HIGH SENSITIVE GAS MICROSENSORS BASED ON SULFONATED CNTS AND CNTS/POLYANILINE MIXTURE

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REZUMAT. Un senzor este definit ca un dispozitiv care detectează o cantitate variabilă, de obicei un stimul neelectric şi o transformă în semnale electrice care sunt înregistrate. Performanţele de măsurare sunt definite de caracteristicile de sensibilitate, selectivitate, precizie şi stabilitate a senzorului. Din cauza gradului ridicat de selectivitate şi sensibilitate, senzori electrochimici reprezintă o metodă analitică foarte promiţătoare. Utilizaţi în asigurarea condiţiilor de siguranţă la locul de muncă, în inginerie medicală, analiză de mediu sau sectorul alimentar, senzorii oferă aplicaţii în domenii largi de interes. Dezvoltarea senzorilor electrochimici bazaţi pe nanomateriale, reprezintă un avantaj de amplificare a semnalului şi o rezoluţie înaltă de detecţie, datorită straturilor active de conductivitate superioare, stabilitate termică şi rezistenţă la stres mecanic. Două structuri de microsenzori de gaz, pe baza de nanotuburi cu un singur perete (SWCNT), au fost obţinute şi folosite pentru detectarea unor gaze diferite, cum ar fi CO, NH_3, CO_2. Pe o structură de electrod de aur interdigitizat au fost depozitate, ca straturi active nanotuburile de carbon sulfonate (s-CNT) şi mixturi de nanotuburi de carbon (CNT) / Polianilină (Pani). Microsenzorii obţinuţi, sunt caracterizaţi prin activitate electrochimică ridicată şi prezintă o stabilitate îmbunătăţită, reprezentând o soluţie pentru un sistem eficient de senzori de putere mică, cu aplicabilitate practică în domeniul monitorizării mediului, asistenţei medicale, automatizarii, controlul proceselor industriale, etc.

Cuvinte cheie: microsenzori, nanomateriale, senzor electrochimic, monizarea mediului.

ABSTRACT. A sensor is defined as a device which detects a variable quantity, usually a non-electric stimulus and converts it into electrical signals that are recorded. Measurement performances are defined by the sensitivity, selectivity, accuracy and stability characteristics of the sensor. Because of their high degree of selectivity and sensitivity, electrochemical sensors represent a very promising analytical method. Used in occupational safety, medical engineering, process measuring engineering, environmental analysis, food sector, they provide wide application fields of interest. Electrochemical sensors development based on nanomaterials, represent a signal amplification advantage and high detection resolution due to active layers superior conductivity, thermal stability and mechanical stress resistance. Two gas microsensors, based on SWCNT, were obtained and used for different gases detection, like CO, NH_3, CO_2. On an interdigitized gold electrode structure were deposited, as active layers, sulfonated carbon nanotubes (s-CNTs) and carbon nanotubes (CNTs)/Polyaniline (PANi) mixture, respectively. The obtained microsensors, characterized by high electrochemical activity and improved stability, could be a solution for an efficient low-powered sensor-system with practical application in the field of environmental monitoring, healthcare, automation, industrial process control, etc.

Keywords: microsensor, nanomaterials, electrochemical sensor, environmental monitoring.

1. INTRODUCTION

A sensor is defined as a device which detects a variable quantity, usually a non-electric stimulus and converts it into electrical signals that are recorded. Measurement performances are defined by the sensitivity, selectivity, accuracy and stability characteristics of the sensor. According to the type of energy transfer, sensors are classified as thermal, electromagnetic, mechanical, and electrochemical. Because of their high degree of selectivity and sensitivity, electrochemical sensors represent a very promising analytical method. Used in occupational safety, medical engineering, process measuring engineering, environmental analysis, food sector, they provide wide application fields of interest. Electrochemical sensors development based on nanomaterials, represent a signal amplification advantage and high detection resolution due to active layers superior conductivity, thermal stability and mechanical stress resistance. Nanomaterials in principle take advantage of a larger surface area for molecules that are intended to be immobilized in order to determine a variation of an electrical signal. As result this phenomena increases the number of

binding sites available for specific chemical analyte detection. Various types of nanomaterials are used for electrochemical sensors development.

Carbon nanotubes (CNTs) are one of the most exciting materials because of their unique electronic, chemical, and mechanical properties [2]. Multi-walled (MW) and single-walled (SW), represent two groups of CNTs, which can be synthesized by electrical arc discharge, laser vaporization, and chemical vapor deposition methods. CNTs behave as either metals or semiconductors, depending on the diameter and the degree of helicity [4]. Characterized as electrochemically inert materials, CNTs possess distinct electrochemical properties because of their unique electronic structure. The CNTs carbon atoms sidewalls and tubes end of geometrically different; their behavior resembling the basal plane and edge plane of highly oriented pyrolytic graphite. In the case of edge-plane defect sites, the rate of electron transfer is high due to the acid-treated aligned s-SWNTs electrochemical properties.

Polyaniline (PANI) is a conjugated conducting polymer characterized by an alternation of saturated and unsaturated carbon-carbon bonds, leading to the presence of non-localized electrons {π-electrons} [5],[2]. In practical application as a pseudocapacitive material PANI is limited by the volume changes that take place during charge-discharge procedure, thus showing poor cycling stability. The crosslinked conducting CNTs/PANI mixture has been synthesized through chemical and electrochemical processes. Molecular chain structure of the mixture was modified conveniently by structural derivations and electrochemical cycling. For the mixture, the obtained active layer of the sensor showed high sensitivities and short response time at room temperature and different relative humidity values.

Construction of efficient electrochemical sensors using the s-CNTs and also CNTs/PANI active layers is very promising in that they promote electron-transfer reactions between molecules, layers and doping substance. The advantage of polymer-based gas sensor over metal oxide sensors is conferred by the capability of the polymer films to detect and identify various constituents in the gas sample in addition to target analyte.

Microsensors based on nanomaterials doped active layers represent an efficient low-powered detecting solution for different monitoring systems, depending on the measured chemical analyte.

2. PREPARATION METHODS OF GAS SENSING MICROSENSORS

The aim of the present work was to compare the chemical sensing properties of s-CNTs and CNTs/PANI sensors structures made of the same CNT material in order to understand the sensing principle and to characterize the microsensors individually. The obtained structures act like resistive sensors and were tested under the stream of three different gases in pure N2 atmosphere by measuring their response under the form of electrical resistances changes. Both selected CNT material mixtures showed significant sensitivity for the same gas vapors.

For the sulfonated CNT the mixture was prepared trough protonation. Taking in account the fact that single walled carbon nanotubes (SWNTs) possess a large polydispersity in chirality, and length, they are difficult to separate due to the fact that strong tube-tube van der Waal attractions hinder their dissolution as individuals. These problems have been overcome by the direct protonation of the tubes by superacids like sulfuric acid (H_2SO_4 96%), were the pristine nanotubes fully disperse as individuals. Generically the group purified SWNTs (1 mg) were placed in 10 mL of concentrated sulfuric acid and sonicated in a water bath sonicator for 50 minutes at room temperature. The mixture was heated to 60°C and stirred for 3 h. The final preparation step was to heat-up the nanotubes at 250°C for 2 h. The obtained mixture was placed in 10 mL of distilled water.

Drop casting method has been applied on the interdigitated structure by fully covering with sulfonated SWNT mixture the gold electrodes surface [6]. The casted surface presented in figure 2.1 was dried for 24 h at room temperature in clean air.

Fig. 2.1. Obtained sulfonated CNT (s-SWNT) sensor interdigitated structure.

For the CNTs/PANI mixture several chemical and electrochemical methods were used in preparation. One of the efficient methods for obtaining the studied mixture was the electrochemical oxidative polymerization process of aniline. The protonation for PANI was achieved in an equimolar proportion of sulfuric acid (H_2SO_4 96%) medium, where aniline becomes an anilinium cation. Two mixture of aniline with H_2SO_4 were prepared for 0.1 M, respectively 0.2 M equimolar proportions. The oxidation state of the aniline determines the degree of polymerization and the conductor and/or insulator characteristics under certain experimental conditions for the PANI solution. In the first redox form, aniline is converted

in fully reduced leucoemeraldine base that acts like an insulator [1],[5]. The next oxidation form of the aniline is emeraldine base and is the only redox form that acts like as conductor. The transformation into emeraldine base of the leucoemeraldine, was performed taking into account the slow oxidation of amino groups by air oxygen. This reaction is reversible and it can be stabilized by keeping lower oxidation through crosslinking and intrachain oxidative cyclization [6],[7]. The polymerization of aniline solutions in leucoemeraldine base with slow oxidation was completed within 15 min at room temperature. The oxidation of aniline is exothermic so the temperature of the reaction mixture can be used to monitor the progress of reaction [2],[6]. Purified SWNTs (1 mg) were placed in each prepared solutions of PANI mixture (10 mL) and sonicated in a water bath sonicator for 2 h at room temperature. Potentiostatic method was applied for sensor manufacture. Depositions of polymer films were carried out electrochemically by varying acid concentrations as well as monomer(distilled aniline). The polymerization taked directly place over the interdigitated gold electrodes support of the sensor by oxidation at (750-1400)mV while potential was increasing followed by a de-protonation at (500–150) mV in the reverse direction of potential for 0.1 M and 0.2 M H2SO4 concentrations in order to align the PANI+CNT and to form multilayers of nanotubes and PANI between the 2 electrodes.The obtained mixtures were drop casted on two interdigitated gold structures, one for each solution. The casted layers were dried and activated for 24 h at room temperature in clean air (fig. 2.2).

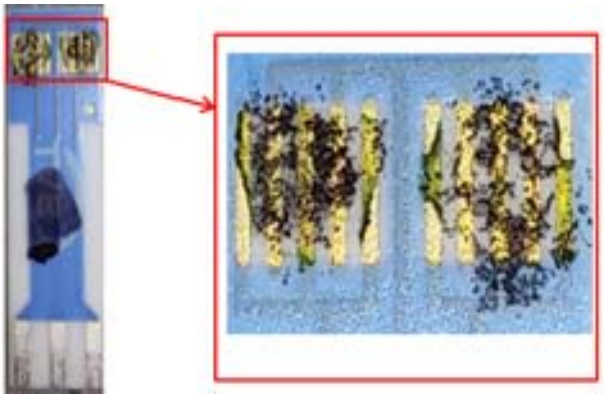

Fig. 2.2. Obtained pani mixture sensor interdigitated structure.

3. MICROSENSORS TESTING SYSTEM

A dedicated gas handling system for sensors testings (fig.3.1.) was designed and constructed tacking into account different methods for the sensors connections and used data acquisition systems. Nitrogen was used as the carrier and diluting gas forming in the test chamber a stable atmosphere [7],[8], [9]. Calibrated samples of CO, NH3, CO2 gas at ambient temperature were injected in the known atmosphere of our experimental apparatus.

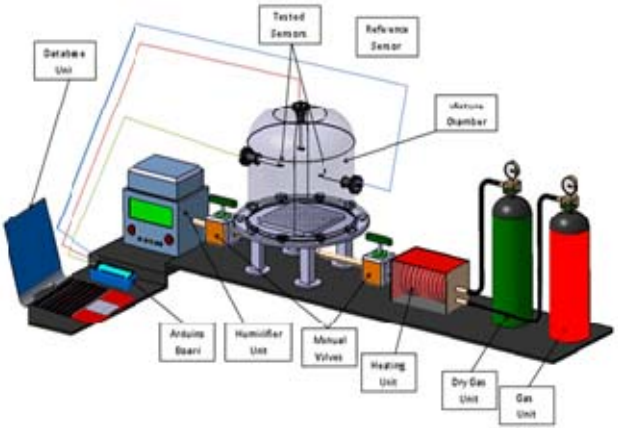

Fig. 3.1. Dedicated gas handling system for sensors testings.

Measurements were made with an Arduino Mega 2560 microcontroller board based on the ATmega2560 chipset (figure 3.2.). This microcontroller board has 54 digital input/output pins, 16 analog inputs, 4 UARTs (hardware serial ports), a 16 MHz crystal oscillator, a USB connection, a power jack, an ICSP header, and a reset button. It was connected direct to a computer pins, 16 analog inputs, 4 UARTs (hardware serial ports), a 16 MHz crystal oscillator, a USB connection, a power jack, an ICSP header, and a reset button. It was connected direct to a computer with a USB cable and data aqusition was made using Parallax Data Acquisition tool (PLX-DAQ). For the measurement system board (fig.3.3.) represented by the Arduino Mega 2560 power pins were set-up as follows:

• **Vin** represents the input voltage to the board when it's using an external power source (as opposed to 5 volts from the USB connection or other regulated power source). Voltage can be supplied through this pin, or, if supplying voltage via the power jack, access it through this pin.

• **Vcc 5 V** – this pin outputs a regulated 5 V from the regulator on the board. Maximum current draw is 20 mA.

• **Vcc 3.3 V** – this pin outputs a regulated 3.3 V from the regulator on the board. Maximum current draw is 50 mA.

• **GND** represents the Ground pins.

• **IOREF** – Describes the pin on the board that provides the voltage reference with which the microcontroller operates. A properly configured shield can read the IOREF pin voltage and select appropriate power source or enable voltage translators on the outputs for working with the 5V or 3.3V

The experimental set-up for the proposed gas sensing sensors characterization included also a DTH22 digital humidity and temperature sensor references. Accuracy resolution achived is about ±0.1% in resistivity measurement. The results were obtain after several inputs of nitrogen with low humidity level in the closed controlled chamber. The temperature was keept in a range near 23,5 ◦C– 25 ◦C. The DHT22 AM2302 sensor reference data aquisition is independent from the one of the tested sensors and it does not interfere in any way because the values are collected on the digital input.

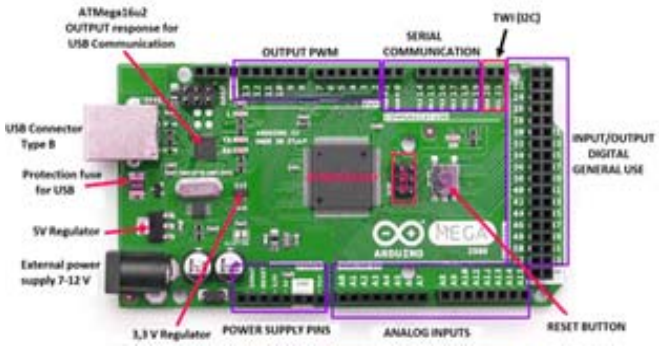

Fig. 3.2. Measurement system for proposed gas sensing sensors characterization.

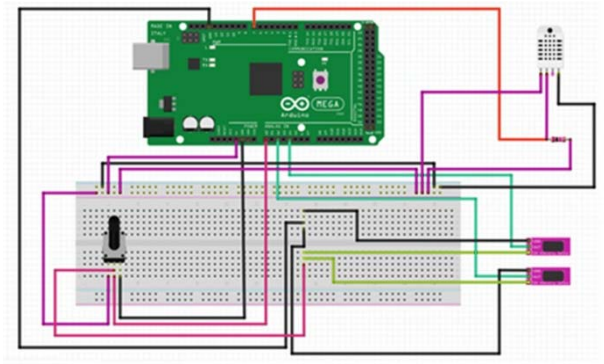

Fig. 3.3. Measurement system for proposed gas sensing sensors characterization.

4. RESULTS AND DISCUSSIONS

Reduction of resistance was recorded for increased proportions of CNTs, resulting in good contact (better conductivity) and the well-formed CNT network inside PANI. PANI/CNTs composite film onto sensors substrate show symmetric behavior of the applied forward and reverse bias voltage. The curves exhibit non-linear feature and this is an indication the prevalent conduction mechanism is non-Ohmic in nature and it may reveal for existence of different kinds of conduction mechanisms. The interaction of CNTs with nitrogen of PANI, leading to an expansion of compact PANI chains into more stretching conformations.

Our results showed that PANI 0,1M and PANI 0,2M can be used as sensitive material for different gases detection and have an active selectivity characteristic. The experimental set-up can be considered a concept of laboratory equipment, designed and optimized to perform a variety of automated measurements, gas analyses, incorporating a precision current source and a precision voltmeter together with a simple acquisition solution.

The resistance evolution of resulting structures, as a function of different gases concentrations is presented in figure 4.1. , 4.2. and 4.3. The obtained results, proves that the prepared sensors have different rezistivity values for the gases, with high sensitivity and selectivity potential regarding the the measured chemical analyte.

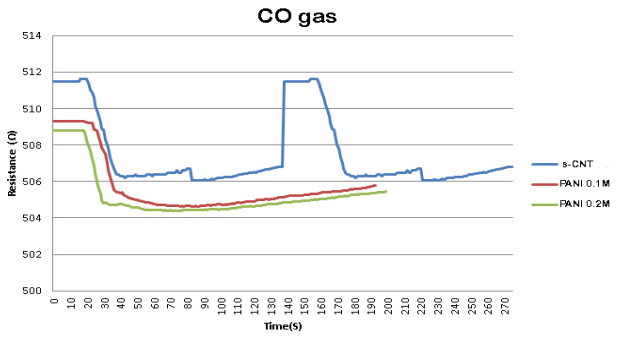

Fig. 4.1. Resistance evolution of resulting structures, as a function of CO gas concentrations.

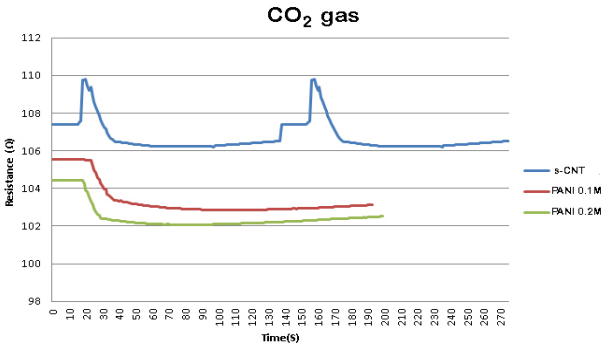

Fig. 4.2. Resistance evolution of resulting structures, as a function of CO_2 gas concentrations.

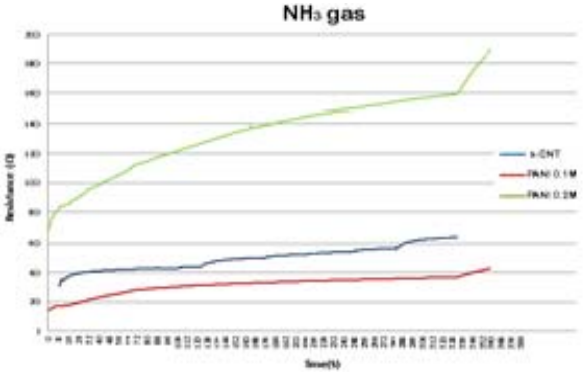

Fig. 4.3. Resistance evolution of resulting structures, as a function of NH_3 gas concentrations.

5. CONCLUSIONS

As conclusion, maximum potential for developing s-CNTs and PANI/CNTs based sensor technology consists in the development of compact, low power, mobile sensor arrays that allow detection and screening for multiple chemical analytes. Additionally, operating at room-temperature, the requirement of complex heating parameter for regeneration process will be partial eliminated resulting low power consumption and improvement for the sensor battery lifetime. Manufacturing cost will decrease and wireless technology implementation will allow production of large wireless sensor networks. These prospects predict the achievement of a sensor material with superior sensitivity, reduced size, and light weight, compact with extended life for innumerable applications.

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