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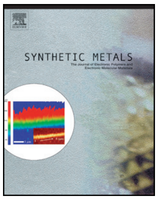

# Functionalized polyanilines made by nucleophilic addition reaction, applied in gas sensors field

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ABSTRACT

Resistive sensors for organic volatile compounds are built using functionalized polyanilines. The functionalization of polyaniline (PANI) is achieved by nucleophilic addition with thiols and is confirmed by X-ray Photoelectron Spectroscopy. The modified polymers tested as resistive sensors change the polymer sensitivity to volatile compounds. PANI shows a signal that increases when the chain length increases, however, functionalized polyanilines show a completely different behaviour. The sensitivity to long chain alcohols increases when PANI is modified with long alkyl chains, the opposite behaviour occurs when more hydrophilic groups are bonding to the polymer. We conclude that the different sensitivity of the functionalized polyanilines to the same volatile molecule allows identifying the analyte. In that way, multisensor arrays based on these materials could be used as an electronic nose. To explain this behaviour measurements of contact angle were performed. The data reveal that all modified polyanilines are more hydrophobic than PANI, this is likely to be due to the presence of the sulphur atoms. Therefore, we conclude that the hydrophobic/hydrophilic nature of the surface plays an important role but is not decisive in the sensor response. Also, Van der Waals interactions between the alkyl chains bound to de PANI and present in the sensed alcohols play an important role. Accordingly, the sensitivity for a plain alkane (heptane) increases strongly when PANI is modified with long alkyl chains.

## 1. Introduction

Gas sensing is important in environmental control, explosives detection, aroma identification and health diagnostics [1]. Specifically, volatile organic contaminants should be detected to control the concentration and the exposure of humans [2]. Conductivity sensors are based on a change of conductance (or resistance) due to a physical interaction of the sensing material with the volatile compounds [3]. Semiconducting oxides (e.g. $SnO_2$) are usually used for such purpose but they have to be heated above 200 °C to have a measurable conductance [4]. Other conducting materials, such as conducting polymers [5], carbon nanotubes [6] and graphene show measurable conductivity at room temperatures (e.g. 25 °C) [7]. Therefore, they have been widely used to build sensors for volatile organics [8,9]. Sorption (surface adsorption and bulk absorption) of a volatile organic compound on a conducting polymer could induce different processes, which change the conductivity [10,11]. The resistance changes ($\Delta R$), results from sorption of an analyte can be divided into three components: $\Delta R = (\Delta R_{ele} + \Delta R_{hop} + \Delta R_{ion})$; $\Delta R_{ele}$ is the change intrinsic resistivity of conducting polymer chains. The analyte interaction could change the polarons and bipolarons density of these materials, affecting the total resistivity. $\Delta R_{hop}$ is the resistivity change in electron hopping between polymer chains, which could be modulated by the presence of the analyte. The analyte could cause physical swelling of the film and therefore increase the interchain distance, making the hopping more difficult [7]. The polarity of the analyte could screen the charge carriers, decreasing the resistivity. $\Delta R_{ion}$ is the change in ionic resistivity across the polymer layer. Since the conducting polymer

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has mobile counterions balancing the charge, the ions could transport charge between the electrodes. If charged groups (e.g. —COO$^-$) are present, the ionic contribution could be more important. Again, polar analytes could screen the ion charges and affect the resistivity. The effect of the analyte on the electronic properties of the polymer is usually negligible when it is compared with the effect on the hopping [12]. However, the swelling could be very small due to the relative rigidity of the polymer chains.

For sensor applications, it is important to be able to produce sensing materials, which have a large sensitivity to a specific analyte. In single sensor applications, the material should show a high sensitivity for one analyte while it should show low sensitivity for the others present in the same sample. In multiple sensor applications (electronic noses) different sensitivity for different analytes is required. In that sense, the exposure of various sensors to a given analyte generates a defined signal pattern, which is different from the patterns produced by other analytes. In any case, the ability to tailor the sensitivity to the analyte is very relevant. As it was pointed before, the arrays of conducting polymers show relatively low diversity in affinity toward a very diverse set of analytes, thereby producing less than an optimal separation of many analytes in the sensor array data space [13]. It is reasonable to assume that the functional groups incorporated into the conducting materials affect its sensitivity to different volatile organic compounds. Indeed, it has been shown that different copolymers of pyrrole show different response than the homopolymer [14]. Moreover, different schemes can be used to produce conducting polymers bearing different functional groups. Among them, the different monomers polymerization [14,15], and the homopolymer formation in the presence of different counterions (e.g. polypyrrole) have been employed [16,17]. Both methods present a serious disadvantage; they need a precise polymerization condition, making the method difficult and hard to reproduce. The functionalization of a preformed conductive polymer film only requires setting the conditions for the reaction, since the base film is the same. In this field several researchers and our research group have been worked extensively in the development of methods for post-functionalization of conductive polymer films [18–24].

In the present work, we describe the use of different functionalized polyanilines as sensing materials for model volatile compounds (alcohols and alkanes). It is shown that the response is affected by the hydrophobic/hydrophilic properties of the material surface and the polarity of the volatile molecules. When different alcohols are sensed, PANI shows a signal that increases as the chain length increases. Moreover, the results suggest that hydrophilic or hydrophobic groups incorporated on the PANI backbone change the sensitivity to different alcohols. At the same time, it is shown that the sensitivity for heptane is larger when a polyaniline is modified with long alkyl chains. The data prove that the hydrophobic/hydrophilic nature of the sensor surface and its sensitivity to volatile molecules cannot be directly predicted taking into account only the nature of the added functional group. Further, the use of functionalized polyanilines as sensors allows identifying one analyte from a mixture, due to these sensors show different sensitivity to each one of them. In that way, multisensor arrays based on these materials could be used as an electronic nose.

## 2. Materials and methods

Aniline (Merck) was distilled under reduced pressure before polymerization. Ammonium persulphate (Aldrich) was used as received from the manufacturer. All aqueous solutions were prepared using twice-distilled water. All the other reagents were of analytical quality.

### 2.1. Polyaniline films synthesised onto woven cloth of Polyethylene-terephthalate (PET)

PANI (emeraldine form) was prepared by oxidation of aniline (0.1 M) in 1 M HCl with ammonium persulphate (equimolar to aniline) following the procedure published elsewhere [25,26]. The reactor was immersed in an ice-water bath to keep the temperatures below 5 °C. In order to produce PANI woven cloth of PET [27], 4 × 4 cm$^2$ pieces were immersed in the polymerization solution. The woven cloth of PET was used to increase the total surface area for a given geometric area. Thin films (200–600 nm) of PANI were formed on these substrates [28]. After the polymerization finished, the PANI films on the woven cloth of PET were washed for 15 min in pure water to ensure that no reactant was retained in the film. The bulk PANI synthesised in the same conditions was washed several times with bidistilled water.

### 2.2. Polyaniline bulk and film functionalization

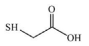
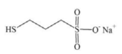
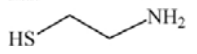
A solution (50 mL) 0.5 molar of the each nucleophile agent was prepared, the polyaniline films and 0.5 g of PANI bulk were dispersed in the nucleophile solution and refluxed during 2 h at 60 °C. The reaction mixture was cooled; the films were extracted and washed with successive portions (250 mL) of deionized water. The PANI bulk were filtered and washed with successive portions (500 mL) of deionized water. Then, the films were dried under dynamic vacuum for 24 h. The modified PANI bulk was dried under dynamic vacuum at 50 °C for 48 h. The nucleophiles used to modify the polymer are described in Table 1 and in Scheme 1 the reaction of functionalization are depicted.

The characterization of the modified PANI was performed using X-ray photoelectron spectroscopy (XPS) using the modified PANI bulk, and the surface modification was investigate using contact angle measurement of the PANI films.

### 2.3. Measurement set-up

The electrical resistance of sensor materials stripes were measured along the specimen length (the materials were cuts out in pieces of 15 mm of length and 5 mm of width) by the two-point technique using a multimeter Sefram 7338. The stripe was placed on a planar holder with copper electrodes fixed on both sides of the specimen. Time-dependent electrical resistance measurements were performed during adsorption and desorption cycles. In the former case the holder with the specimen was quickly transferred into an airtight erlenmeyer flask (0.500 L) saturated with vapors of the respective analyte due to the presence of a 0.050 L of the analyte at the flask bottom. The measurements were conducted in saturated vapours at atmospheric pressure and temperature 25 °C. After 6 min of measurement, the holder was promptly removed from the flask and for the next 6 min the sample was measured in the desorption mode. These cycles were repeated

**Table 1**
Nucleophiles used for modification of polyaniline.

| Molecule | Shorthand | Chemical structure |
|---|---|---|
| Thioglycolic acid | TIO |  |
| Sodium mercaptopropansulfonate | MPS |  |
| Dodecanothiol | DOT |  |
| Cysteamine | CIA |  |