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Printed flexible gas sensors based on organic materials

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Abstract

Functional ammonia, humidity and nitrogen dioxide sensors were fabricated by screen and gravure printing on flexible poly(ethylene terephthalate) (PET) substrates. Ammonia and humidity sensors were based on resistive principle (chemiresistors) while an electrochemical sensor was used for nitrogen dioxide detection - a semi-planar, three-electrode topology with polymer electrolyte containing organic ionic liquid was utilized. New type of polyaniline hydrochloride colloid was used as a sensitive layer for ammonia detection whereas a thin film of poly(3,4-ethylenedioxythiophene):poly(sodium 4-styrenesulfonate) (PEDOT:PSS) was used for the humidity sensor. All sensors were completely prepared by printing technologies which enables future compatibility with R2R fabrication process intended for mass production of low cost and all-organic flexible gas sensors.

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Keywords: Printed sensor; ammonia; nitrogend dioxide; humidity, organic materials

1. Introduction

Gas sensors and systems have become essential in the protection of human health in several areas such as industrial manufacturing, personal safety protection and environmental monitoring. Especially the detection of hazardous and toxic gases (e.g. NO_2 and NH_3) and other parameters (e.g. temperature and humidity) is currently a natural part and parcel of a measurement procedure determining quality and comfort of human environment. Traditional metal oxide and electrochemical sensors are poorly integrated into low cost, battery-powered flexible

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devices intended for the future applications in The Internet of Things. Therefore, a growing attention has been paid to the use of organic materials and printing technologies [1] allowing the preparation of thin organic sensitive layers or organic-based electrolytes for printed chemiresistors [2-4] or electrochemical sensors [5-7], respectively. These organic-based sensors usually work at room temperature, exhibit low power consumption and can be fabricated on flexible substrates by using cost effective printing techniques. This fact makes them attractive for logistic sector (cold chain, monitoring of perishable goods during transport) and multi-sensor devices and systems which monitor environmental air-pollution or protect humans from dangerous concentrations of hazardous and toxic gases.

In this study, ammonia, humidity and nitrogen dioxide sensors intended for the above-mentioned applications are presented. All sensors show good sensitivity, reversibility and stability of the response in the tested range and they were newly fabricated by gravure and screen printing.

2. Sensor fabrication and measurement setup

2.1. Ammonia and humidity sensor

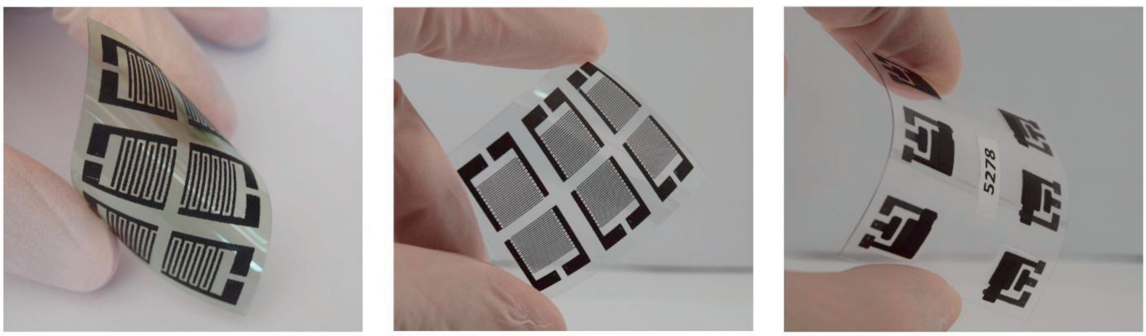
Chemiresistive ammonia and humidity sensors (Fig. 1a,b) were fabricated by gravure printing (Norbert Schläfli Labratester) of organic-based sensitive layers on flexible PET foil (unless otherwise stated, Melinex ST504, thickness 175 μm). Novel type of polyaniline (PANI) hydrochloride, which was synthesized in chloroform in the presence of surfactant, was used for the ammonia sensor while aqueous dispersion of poly(3,4-ethylenedioxythiophene):poly(sodium 4-styrenesulfonate) (PEDOT:PSS) was used for the humidity sensor. Subsequently, carbon interdigital electrodes (IDE) were screen printed (EKRA E1) onto both active layers. The layout of the IDE structures were 500/500 μm (gap/finger width) and 200/200 μm for the ammonia and humidity sensor, respectively.

2.2. Nitrogen dioxide sensor

Fully printed nitrogen dioxide sensor was solely fabricated by screen printing technology (Fig. 1c). Fabrication process consisted of three basic steps: (i) printing of bottom electrode structure (counter and pseudoreference electrode), (ii) printing of the organic-based electrolyte layer, (iii) printing of the working electrode. The sensor layout was thoroughly described in our previous work [5,8], where material specification and printing process were discussed in detail.

2.3. Sensor testing

All sensors were characterized by means of gas test system for parallel measurement up to six samples. It consisted of a test chamber, five mass flow controllers, a PC and two gas tanks: (i) reference gas mixture (100 ppm NO_2 or 1000 ppm NH_3 for our experiments), (ii) synthetic air. Required gas concentrations were prepared by mixing



a) b) c)

Fig. 1. (a) ammonia sensors; (b) nitrogen dioxide sensors; (c) humidity sensors.

reference gas with humidified synthetic air. All measurements were performed under the following conditions: 22 °C, 40% RH and analyte flow rate = 1 l/min. The lowest practically detected concentrations (the limit of the gas test system) that can be practically achieved under the conditions mentioned above are presented in Table 1. Chemiresistive ammonia and humidity sensors were measured by using precision LCR meter (Agilent E4980A, sinusoidal measuring voltage, 1 V RMS, 1 kHz). Electrochemical nitrogen dioxide sensor was measured by digital multimeter (KEITHLEY 2700) connected to 6 channel potentiostat board assembled in our laboratory.

3. Results and discussion

Chemiresistive ammonia and humidity sensors are based on impedance change of the active layer under the analyte exposure. The increase of the impedance of the ammonia sensor (Fig. 2a) based on novel PANI colloid can be explained by the conversion of conducting PANI salts to non-conducting PANI base [9]. Generally, it can be concluded, that sensitivity, response stability and dynamic properties of chemiresistors depend on both IDE layout and structure of the active layer. Morphology, porosity and thickness of the sensitive layer play also an important role when detection principle is associated with adsorption/desorption processes on solid/gas phase interface. This suggestion is supported by the shape of the calibration curve of the NH_3 sensor (Fig. 2b) which can be well fitted by Freundlich adsorption isotherm. The decrease of the impedance of the humidity sensor (Fig. 2c) is based on the dissociation of OH groups in PSS chain and the formation of free charge carriers in PEDOT chain. This mechanism can also explain a great disproportion between response/recovery times (t_{90}/t_{10} in Table 1) because the OH groups dissociation is quite fast while the diffusion based reverse process is much slower. It should be also noted that the probability of dissociation depends on the ratio of PEDOT to PSS. Thus the sensitivity of such sensor can be tailored

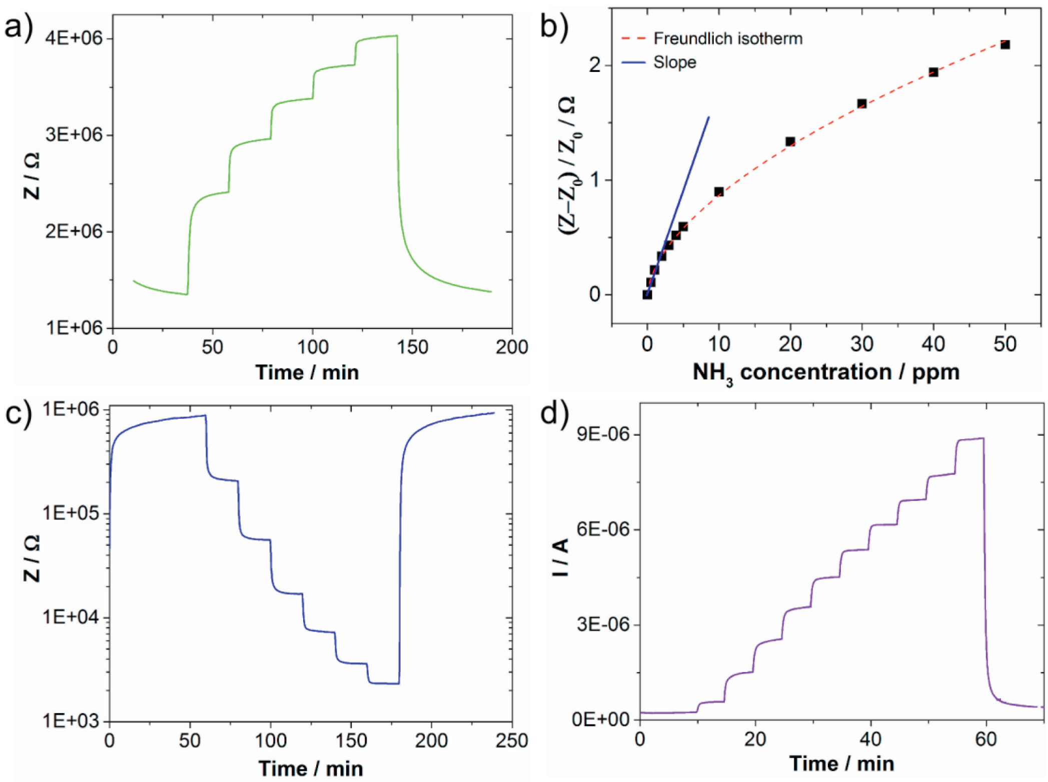


Fig. 2. (a) ammonia sensor response to stepwise increases from 0 to 50 ppm NH_3 (1 step = 10 ppm NH_3); (b) calibration curve of the NH_3 sensor (blue line – slope of the calibration curve in the quasi-linear region, red dashed line – fitting curve according to Freundlich isotherm); (c) humidity sensor response to stepwise increases in the range of 20-80% RH (1 step = 10% RH); (d) nitrogen dioxide sensor response to stepwise increases in NO_2 concentrations: 1, 3, 5, 7, 9, 11, 13, 15, 17 and 20 ppm NO_2.

Table 1. Sensor parameters.

Parameter	NH_3 sensor	NO_2 sensor	RH sensor
Detection principle	chemiresistive	electrochemical	chemiresistive
Tested range	0-50 ppm	0-20 ppm	20-80 %
Theoretical limit of detection (LOD)/the lowest practically detected concentration*	30/500 ppb	20/200 ppb	0.05/1 %
Response/recovery times (t_{90}/t_{10})**	6/17 min	70/60 s	< 30 s/18 min
Hysteresis***	13%	5%	15%

** Limit of the gas test system.*
*** Calculated as an average value from five repeated exposures to 10 ppm for NH_3 sensor, 2 ppm for NO_2 sensor, 60% for RH sensor.*
**** The maximum value in the tested range.*

through this ratio to particular application. Response times, LOD and hysteresis in Table 1 were determined using the procedure described in our previous work [5]. The slope of the calibration curves for ammonia and humidity sensors were determined from linear parts of the dependencies (see line in Fig. 2b) as described in Refs. [3,10,11].

4. Conclusion

We demonstrate successful fabrication of fully printed sensors on flexible PET substrates for the detection of ammonia, humidity, and nitrogen dioxide. All sensors were prepared by gravure and screen printing without using metal-based printing pastes which reduces the production cost and makes these sensors ideal candidates for mass production. Additionally, the use of organic materials as sensitive layers and the absence of metallic electrodes enable to produce all-organic, “green” sensors that can be environmentally disposed of after their life cycle.

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