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Acetaldehyde Chemical Sensor based on Molecularly Imprinted Polypyrrole.

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Abstract

This paper presents a chemical sensor based on molecularly imprinted polypyrrole for acetaldehyde detection. This molecule belongs to the family of volatile organic compounds (VOC's) and is known for its toxicity. The sensor working principle is the measurement of conductivity variations of polypyrrole films deposited on interdigitated electrodes. The molecularly imprinted polypyrrole (MIP) films are deposited on the electrodes by direct electropolymerization in a bath containing pyrrole monomer, acetonitrile as solvent and acetaldehyde as template. Non imprinted polypyrrole (NIP) films are prepared in the same conditions without template. The behaviour of both films is compared by mass adsorption measurements using a quartz crystal microbalance and impedance measurements as well. The MIP-based sensors show a rapid and reversible response to acetaldehyde in the ppm range while NIP gives an insignificant signal.

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Keywords:

1. Introduction

Acetaldehyde is considered as carcinogenic and toxic. The TWA threshold limit (exposure for 8 hours workday and a 40 hours workweek) is 100 ppm and 150 ppm for short term (15 min) exposure for acetaldehyde [1]. The main sources are essentially incomplete combustions or emissions from paints, linoleum, varnishes [2]. Several

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technologies were considered for its detection by using metal oxides [3] or quartz crystal microbalance (QCM) coated with polymers [4] for instance. Among polymers as sensitive layers, Molecularly Imprinted Polymers (MIPs) present very interesting characteristics. In brief, MIP's are obtained from a polymerization initiated in the presence of a chosen template molecule that will be extracted afterwards. Functional monomers bind to the target molecule (template) thanks to specific interactions (hydrogen bonds for instance) and are polymerized with a crosslinker. The so formed polymer encapsulates the template. The removal of the template creates specific recognition sites complementary in shape, size and chemical functionality to the template molecules [5] in the polymer matrix which have a good affinity to the target molecule. The MIPs demonstrate the following advantages: high selectivity and affinity for target molecules; high physical robustness, strength, resistance to temperature and pressure; inertness towards acids, bases, metal ions and organic solvents; long-term stability and operating at room-temperature. By the possibility of synthesis of specific polymers able to recognize biological and chemical molecules according to the "key-lock" system [6], Molecular Imprinting Technology (MIT) is a versatile and promising technology for practical applications in many areas, such as antibody receptors [7,8], protein separation [9-11], pollutant determination [12], catalysis [13, 14], drug delivery [15] and chemical sensors [16-19].

In this work, the sensor is a chemoresistor and it consists in a MIP sensitive layer, polypyrrole (PPy) deposited on a pair of interdigitated gold electrodes laying on a SiO_2/Si substrate. As polypyrrole is a semiconductor, its conductivity can therefore be modified by the adsorption of a gas. The signal is the change in conductivity of the sensitive layer in contact with acetaldehyde in the atmosphere. The aim is to take advantage of the remarkable characteristics of MIPs and the simplicity of chemoresistors. MIP Polypyrrole can be synthetized by various methods but, as the sensitive layer has to be deposited on metal electrodes, electropolymerization seems convenient to insure adhesion. For comparison, non-imprinted PPy films called NIP were prepared under the same conditions but without template. The behaviours of MIP and NIP are compared by impedance measurements and mass adsorption measurements with a quartz crystal microbalance.

2. Experimental

The sensors consist in gold interdigitated electrodes deposited on a SiO_2/Si substrate (Fig. 1). The chips are bonded in a 2 pin-TO header (the third pin is the ground). The sensitive film will be directly grown by electropolymerization on the electrodes. The width and the finger spacing of the electrodes is 2 µm, a 5-µm-thick MIP film can cover the metallic electrodes with a continuous film. The advantages of this method are a good adhesion and the fact that the sensitive layer is deposited only on the useful area avoiding further photolithography steps.

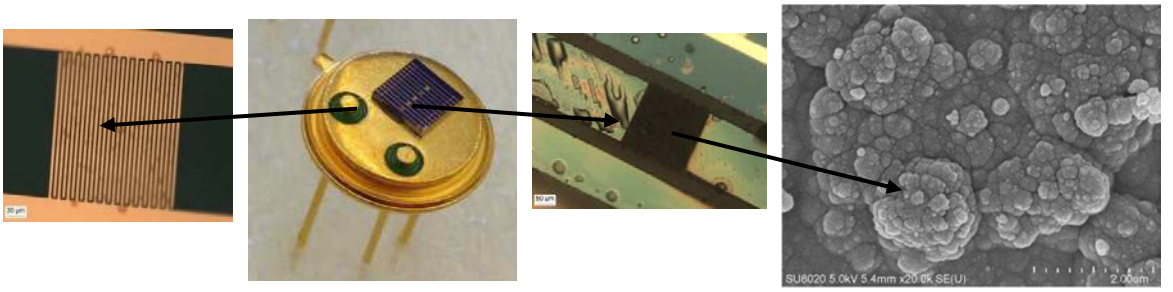

Fig. 1. Picture of the fabricated sensors: a) electrodes before deposition b) general view c) electrodes covered with MIP PPy film d) SEM picture.

The MIP films are deposited by direct electropolymerization (in pulsed mode) on the electrodes in a bath containing: 50 ml of acetonitrile (99.8% anhydrous), 0.62 g of sodium perchlorate, 0.335 ml of pyrrole monomer and 50 µl of acetaldehyde. All reactants were purchased from Sigma-Aldrich. A 3-electrodes setup is used having an Ag/AgCl reference electrode and a stainless steel counter electrode as cathode. The gold electrodes are the working electrode (anode). After placing the sensor in the solution, the electropolymerization was launched according to the following program: 1.8 V for 0.1 s, 0 V during 0.1 s (4000 pulses).

The molecular template extraction was carried out by dipping the samples in a mixture of acetic acid (1/3) and methanol (2/3) for 8 h. All the films present a typical cauliflower structure like can be observed by SEM (Fig. 1d).

For comparison, NIP films were prepared in the same conditions but without template. The behaviors of the MIP and NIP are compared by impedance measurements and mass adsorption measurements with a quartz crystal microbalance (films were electrodeposited on QCM substrates in the same conditions).

3. Results and discussions

The sensors and quartz crystals were placed in a gas cell and exposed to acetaldehyde gas at various concentrations in humid air (50 % RH at 22 °C) thanks to mass flow controllers imposing a constant total flow of 1000 ml/min.

Fig. 2 shows the relative mass uptake of the films after acetaldehyde injections in moist air. A rapid and reversible response can be observed with the MIP while almost no mass uptake can be found with the NIP. Fig. 3 shows the sensor conductance versus acetaldehyde concentration at room temperature in moist air. A significant response in the ppm range is observed for the MIP while the corresponding NIP shows almost no response showing the MIP effect. In our case, PPy is almost intrinsic and presents a low conductivity. Adsorption of acetaldehyde, an electron donor, allows the increase of electron concentration leading to a conductivity increase. The response time is 3 min and recovery time is about 3 min, corresponding to what is observed with the mass evolution.

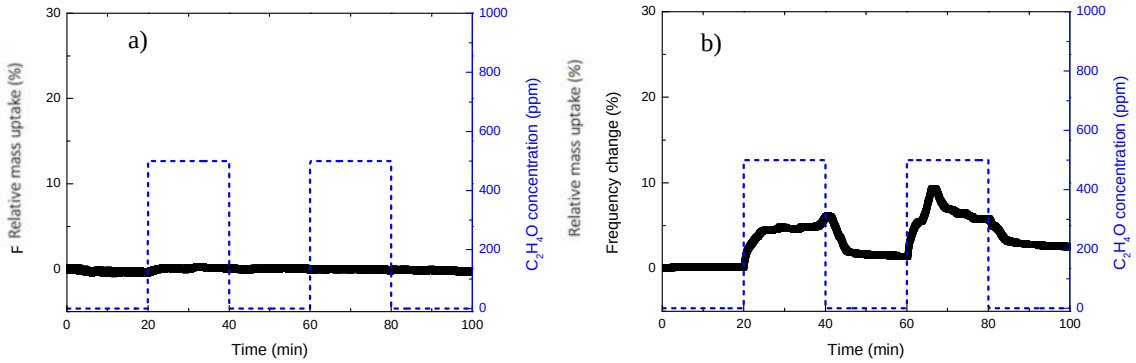

Fig. 2. Relative mass uptake after 500 ppm acetaldehyde injections in moist air a) NIP b) MIP

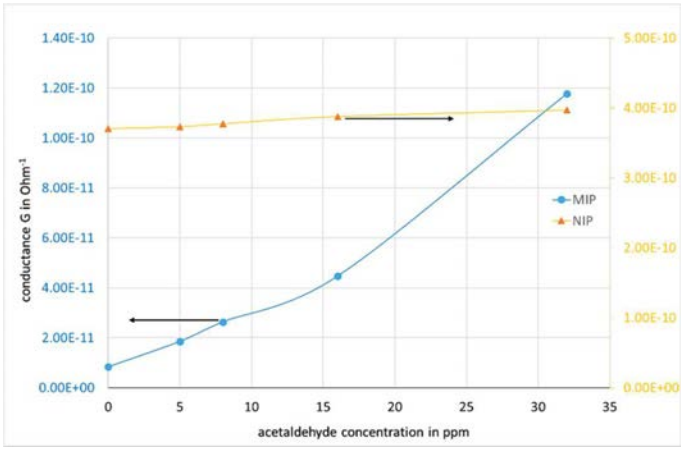

Fig. 3. Conductance versus acetaldehyde concentration in moist air (50 % relative humidity @ 20 °C)

4. Conclusions

This paper presents a chemoresistive sensor based on molecularly imprinted polypyrrole for acetaldehyde detection. The MIP films are deposited on the electrodes by direct electropolymerization. Non imprinted polypyrrole (NIP) films are prepared in the same conditions without template. The MIP-based sensors show a rapid and reversible response to acetaldehyde in the ppm range at room temperature while NIP gives an insignificant signal proving the MIP effect. This kind of sensor can be useful for VOC monitoring.

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