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Detection of volatile organic compounds using a polythiophene derivative

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Conjugated polymers have been subject of great interest in the recent literature from both fundamental point of view and applied science perspective. Among the several types of conjugated polymers used in recent investigations, polythiophene and its derivatives have attracted considerable attention over the past 20 years due to their high mobility and other remarkable solid-state properties. They have potential applications in many fields, such as microelectronic devices, catalysts, organic field-effect transistors, chemical sensors, and biosensors. They have been studied as gas and volatile organic compounds (VOCs) sensors using different principles or transduction techniques, such as optical absorption, conductivity, and capacitance measurements. In this work, we report on the fabrication of gas sensors based on a conducting polymer on an interdigitated gold electrode. We use as active layer of the sensor a polythiophene derivative: poly (3-hexylthiophene) (P3HT) and analyzed its conductivity as response for exposure to dynamic flow of saturated vapors of six VOCs \([n\text{-}\text{hexane, toluene, chloroform, dichloromethane, methanol, and tetrahydrofuran (THF)}]\). Different responses were obtained upon exposure to all VOCs, THF gave the higher response while methanol the lower response. The influence of moisture on the measurements was also evaluated.

1 Introduction The growth of population and industrial development gave rise to unprecedented air pollution that can cause harm to humans and the environment. Efforts to reduce this pollution include recognition of the problem, collection of information, definition of sources and causes, and the selection and implementation of the appropriate solutions [1]. In order to control the emission levels of pollutants, portable devices using arrays of gas sensors have been developed over recent years [2–4]. These so-called electronic noses (e-nose) are mainly based on selective layers made from metal oxide semiconductors [3, 5–7]. However they have been shown some drawbacks, which include their poor selectivity and sensitivity, high operation temperatures, and instability because of response to humidity [8].

Conjugated polymers have been proposed as alternative materials to improve these properties. The easy synthesis, the diversity, and the sensitivity at room temperature are the main advantages of these polymers over inorganic materials [7–10]. Among the several types of conjugated polymers used in recent investigations, polythiophene and its derivatives have attracted considerable attention due to their good environmental and thermal stability, their high mobility, and other remarkable solid-state properties [11]. Polythiophenes can be obtained from chemical or electrochemical polymerizations and have been used as sensing materials for different gases and vapors like NO\(_x\) [12, 13] and volatile organic compounds (VOCs) [14–16]. VOCs include a variety of chemicals that significantly evaporate under normal conditions [1]. They have been contributed to air pollution and they are suspected to cause cancer in humans. Therefore, the control of VOCs emission levels is currently of wide interest.

The interaction of these analytes with polythiophene films can cause changes in their color, mass, work function, and electrical conductivity [7, 12–16]. Of particular interest is the study of the last property that is relatively easily and inexpensively to be used in sensors.

In this paper, we report on the use of P3HT for VOCs electrical detection. The sensing measurements were undertaken on an interdigitated electrode by measuring the current.
versus time with applied voltage at room temperature. The effect of different VOCs on the electrical properties of P3HTs is investigated and their potential application as electrical sensor is discussed.

2 Experimental

We use as active layer of the sensor a polythiophene derivative: poly (3-hexylthiophene) (P3HT), Fig. 1(A). This material was synthesized via oxidative polymerization using ferric trichloride. The monomer was dissolved in nitromethane and solid ferric chloride was added quickly to the mixture by a powder addition, funnel under nitrogen atmosphere and magnetic stirring. In the next step, chloroform was added to the mixture which was magnetic stirred for 4 h. The polymer was isolated by precipitation into methanol. The solid was dissolved in chloroform and insoluble products were removed by filtration. The soluble fraction was treated with aqueous ammonia solution and EDTA for dedoping and the dedoped polymer was precipitated into methanol. The number-average molecular weight ($M_n$) value of dedoped polymer, estimated by HPSEC in tetrahydrofuran (THF), were around 10,000 g/mol.

P3HT (15 mg mL$^{-1}$ in chloroform) were spin-coated (1000 rpm, 60 s, 25 °C) onto a glass substrate and a glass substrate coated with the interdigitated chromium–gold array. Patterned Au electrodes were prepared by photolithography, where 25 pairs of lines act as electrode contacts. The length of the electrodes, their thickness, and the distance between them are 800 μm, 100 nm, and 100 μm, respectively [Fig. 1(B)]. Spin-coated films onto interdigitated array were about 100 nm thick.

UV–Vis absorption measurements of the film were carried out in a HITACHI U-2001 spectrophotometer in the range between 350 and 800 nm. The emission spectra of this film were recorded in a SHIMADZU 5301RFPC spectrofluorometer. The sample was optically excited at 490 nm. The response characteristics of the micro gas sensor films were then investigated against various test gases. The response behavior of P3HT sensors were characterized by measuring the current versus time with a fixed applied voltage (5 V) at room temperature with a Keithley 238 high voltage source-measure unit, in dark. The sensors were tested in a homemade test chamber in the presence of volatile gases such as n-hexane, toluene, chloroform, dichloromethane, methanol, and THF in dynamic flow, dragged by nitrogen. Prior to data acquisition the sensing units were left under pure N$_2$ flow for ~60 min in the chamber to reach a stable reading.

3 Results and discussion

Figure 2 show the UV–Vis spectrum for a P3HT spin-coated film on glass, featuring $\lambda_{\text{max}}$ at 490 nm, which are related to transitions between delocalized $\pi$–$\pi^*$ states. The region below 350 nm was not recorded since the glass substrate absorbs strongly at this region, therefore only one peak could be observed in the UV–Vis spectrum. The PL spectrum of P3HT film displays a zero-phonon peak ($I_0$) at 640 nm and no vibronic peaks were observed probably due to the high optical quality of the film. These values are close to those reported in the literature for regiorandom P3HT films [17].
Figure 3 shows the normalized current changes for P3HT sensors upon exposure to different VOCs. Normalization has been used to analyze and compare polymers sensors data with different initial currents [18]. In this case, the normalizations were performed using each sensor current immediately before the VOC exposition (t ~ 600 s). The system was designed to be always vapor saturated during the exposures. Considering the effect of moisture on the sensitivity, a test was carried out using water vapor injection and the results show that the moisture did not influence the conductivity of P3HT film.

For others vapors tested it was observed a negative response, indicating that the conductivity of the material decreases in the presence of the VOCs, since the conductivity is directly proportional to current value. The sensors demonstrated a fast response to all vapors. The methanol vapor showed the minimum response and THF vapor the maximum one. For n-hexane and toluene, which are non-polar and weak solvents for P3HT, results show intermediary responses (between methanol and THF).

The sensors current values did not return to the initial ones after the chamber was flushed for 10 min with nitrogen, showing that these changes are partially reversible with different degrees of hysteresis. Most of these hysteresis can be attributed to irreversible attachment of VOCs at P3HT and/or irreversible effects of VOCs on the conduction mechanisms of these films. The nitrogen flow can also promoted small decreases of P3HT current with the time (ca. 4% for the analysis period) that can also contribute to these hysteresis.

To better understand the response effects, conduction mechanisms of the polymers must be conceived. In the room temperature regime, polaron hopping conduction is the most accepted model of transportation mechanism inside the conjugated polymer [14, 15]. The interaction between the organic material and gas molecules results in an increase or decrease of polaron densities on the band gap of the polymers. Furthermore, exposure of the conducting polymers to chemical solvent vapors can cause polymer swelling, resulting a decrease in the electrical conductivity.

The P3HT responses for some VOCs are the result of weak physical interactions between analytes and polymers causing swelling of the polymer films [19]. Swelling of the polymer matrix due to absorption of organic vapors may also increase the distance between polymer chains, thereby decreasing the hopping conduction. This effect is the most probable mechanism that can explain the electrical behavior of the sensor.

This swelling effect depends on the interactions between polymer and vapor and the polymer solubility. This process can influence the aggregation of the polymer chains, changing their conformation and sometimes cannot be completely reversed only by passing a nitrogen flow. The highest response for THF is probably caused by the swelling effect, since THF is a polar analyte and a strong solvent for P3HT. The analyte molecules can penetrate into the polymer film and enlarge the spacing between the polymeric chains, resulting in a lower conductivity. The poor sensitivity to methanol, which is not a solvent for P3HT, is probably caused by the absence of the swelling effect. Similar effects were observed for optical VOCs detection using P3HT as active layer. The complete set illustrates the variety of responses and it was not possible to directly correlate the responses intensities with any properties of these analytes, such as dielectric constants or dipole moments for example [20].

4 Conclusions In summary, we have demonstrated that a polythiophene derivative, P3HT, is a promising material for use in VOC sensors. Sensing mechanisms involving various physical interactions between the polymers and analytes, and further experiments are necessary to better identify and understand those mechanisms. The simple preparation approach, which can offer excellent properties as well as the low-cost interdigitated electrodes, suggests that this polythiophene derivative film-based device could be used in the gas sensors field, such as in electronic noses.

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References


