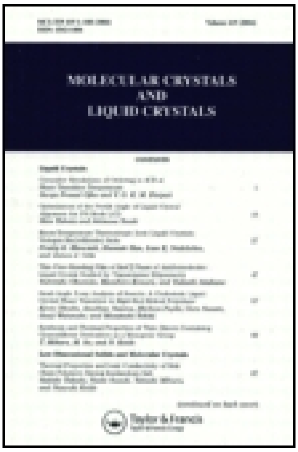

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Ultrathin Conducting Polymer Films as Sensors of Volatile Compounds

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Ultrathin Conducting Polymer Films as Sensors of Volatile Compounds

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The self-assembly technique was used to prepare polymeric thin films composed of bilayers of polypyrrole (PPY) doped with different counter-ions and poly(3-thiophene acetic acid) (PTAA), directly on conducting glass electrodes. The electrical conductivity of these thin films - which have a relative high degree of structural order and large surface to volume ratio – responds in a very fast manner to the exposure to vapors of simple organic solvents (methanol, ethanol, carbon tetrachloride and benzene). The changes in the fractional difference of individual films disposed as an sensor array were measured and the Principal Components Analysis (PCA) was used to correlate the corresponding collective pattern to the specific volatile compound.

Keyword: polypyrrole, gas sensors, self-assembly, thin films.

INTRODUCTION

Thin films of conducting polymers have a large potential for different technological applications such as photo- and electro-luminescent devices and in corrosion protection of surfaces[1]. In the last few years, it has been demonstrated that the characteristic change of the electrical properties of conducting polymer samples upon exposure to different volatile organic compounds can be exploited to develop electronic noses[2]. Aroma sensors are potentially useful for quality control of beverages and food products and for environmental monitoring[2,3]. In this type of device, a set of individual sensors is interfaced to a pattern recognition system capable of analyzing and interpreting the data simultaneously received from the different units.

In this communication we show that thin organic films prepared by self-assembly techniques[4] represent promising materials for the preparation of more efficient sensors. We have examined the response of self-assembled polymeric films composed by a varying number of bilayers of PPY (doped with different counter-ions) and PTAA films to polar (methanol and ethanol) and non-polar (carbon tetrachloride and benzene) compounds. Due to their inherent large surface to volume ratio, thin films exhibit a fast response to the adsorption and desorption of volatile compounds and could eventually lead to the development of instruments operating in real time.

EXPERIMENTAL

Pyrrole (Aldrich, USA) was freshly distilled under reduced pressure and stored in a refrigerator in the dark for later use. Also from Aldrich were the chosen doping agents p-toluenesulfonic acid monohydrate (pTSA), lithium perchlorate (PER), 4-octylbenzenesulfonic acid, sodium salt (OBS), and anthraquinone-2-sulfonic acid sodium salt (ASA). Ferric chloride was used as oxidant. All reagents were of analytical grade and used as received. In all cases, deionized water (Nanopure, USA) was the solvent. The following volatile organic compounds were used for the sensitivity tests: methanol and ethanol (Quimex, Brazil), carbon tetrachloride (Aldrich, USA) and benzene (Merck, Germany). The Lancaster method[5] was adopted for the synthesis of PTAA.

The ITO electrodes used as substrates were prepared in the standard manner[2,7]. To form the first polymeric bilayer accordingly to the self-assembly technique[4], the substrates were first dipped for 5 minutes in a beaker containing the polyanion solution to allow the adsorption of the first negative polymeric layer. After an intermediate cleaning step, when the substrate was immersed for another 5 min in an acidic solution for removal of residual polymer, the procedure was repeated using the polyanion solution. After a new immersion in acidic solution for the same amount of time, the substrate was taken out and allowed to dry in a N_2 flux. The entire process was then repeated to produce the desired number of bilayers; for this study, similar films with 4 and 8 bilayers were prepared for effects of comparison of the sensitivity.

In the polymerization reactions required to prepare the four different types of films to be used in the tests, pyrrole (0.02 mol/L) was used as the polycation in an aqueous solution (20 mL) with pH = 2 containing $FeCl_3$ (0.006 mol/L) and the doping agent (PER, ASA, OBS, PTSA) always at the same concentration (0.005 mol/L), and PTAA was the polyanion used in a 20 mL solution with concentration 4,0 x 10^{-4} mol/L and pH = 5

RESULTS AND DISCUSSION

A simple array of only four different self-assembled thin films seems to be sufficient to permit the discrimination between different volatile compounds. The parameter adopted to compare the response of a given film to different vapors was the fractional difference FD[2,7] in its electrical resistance.

Four volatile substances were analyzed in this work: methanol, ethanol, benzene and carbon tetrachloride. To better examine how the number of deposited bilayers affects the response time of the films, for each type of counter-ion used we have prepared films with 4 and 8 PPY/PTAA bilayers. As it could be expected, the 4-bilayers films presented a shorter response time than the corresponding 8-bilayers films. In Figure 1 we compare the level of response of the four different sensors (identified by the respective doping agent) when exposed to carbon tetrachloride for 1 min. and for 10 minutes.

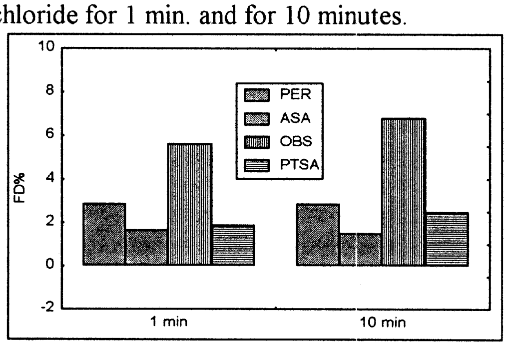

FIGURE 1: Sensitivity (FD%) of the four differently doped 4-bilayers films after 1 min (left) and 10 min (right) of exposure to carbon tetrachloride.

Although only after 10 minutes were the sensors' signals completely stabilized, one can see that after the first minute of exposition the percent fractional difference pattern remains practically unaltered. Hence, 1 min. seems to be the minimum time required for an array consisting of these 4 different films to recognize this particular organic solvent in an efficient manner.

In Figure 2 we can observe the sensitivity pattern of differently doped 4- and 8-bilayers films (identified by the respective doping agent) after 10 min of exposure to carbon tetrachloride vapor.

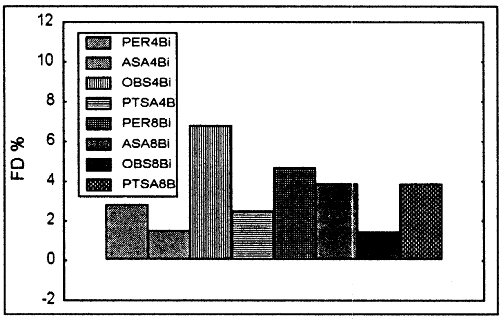

FIGURE 2: Sensitivity (FD%) of identically doped films with 4- (first four bars from the left) and 8-bilayers (last four bars) after 0 min. of exposure to carbon tetrachloride.

The highest [lowest] response of all films was towards methanol [benzene]. The corresponding values of FD% after 10 minutes of exposure to methanol and benzene are plotted in Figures 3 and 4, respectively. From the data in these figures, one can note that while the films doped with PER and PTSA had a sensitivity to methanol approximately six times greater than that to benzene, the difference in discriminating power was reduced to a factor of approximately three for the films doped with ASA and OBS.

The differences in the individual responses of the polymeric films to the volatile compounds do not provide sufficient information for the level of discrimination required for an electronic nose. It is essential to be able to compare the evolution of the individual sensitiveness and to identify overall patterns more specific of each volatile compound. Principal Components Analysis (PCA)[6] is a projection method that we have previously used to discriminate response patterns of polymeric films towards simple and complex aromas[2,3].

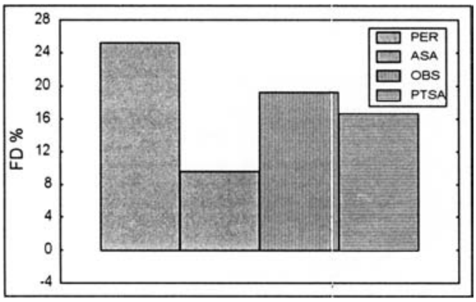

FIGURE 3: Sensitivity (FD%) of the different 4-bilayers films towards methanol after 10 min of exposure.

In Figure 5 we plot the scores plots obtained from a PCA of the FD% data of the different 4-bilayers films after 1 min of exposure to methanol (Met), ethanol (Etha), benzene (Ben) and carbon tetrachloride (TC) vapors, using only the first two principal components, PC1 and PC2.

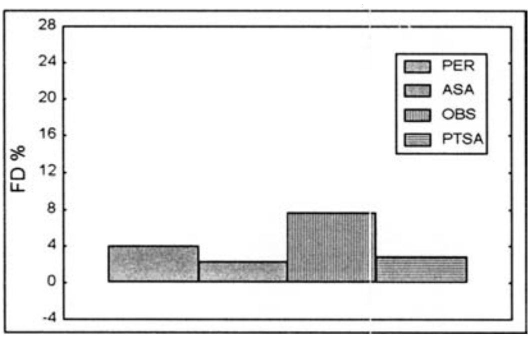

FIGURE 4: Sensitivity (FD%) of the different 4-bilayers films towards benzene after 10 min of exposure.

One can see that these compounds are visually separated in two groups: TC and Ben, closely situated at the left, and Etha and Met, at the right. The variance explained using just these first two components was 99,36 %; however, since there was a very good separation of the substances only along the PC1 axis (responsible for 97,66% of the information), one could neglect the second principal component without any significant loss of information.

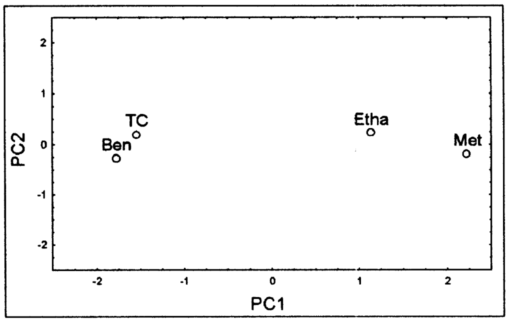

FIGURE 5: PC1 and PC2 scores plot obtained from the FD% data of the different 4-bilayers films after 1min of exposure to the vapors of the compounds examined.

CONCLUSION

Thin organic films prepared by self-assembly deposition of PPY/PTAA bilayers have demonstrated a fast response (~1 min) to the presence of vapors of both polar and non-polar compounds. Using a Principal Components Analysis, just the first two components were sufficient to discriminate the compounds analyzed and well separate the polar from the non-polar compounds.

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