques for depositing films including: electropolymerization [24], spin casting [25,26] and laser deposition [27,28]. Several reports of doped PANi films applied to the detection of formaldehyde or acetaldehyde have appeared in the literature [29–31], however, these approaches, often using metal atom doping of the polymer, are more complex than that described here in which PANi is employed to directly measure the target concentration in concert with a second polymer included in composites to improve the porosity and targeting of the sensing material.

Sensing using conductive polymer films can be performed either by coating the surface of an electrode with the doped polymer and measuring the cell potential with reference to a redox electrode or by making a true planar, chemiresistive structure. The latter has advantages in that it can be used with a variety of conductive polymers or composites, may be designed to create higher values of resistance (signal), and has the potential for rapid detection; these planar structures may be designed with good time response by an appropriate choice of geometry and materials. Alternatively, one may substitute a dielectric polymer for the conductive polymer and develop a capacitance based sensing element. We have utilized a capacitive sensor for amino acids, but because of the reactive nature of formaldehyde with PANi, chose the resistance device as the best solution. In the research described here, we employed a spin casting method for preparing the thin films on lithographically produced electrodes. These PANi conductive films have been characterized and shown to be sensitive to vapor phase formaldehyde in a laboratory setting.

2. Experimental

2.1. Materials

Poly(aniline) was purchased from Polysciences, Inc. as the undoped, emeraldine base form with a molecular weight of 15,000 and a conductivity of 10^{-10} S/cm. Branched poly(ethyleneimine), PEI, with a molecular weight 70,000 was obtained from Alfa-Aesar as a 30% aqueous solution. Both polymers are shown in Fig. 1. Formic acid, >98%, was purchased from EMD Chemicals and used to dissolve the polymers prior to spin casting. Formaldehyde was purchased from Fisher Scientific as formalin solution (37% formaldehyde/10% methanol/53% water). All reagents were used as received without any further treatment.

2.2. Preparation of PANi/PEI composite solutions

The polymer films for detecting formaldehyde were spin-cast composites of PANi and PEI. PANi in its conductive form is insoluble. However, the emeraldine base may be dissolved in several

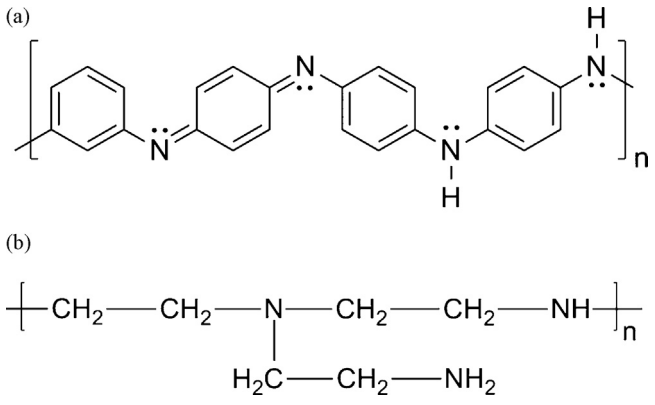

Fig. 1. Molecular drawings of the emeraldine base of PANi (a) and PEI (b).

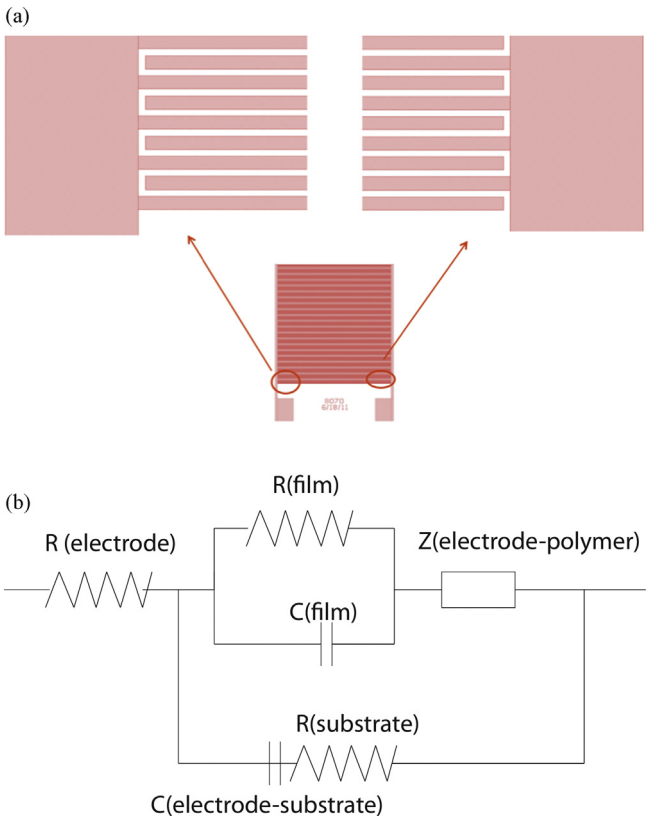

Fig. 2. (a) Schematic diagram of the lithographic circuit for the sensor. Interdigitated electrodes: 40 μm with a spacing of 20 μm; (b) schematic diagram of proposed equivalent circuit for the interdigitated electrode.

solvents, including the formic acid used in this research; PEI is also soluble in formic acid. The formic acid solvent also acts as a primary dopant for PANi. Based on previous experiments, the spin casting solution was produced as a 5% by weight solution in each of the two polymers. PEI serves to create a more porous film as demonstrated in the characterization subsection. A number of functionalized PANi derivatives have been reported in the literature, however, our goal is an inexpensive sensing device for the target formaldehyde. The use of a specialized polymer would considerably raise costs. Hence, we have restricted development to readily available materials.

2.3. Fabrication of conductive devices

The conductive sensors were constructed on oxidized silicon substrates with the PANi/PEI composite film as the active element above the electrode. The production method is briefly outlined below.

Prime grade silicon wafers with a 5000 Å thermally deposited oxide layer were used for the substrate. The oxide layer insures isolation of the interdigitated electrodes from the silicon surface. These films were patterned by photolithography and subsequently wet etched to produce the final electrodes with a total area of 376 mm^2, following vapor deposition of 1000 Å of chromium and the 200 Å overlayer of nickel. Chromium is usually employed as the initial metal layer in order to improve adhesion of the actual conductive layer and this was its use in the current work as well. The selection of nickel as the conductive layer was somewhat arbitrary, however, its conductivity is within a factor of three of that of gold and its use for the contact pads provided a soft, but rugged connection to the sensor mounting clips. Lift off was accomplished using acetone, with final rinses of water. The electrode was patterned into an interdigitated grid, as shown in Fig. 2, with 40 μm fingers