

## Tuning the molecular sensitivity of conductive polymer resistive sensors by chemical functionalization.

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**Abstract.** Polyaniline thin films are chemically functionalized by nucleophilic addition of thiols bearing different functional groups: carboxylic, amine, -dodecyl and sulfonic. The modification is tested using FTIR and XPS spectroscopy. Then, the films are used as resistive sensors for different volatile organic compounds in a static measuring system. The sensitivity of conducting polymers to alcohols and heptane is strongly affected by the chemical functionalization of the materials. Polyaniline show an increasing signal when the chain length of different alcohols is increased. The incorporation of hydrophilic groups on the PANI chains seems to maintain the trend. On the other hand, the polymer modified with a long alkyl chain (PANI-DOT) show negative response for methanol and the signal increases up to propanol to decrease for longer chains. PANI-DOT show the largest signal for heptane of all polymers tested. Therefore, the functional group attached to the conductive polymer chain can be used to tune the molecular sensitivity of the resistive sensor

### Introduction

Sensing of volatile organic compounds (VOCs) is important in environmental control, explosives detection, aroma identification and health diagnostics.[1] Specifically, contaminants should be detected to control concentration and exposure of humans.[2] Resistive sensors are based on a change of electrical resistance due to interaction of the sensing material with the volatile compounds. Conducting oxides (e.g. SnO<sub>2</sub>) are usually used for such purpose, [3] but they have to be heated above 200 °C to have a measurable conductance. On the other hand, conducting polymers has measurable conductivity at normal (e.g. 25 °C) temperatures. Therefore, they have been widely used to build sensors for volatile organics.[4] Sorption (both surface adsorption and bulk absorption) of a volatile organic compound on a conducting polymer could induce different processes which change the conductivity.[5]:

$$\Delta\sigma = (1/\Delta\sigma_{\text{ele}} + 1/\Delta\sigma_{\text{hop}} + 1/\Delta\sigma_{\text{ion}})^{-1} \quad (1)$$

$\Delta\sigma_{\text{ele}}$  is the change in conductivity of the polymer chains (intrachain) due to the interaction of the analyte affecting the electron density on the polymeric chains.  $\Delta\sigma_{\text{hop}}$  is the change in electron hopping (interchain) between polymer chains which could be modulated by the presence of the analyte in the film. The analyte could cause physical swelling of the material and therefore increase the chain to chain distance, making the hopping more difficult. Additionally, the polarity of the analyte could screen the charge carriers in the different chains, affecting the conductivity.  $\Delta\sigma_{\text{ion}}$  is the change in ionic conductivity across the polymer layer. Since the conducting polymer has mobile counterions balancing the charge, the ions could transport charge between the electrodes. Again, polar analytes could screen the ion charges and affect the conductivity. The intrachain conductivity is usually much larger than the electron hopping. Therefore, the effect of the analyte on the

electronic properties of the polymer chains is usually negligible when compared with the effect on hopping. Moreover, the swelling could be small due to the relative rigidity of the polymer chains. However, significant swelling/deswelling of a polymer is not usually a reversible process and could induce hysteresis. Volatile sorption could be strongly affected by the presence of functional groups on the polymer chains, due to interactions between the analyte and the groups. It is possible to produce conducting polymers bearing different functional groups by copolymerization,[6,7] The method require to adjust the polymerization conditions in each case. On the other hand, functional groups can be attached to conducting polymers by well known organic chemistry reactions.[8] The functionalization of a preformed conductive polymer film only requires to set the conditions for the reaction since the base film is the same.[9,10,11,12,13] In the present communication, we describe the use of different functionalized polyanilines as sensing materials for model volatile compounds (alcohols and alcanes).

### **Experimental Part**

Aniline (Merck) was distilled under reduced pressure prior to 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. Polyethylene (PE) and Polypropylene (PP) films (1 mm thick) were purchased from Goodfellow and used as transparent substrates.

#### **Polyaniline film synthesis.**

PANI (emeraldine form) was prepared by oxidation of aniline (0.1 M) in 1M HCl with ammonium persulphate (equimolar to aniline) following the procedure published elsewhere.[14] The reactor was immersed in an ice-water bath to keep the temperatures below 5 °C. In order to produce PANI onto polyethylene (PE) or poly(ethylene terephthalate) (PET). In the later case, woven cloth of PET is used to increase the total surface area for a given geometric area. 4x4 cm squares of each polymer film were immersed in the polymerization solution. Thin films (200-600 nm) films of PANI form on the substrates.[15] After the polymerization finished, the films of PANI on the plastic substrates were washed for 15 min in pure water to ensure that no reactant was retained in the film.

#### **Polyaniline film functionalization.**

The functionalized PANI films were produced by coupling of diazonium ions with PANI thin film.[9] The amines were diazotized with sodium nitrite and concentrated HCl in an ice bath.[11] PANI films were suspended in TRISs buffer (pH = 8) and mixed with the diazonium salt solution in an ice bath. The modified films were washed first with 1 L of 1 mol L<sup>-1</sup> HCl solution and then with 1 L distilled water. Then the films were dried (dynamic vacuum for 48 h). The nucleophiles used are: thioglycolic acid (HSCH<sub>2</sub>COOH, TIO), Sodium mercaptopropansulfonate (HSCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>H, MPS), dodecanthiol (HSC<sub>12</sub>H<sub>23</sub>, DOT) y Cysteamine (HSCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, CIA).

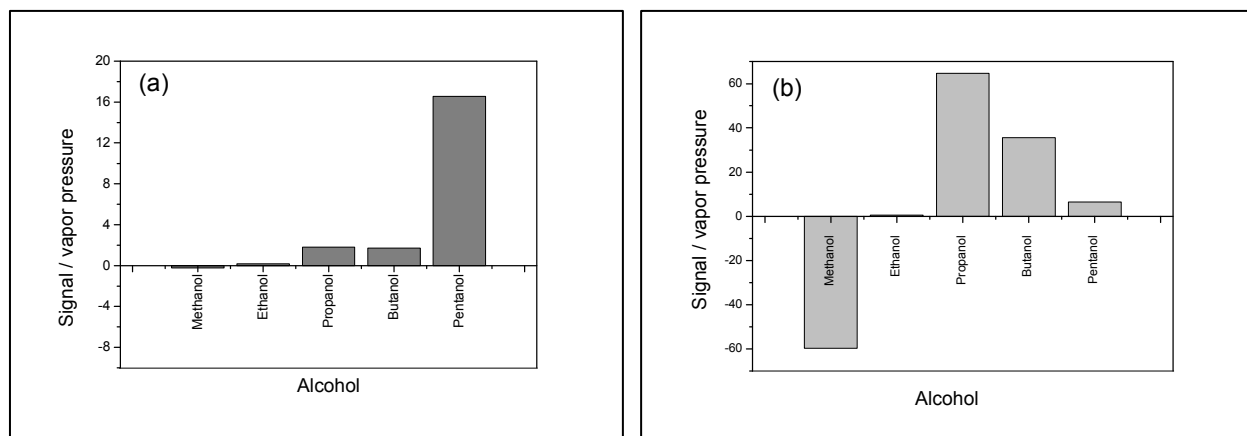
#### **Measurement set-up.**

The cloth covered with sensitive material is cut into 1.5 x 1 cm rectangles, which are contacted in the extremes by pressing copper plates. The sensors are placed inside a sample chamber made of a closed 250 ml Erlenmeyer flask, which is thermostated in a water bath. 25 ml of liquid sample are set inside the flask and left to equilibrate with the head space at the set temperature. In this static set-up the equilibrium conditions can be achieved. The response signal of the sensor was measured with a multimeter connected to a PC via an USB connection and a two probe method was employed for the measurement.

### **Results and Discussion**

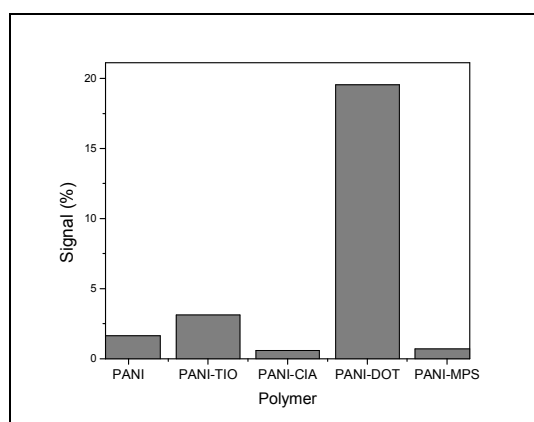
A typical resistance-time response for repetitive exposures to methanol shows a different resistance response to the same compound. The difference could arise from different degree of interaction

between methanol and the film and/or different effect on the conductivity. In principle, the conductivity changes could be due to changes in the charge carrier mobility in the polymer chains (an electronic effect) or to changes in the interchain hopping (a swelling effect). Both effects require the interaction of the volatile molecules with the polymer chains. In Fig. 1 it is shown the response of functionalized PANI films to different alcohols. As it can be seen, the materials are sensitive to the presence of the organic molecules and the sensitivity depends on the molecule. Interestingly, increasing the chain length (decreasing polarity) of the alcohol induces an increasing signal (Figure 1.a) for the polymer functionalized with a hydrophilic group ( $-\text{NH}_2$ ).



**Fig. 1.** Comparative normalized resistance signal (at saturation) obtained by exposing to different alcohols, sensors made of: (a) hydrophilic polyaniline (PANI-CIA, functionalized by reaction with cysteamine). (b) hydrophobic polyaniline (PANI-DOT, functionalized by reaction with dodecanthiol). Each signal is normalized to the vapor pressure of the volatile at the measurement temperature ( $25\text{ }^{\circ}\text{C}$ ) for comparison.

On the other hand, when a hydrophobic polyaniline is produced by incorporation of an alkyl radical ( $-\text{C}_{12}\text{H}_{23}$ ), reacting the PANI with dodecanthiol, (PANI-DOT), the trend is different. As it can be seen in Figure 1.b, the signal begins in a negative value (methanol), increases with the chain length of the alcohol till propanol and then decreases. It seems likely that better solvation of the film having alkyl chains are achieved by the alcohols with intermediate alkyl chains. However, it should be expected for alcohols with longer chains to solvate better the PANI-DOT.



**Fig. 2.** Comparative resistance signal (at saturation) of different functionalized polyanilines when exposed to saturated vapor of heptane, at  $25\text{ }^{\circ}\text{C}$ .

While the effect of alkyl chain length in alcohols is less clear, when the sensors are exposed to an alkane (heptane) lower signal levels are shown overall but a clear signal effect of the sensor material is observed. The sensor based on a hydrophobic polyaniline (PANI-DOT) show a signal nearly 5

times larger than other polymers. It seems that strong van der Waals interactions between the volatile alkane and the long alkyl chains of the attached functional groups induce a strong signal.

### Conclusions

Functionalized polyanilines can be easily prepared by nucleophilic addition of different thiols to polyaniline. The polymers show finite resistance and are sensitive to different volatile molecules. There is an effect of alkyl chain length when the sensors are exposed to alcohols, which is more marked with a polyaniline modified by addition of cysteamine (PANI-CIA). On the other hand, when a hydrophobic polyaniline, modified by addition of dodecanthiol (PANI-DOT), is exposed to different alcohols a non monotonic change of signal is observed. However, PANI-DOT shows a signal nearly five times larger than other polyanilines, when exposed to heptane. It seems that strong interaction between the volatile alkane and the attached functional group induces a large signal. The results suggest that chemical functionalization of polyaniline films allows to tune the molecular sensitivity of resistive sensors.

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## **Materials and Applications for Sensors and Transducers III**

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### **Tuning the Molecular Sensitivity of Conductive Polymer Resistive Sensors by Chemical Functionalization**

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