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Low-bandgap Polymers, a New Sensitive Surface for Ammonia Detection

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Summary:

Ammonia (NH_3) gas presents risks to human health and environment, requiring continuous monitoring using reliable sensors. The versatility and the sensitivity to ammonia of conductive polymers make them excellent candidates for use as active layers in sensors. In this study, our goal is to analyze and compare the response of two chemiresistive sensors fabricated using two low-bandgap polymers with distinct functional groups in their side chains to detect NH_3. The manufactured sensors exhibit high sensitivity to NH_3 (0,37%/ppb and 0,27%/ppb, respectively) and a good repeatability.

Keywords: Gas sensors, drop-casting, semiconducting polymers, thin film, chemiresistive sensor

Introduction

NH_3 is a hazardous compound commonly found in products and industrial environments. Even at low concentrations, in parts per million (ppm) levels, this compound can present significant risks to human health and to the environment due to a high level of toxicity and its capacity to react with acids forming harmful aerosols. Therefore, the detection of this gas becomes necessary to mitigate potential environmental and health risks [1].

Conductive polymers (CPs) have appeared as a promising active layer of sensors to detect compounds like NH_3. Compared to metal-oxide semiconductors, CPs present a lower cost, an ease of processing, a high sensitivity, and an ability to work at room temperature [2]. Moreover, the capacity to add/modify functional groups during the synthesis enhances their adaptability and versatility, providing the possibility to target more specific applications.

CPs with narrow bandgaps were widely studied because of their capacity to exhibit intrinsic electrical conductivity without doping and their broad absorption spectrum which can be beneficial for applications in organic devices. For instance, Low-bandgap polymers have exhibited good selectivity and sensitivity in detecting NH_3 when applied in Field Effect Transistor Sensors [3]. This study aims to evaluate the application of those materials in simplest devices such as chemiresistive sensors, known for their low cost and easy implementation.

Materials and Methods

The active layer of the sensors were the low-bandgap polymers poly[4,4'-diethylhexyl-4H - cyclopenta [2,1-b;3,4-b'] dithiophene - alt - 2,5 - didodecyl-3,6 - bis (thiophen-2-yl)pyrrolo[3,4-c]-pyrrole-1,4-dione] (PCPDPDPP_C12) and poly[4,4' -diethylhexyl-4H-cyclopenta [2,1-b;3,4-b'] dithiophene – alt -2,5- di(2-(2-(2-methoxyethoxy)ethoxy) ethyl-3,6-bis (thiophen-2-yl) pyrrolo[3,4-c] -pyrrole-1,4-dione] (PCPDPDPP_TEG), both synthesized according the process described previously [4]. From this point forward, the materials will be referred as C12 and TEG, respectively.

Both polymers were dispersed in Chloroform (1 mg/mL) and agitated using an ultrasonic bath for 2 hours. To make the sensors, 6 µL of the solution was drop-casted onto gold interdigitated electrodes, 50 µm of space between the digits, and allowed to dry for 3 hours at ambient temperature.

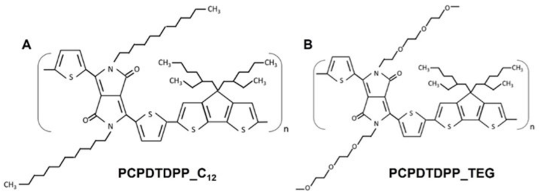

Fig 1 – Molecular structure of the low-bandgap polymers A) PCPDTDPP_C12 and B) PCPDTDPP_TEG.

To characterize the sensors, two cards with 10 devices each were placed inside a treated stainless-steel chamber at room temperature (~23 °C) and monitored by a Sensirion SHT21 temperature and relative humidity (RH) sensor. The NH_3 gas in nitrogen was obtained from Messer (9,70 ppm concentration). The flow rate was set for 4 L/min, with the NH_3 concentration ranging from 50 to 2000 ppb. RH was maintained at 50% using an Omicron gas generation and dilution system, model OMI-SR042A-A. Sensors resistances was measured by the Agilent Data Acquisition/Switch Unit, model 34970A, and NH_3 concentration inside the chamber was monitored by LGR gas analyzer, model 907-0016-0000.

Results

In general, independently of the functional group, all sensors show an increase in the resistance values when exposed to NH_3.

Fig 2 shows the continuous response-recovery curves for NH_3. A direct correlation between the intensity of the response and the concentration of ammonia used in the cycles was noticeable. This increase shows that both materials are sensitive for NH3 and can be used as detectors.

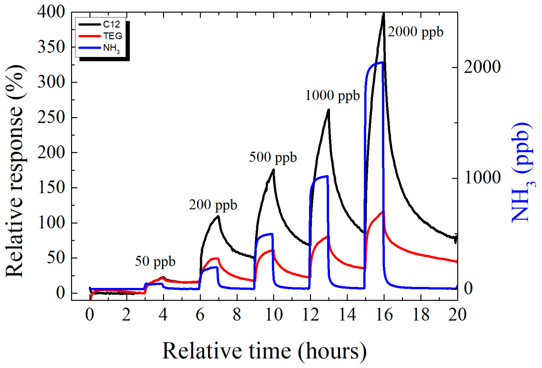

Fig 2 - Response of the PCPDTDPP_C12 and TEG NH_3 sensors at 50% RH in continuous response-recovery curves.

Furthermore, sensors based on C12 polymer proved to be more stable in terms of reproducibility and had lower resistance values (ranging between 0,2 MΩ to 9 MΩ). More TEG sensors were going out of scale due to high resistance values (from 30 MΩ to more than 100 MΩ) causing difficulties in analyzing their reproducibility. The observed difference for resistance values can be attributed to functional groups in the side chains: twelve carbons to C12 and a trietyleneglycol to TEG.

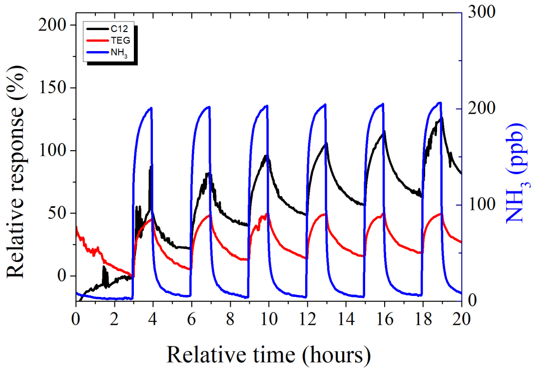

Fig 3 – Repeatability study of the PCPDTDPP_C12 and TEG sensors at 50% RH and 200 ppb of NH_3.

Fig 3 exhibits the repeatability curves response. In terms of repeatability, both sensors demonstrated a low coefficient of variation over the 6 cycles of NH_3, with C12 sensors showing approximately 18% variance and TEG sensors demonstrating around 13%. Moreover, C12 and TEG present a high sensitivity at 0,37%/ppb and 0,27%/ppb for 200 ppb of NH_3, respectively.

To summarize, both sensors exhibited sensitivity to NH_3, displaying good repeatability and sensitivity at 50% RH, with C12 demonstrating superior stability and lower resistance values.

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