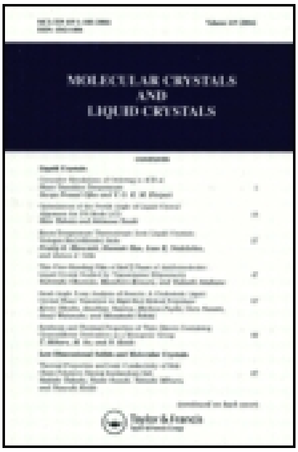

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Polypyrrole Thin Films as Sensors of Volatile Organic Compounds

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Thin films of polypyrrole (PPY), doped with different counter-ions and prepared by *in situ* polymerization on conducting glass electrodes, are used for the development of gas sensors with fast response time. On exposure to a given vapor, each individual film exhibits a fast change of the fractional difference of its electrical resistivity; by adopting a sensor array composed of 4 differently doped PPY films it was possible to detect and identify simple organic solvents. The Principal Components Analysis (PCA) was adopted for the pattern recognition process and the first two principal components were sufficient to produce an explained variance of 98,1%.

Keywords: polypyrrole; gas sensors; in *situ* polymerization; thin films.

INTRODUCTION

Thin films of conducting polymers have a wide range of applications[1]. Recently, there has been considerable interest in the use of conducting polymers – in particular polypyrrole (PPY) and polyaniline (PANI), both as thin films and in composites with conventional polymers – to manufacture sensing devices for organic volatile compounds[2]. A direct comparison of the relative change of the electrical resistance of each individual sensor caused by the exposure to the vapor of a volatile compound can be made, since in this type of device the sensor units are interfaced to a pattern recognition system. Due to their large area to volume ratio, thin films have a fast response to adsorption and desorption of volatile compounds and therefore their use appears as promising strategy for the development of sensing instruments operating in real time.

In situ deposition from aqueous solutions is a simple process for obtaining thin films of intrinsically conducting polymers[3]. The polymeric chain is formed on the substrate directly from a dilute solution containing the monomer and an oxidant. The concentration levels of the monomer and of the dopant, the nature of the dopant and the treatment applied to the substrate's surface are the parameters that most affect the polymerization rate. The polymer is formed in solution and then adsorbed on the substrate's surface, once a critical molecular weight is reached or large aggregates are formed.

In this work we describe a new approach to the development of sensors of volatile compounds based on thin polypyrrole films prepared by the free growth method directly on glass slides covered by a conducting layer of indium tin oxide (ITO). Four different dopants were used to produce distinct films to be tested for the sensitivity towards polar and non-polar compounds.

EXPERIMENTAL

Pyrrole (Aldrich, USA) was freshly distilled under reduced pressure and stored in a refrigerator in the dark. Also from Aldrich were the doping agents p-toluenesulfonic acid monohydrate (pTSA), camphorsulfonic acid (CSA), lithium perchlorate (PER) and anthraquinone-2-sulfonic acid sodium salt (ASA) used. Each of these dopants were used to prepare the 4 different types of films, denoted by S1, S2, S3 and S4, to be used for the testing as aroma sensors. In all cases ferric chloride was the oxidant and deionized water (Nanopure, USA) was the solvent. All reagents had analytical grade and were used as received. The following volatile organic compounds were used for the sensitivity tests: methanol (Met) and ethanol (Eta) (Quimex, Brazil), 1-propanol (P1), 2-propanol (P2), and 1-butanol (But1) and carbon terrachloride (TC) (Aldrich, USA) and benzene (Ben) (Merck, Germany).

The ITO-coated plates were covered with two pieces of adhesive tape, allowing for a lateral separation of 1 mm to leave a thin uncovered patch in the middle of the substrate (Figure 1). The plate was dipped for 2 min into concentrated HCl to corrode the exposed ITO layer, and then washed in abundant deionized water, to remove excess acid. The ITO plates were submitted to a cleaning process which consisted in dipping the substrate first for 5 minutes in a beaker containing chloroform, and then immersing it in pure water for the same amount of time. The procedure was then repeated using acetone and later methanol instead of chloroform, and afterwards the substrate was taken out and allowed to dry in a sterilizer at 110 °C for 1 hour.

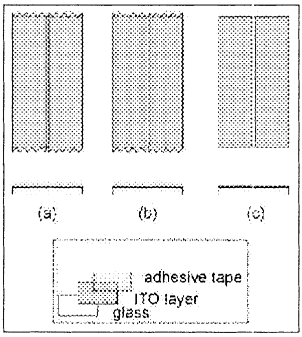

FIGURE 1: Preparation of the ITO substrate.

All polymerization reactions were carried out with the same amount (20 mL) of an aqueous solution containing pyrrole (0.02M), $FeCl_3$ (0.006M) and the doping agent (0.005M). The substrate was vertically dipped into the solution and kept still for 60 minutes to allow the undisturbed free growth of the polymer.

RESULTS AND DISCUSSION

The signal resulting from a sensor-volatile interaction is usually quantified in terms of the fractional resistance difference[2]

$$FD = \frac{R_t - R_0}{R_0},$$

where R_t is the sensor resistance at time t and R_0 is the baseline resistance, i.e. the resistance measured in the absence of the volatile species. The percent fractional resistance difference, FD x 100%, is an effective measure of the sensor's sensitivity. To be efficient as an aroma sensor, an array of sensors made from different polymers must be able to discriminate between different volatile compounds on the basis of their different interacting patterns.

The corresponding fractional differences of the electrical resistance of the sensors used in this work after 10 minutes of exposure to volatile organic compounds are plotted in Figure 2. Although the sensors respond to all seven volatile compounds tested, they do so in varying extents: The highest responses are observed for methanol, and the lowest for benzene.

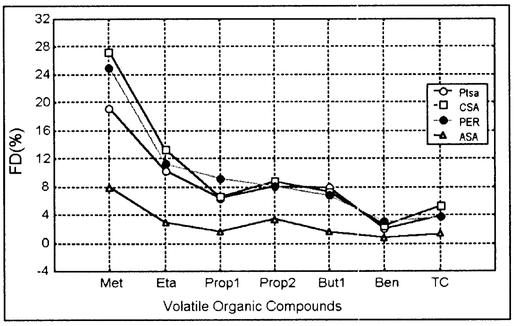

FIGURE 2: Sensitivity (FD%) of each sensor towards volatile organic compounds after 10 min of exposure.

The measured fractional difference of the electrical resistivity of the films was examined using the Principal Components Analysis (PCA)[2] and the use of just the first two principal components (PC1 and PC2) suffice to produce an explained variance of 98,1%.

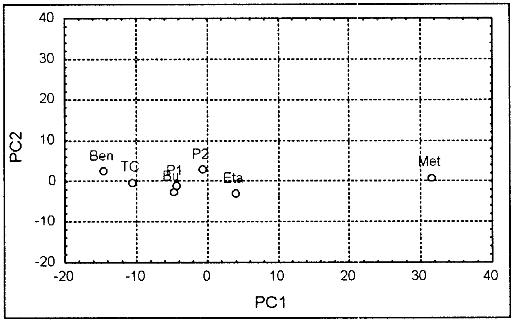

FIGURE 3: PC1 and PC2 scores plot.

From the corresponding scores plot (Figure 3), we can observe that the 4-sensors array composed by the S1, S2, S3 and S4 films was able to discriminate the organic solvents examined. In Figures 4 and 5 we show the corresponding values of sensitivity (fractional difference) of the sensors as a function of the time of exposition to methanol and benzene vapors, for a total exposure time of 60 seconds. In spite of the relative short time of exposure, one can observe that the sensitivity of the sensors experiments a noticeable change (from 3,7% to 13,5 % for methanol and from 0,2 % to 1,00% for benzene).

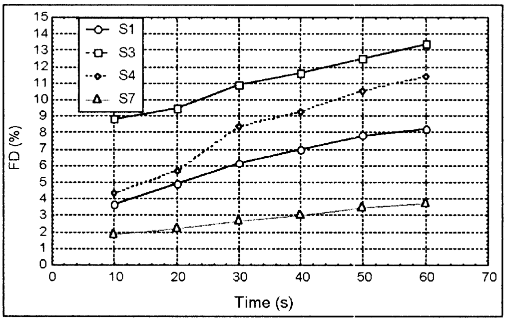

FIGURE 4: Sensitivity (FD%) of sensors towards methanol after 60 s of exposure.

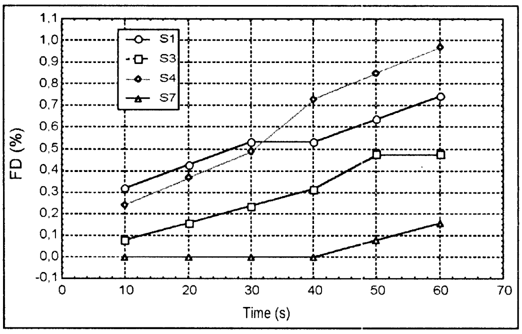

FIGURE 5: Sensitivity (FD%) of sensors towards benzene after 60 s of exposure.

As expected, the thickness of the polymeric film used as a sensor is a determinant factor of the response time of the device[4,5]: Due to the larger surface to bulk ratio, thinner films are likely to exhibit a faster response to the presence of volatile compounds.

CONCLUSIONS

In this work we have described the use of thin polypyrrole films prepared by *in situ* polymerization directly on ITO substrates. The characterization of the sensitivity and selectivity of the sensors was made through the analysis of the variation of their electrical resistances when exposed to the volatile organic compounds. Seven compounds (the homologue series methanol, ethanol, 1-propanol, 2-propanol and 1-butanol, and the non-polar solvents benzene and carbon tetrachloride) were used for the tests, which confirmed the adequate degree of sensitivity of all four films prepared and their fast response time. These results confirm the idea that the use of thin polymeric samples are a promising strategy for the development of real time aroma sensors. An important point, that we plan to elaborate in further work, is that the intensity of the observed responses is larger for the polar compounds than for the non-polar ones.

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