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# s-CNTs and CNTs/PANi – Based Selective Sensors for Detection and Measurement of Pollutants in Industrial Gas Emissions

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***Abstract* – Anthropogenic pollutants are a threat for ecosystem sustainability, especially in heavy industrialized countries. Issues raised by the massive air pollution led to development and implementation of specific methods and equipment for detecting, measuring and controlling pollution directly to the source. Combined actions of multiple pollutants resulted from industrial gas emissions are of particular concern, since they generate negative effects on environment quality and human health, even when low concentrations of each individual chemical are present, that considered separately are not effective. In this work, different types of microsensors, based on SWCNT, were developed and tested for the detection and measurement of classical pollutants resulted from industrial gas emissions, such as CO, $NH_3$, and $CO_2$. Drop casting method and electrochemical cycling have been applied in manufacturing the sensors, by directly deposition on interdigitated electrode gold structures of different active mixture like sulfonated carbon nanotubes (s-CNTs) and carbon nanotubes (CNTs)/Polyaniline (PANi) respectively. Our main objective was to investigate the behavior of the obtained microsensors at room-temperature. Characterized by high electrochemical activity and improved stability, the proposed sensors solutions could represent a viable solution in developing low-powered sensor-systems with innumerable practical applications application.**

***Keywords – polyaniline, sulfonated carbon nanotubes, industrial pollutants sensing, gas microsensor, drop cast method***

## I. INTRODUCTION

Intensified climate change and anthropogenic disturbances are immediate effects of an unbalanced ecosystem. Industrial development generated by an increased demand for high production volume or the low experience in using new materials obtained by complex chemical fabrication processes, along with the intensive agriculture without a sustainable development strategy and the human activity express by consumer needs, produced in the recent years exceeds in waste and environmental pollution. Because these facts represent a critical issue when refer to ecosystem sustainability, special attention should be given to the solutions, methods and equipment that could identify and assess the impact of different pollutants sources. Air pollution can be seen as a complex scenario since it can occur in a short time both locally and globally. Thus, the electrochemical microsensors described in this paper were designed to detect, select and measure specific gases consisted as main elements of local and global air pollution.

Electrochemical sensors represent an optimal approach regarding ambient toxic gas monitoring. This particularly type of sensors operates by reacting with the gas of interest to produce an electrical signal proportional to that gas concentration. Major advantages in using electrochemical sensor for gas detection, compared to any sensor technology, consist in (*i*) their specificity to detect particular gas/vapor at parts-per-million range and (*ii*) their ability to not interfere or to be poisoned by other gases during the detection process. When discussing on the detection quality and resolution of electrochemical sensors, the cross-sensitivity of other gases is considered to be an issue. However with proper design and implementation of a smart electronic transducer, a sensor with superior selectivity characteristics can be obtained.

Insertions of nanomaterials in sensors design represent an advantage in signal amplification and high detection resolution due to the active layers superior conductivity, thermal stability and high surface area over its geometrical dimension. Characterized as electrochemically inert materials, CNTs exhibit distinct electrochemical properties because of their unique electronic structure [1-5].

Polyaniline (PANi) is identified as 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}

[1, 6, 7]. For application as a pseudocapacitive material due to a poor cycling stability, PANi is limited by the volume changes that take place during charge-discharge procedure.

For the presented sensors, the crosslinked conducting CNTs/PANi mixture has been synthesized through chemical and electrochemical processes. Molecular chain structure of the CNTs/PANi mixture was modified by structural derivations and electrochemical cycling processes.

The development of electrochemical sensors using both s-CNTs and CNTs/PANi active layers was based on the favorable effect of electron-transfer reactions between molecules, layers and doping substance. The main advantage of polymer-based gas sensor compared to metal oxide sensors is allocated to the capability of the polymer films to detect and indicate various constituents in the gas sample in addition to target analyte.

## II. PROPOSED MICROSENSORS PREPARATION METHODS

This paper presents an extended and comparative study on the performance of two electrochemical sensors structures, with s-CNTs and respectively CNTs/ PANi active layer, made of the same CNT material. The study was conducted with the aim to understand the sensing principle and to define the microsensors individually.

For the sulfonated CNT (s-CNTs) the active layer mixture was prepared trough protonation method. A purified group of single wall carbon nanotubes (SWNTs) (1 mg) commercialized by Sigma-Aldrich were placed in 10 mL of concentrated sulfuric acid and sonicated for 50 minutes at room temperature. After sonication, the mixture was heated at 60°C and continuously stirred for 3 h. In the final step of preparation the protonated nanotubes were exposed at 250°C, for 2 h. The obtained mixture was diluted with 10 mL of distilled water. Drop casting method was used for fully covering with sulfonated SWNTs mixture the gold electrodes surface of the interdigitated structure (Fig. 1A). The microsensors surfaces presented in Fig. 1B have been dried for 24 h, at room temperature, in clean atmosphere.

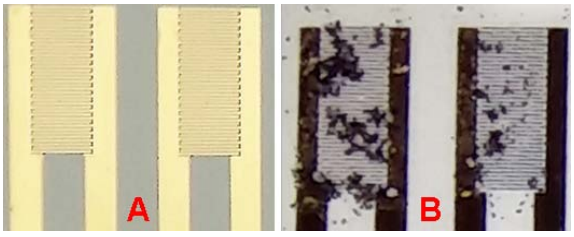


*Fig. 1. Interdigitated structure with gold electrodes (A); Drop casted sulfonated CNT (s-CNT) on the sensor interdigitated structure (B)*

The morphologies for s-CNT active layer composites were investigated by scanning electron microscopy (SEM). The SEM image (Fig. 2) shows the morphology of the sulfonated CNT composite film chemical synthesis after dielectrophoresis process, with application over the electrodes of 1 VDC potential, for 1 minute, to align the SWCNTs and to form multilayers of nanotubes between the interdigitated electrodes.

For the CNTs/PANi sensor (Fig. 3), the active layer mixture was prepared by several chemical and electrochemical methods. Electrochemical oxidative polymerization process of aniline was induced, achiving protonation for PANi in an equimolar proportion of sulfuric acid ($H_2SO_4$ 96%) medium, where aniline transformed in an anilinium cation. Two mixture of aniline with $H_2SO_4$ have been prepared for 0.1M, respectively 0.2M, equimolar proportions. The degree of polymerization and the conductor and/or insulator characteristics of the active multilayer is determined by the oxidation state of the aniline. For obtaining the conductive form of PANi, as emeraldine base, the oxidation process plays a define role in the sensors fabrication step. The transformation into emeraldine base of the leucoemeraldine, was performed taking into account the slow oxidation of amino groups by the oxygen from air.

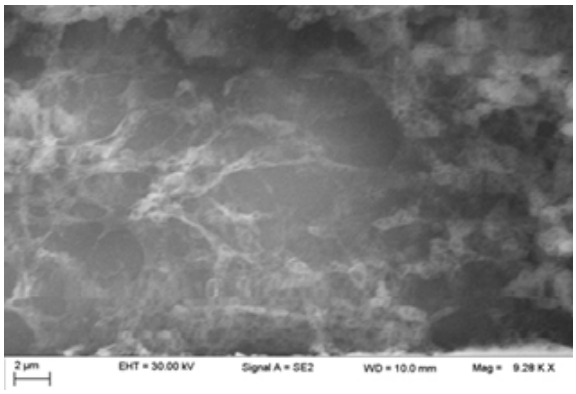


*Fig. 2. SEM image of the sulfonated CNT (s-CNT) sensor interdigitated structure*

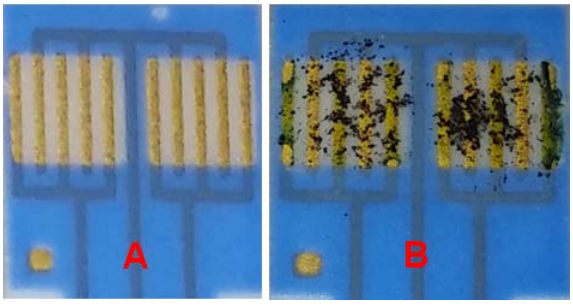


*Fig. 3. Interdigitated structure with gold electrodes (A); Drop casted CNTs/PANi sensor interdigitated structures (B)*

The described reaction is reversible and it can be stabilized by keeping lower and controlled oxidation. The polymerization of aniline solutions in emeraldine base with slow oxidation was completed within 20 minutes in

ice-bath. Due to the fact that aniline oxidation is exothermic, controll and monitoring the progress of reaction determines the polymerisation process quality. Purified SWNTs (1 mg) commercialized by Sigma-Aldrich were introduced in each prepared solutions of PANi mixture (10 mL) and sonicated in water for 2 h, at room temperature. Despite the insoluble nature of PANi in water, PANi/CNTs composites can be readily dispersed in aqueous solutions.

The cyclic voltammetric peak potentials of PANi/CNTs composites will show small and insignificant shifts compared to those of pure PANi, having also a considerable increase in peak currents. The absence of any change in the peak potentials suggests that the mechanism of aniline polymerization is not affected in the presence of CNTs [8, 9].

In Fig. 4, the SEM morphology of PANi-0.1M and SEM morphology of PANi-0.2M, with CNTs composite film synthesis from electrochemical, with cyclic potentiostatic method (-100mV to 1500 mV), are illustrated. The same drop casted method as for s-CNTs active layer was used.

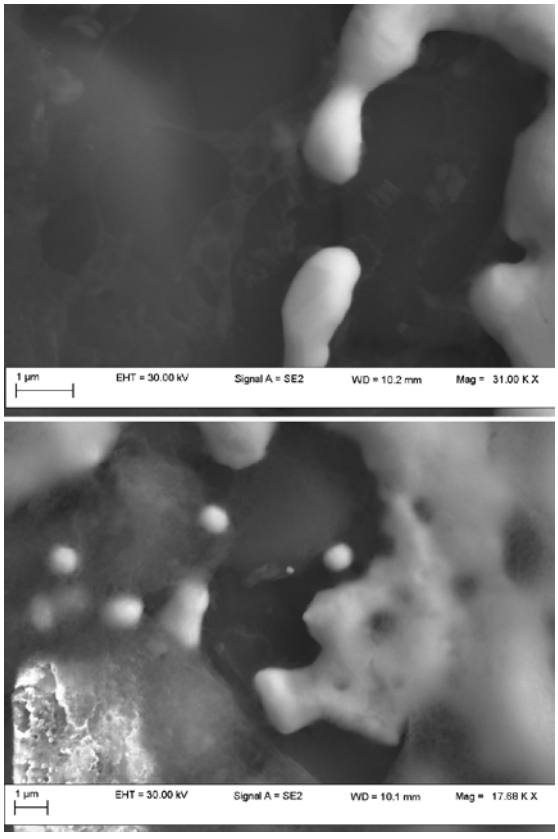


*Fig. 4. SEM image of the PANi/CNTs active layers of: 0.1M PANi/CNTs (A); 0.2M PANi/CNTs (B)*

## III. MICROSENSORS TESTING SYSTEM

Obtained electrochemical microsensors have been tested in a controlled gas chamber handling system with multiple sensors connections possibilities and dedicated data acquisition system (Fig. 5).

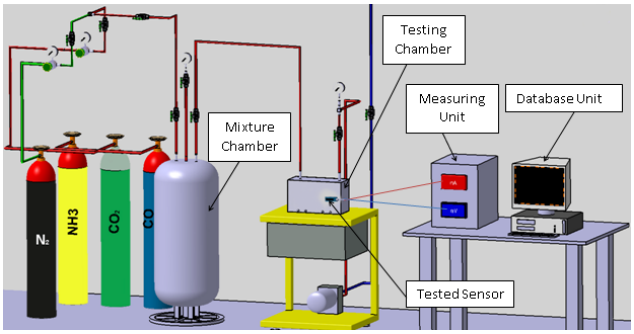


*Fig. 5. Illustration of the controlled gas chamber handling system*

Nitrogen was used as carrier and diluting gas, providing for the test chamber a stable atmosphere [2]. Calibrated samples of CO, $NH_3$, and $CO_2$ gas at ambient temperature were injected in the known atmosphere of our experimental testing gas chamber. For resistance measurement a data logger multimeter was directly connected to a computer with a USB. The experimental set-up for the proposed gas sensing sensors characterization included also a DTH22 digital humidity and temperature sensor as references. Accuracy resolution achieved is about ±0.1 % for resistivity measurement. The results were obtained after several inputs of nitrogen gas with low humidity level in the closed controlled chamber. For all the experiments, the temperature was kept in a range near 23.5 °C - 25 °C. The DHT22 AM2302 sensor as reference data acquisition is independent from the one of the tested sensors and it does not interfere in any way due to the fact that values are collected on different acquisition equipment [1-4].

## IV. EXPERIMENTAL RESULTS

Resistance evolution was recorded for increased proportions of CNTs, resulting in good contact (better conductivity) and well-formed CNTs network inside PANi. PANi/CNTs active layers of the sensors substrate show symmetric behavior of the applied forward and reverse bias voltage [3]. The prevalent conduction mechanism is non Ohmic in nature due to the fact that the curves exhibit non-linear feature indicating that the existence of different kinds of conduction mechanisms is available.

The comparisons of resistance evolution for the microsensors structures with the specified active layer mixtures, as a function of chosen analyte in different concentrations, is illustrated in Fig. 6, Fig. 7, and Fig. 8. The obtained results indicate that the microsensors exhibits different resistivity values for the gases, with a high sensitivity and selectivity potential regarding the measured chemical analyte.

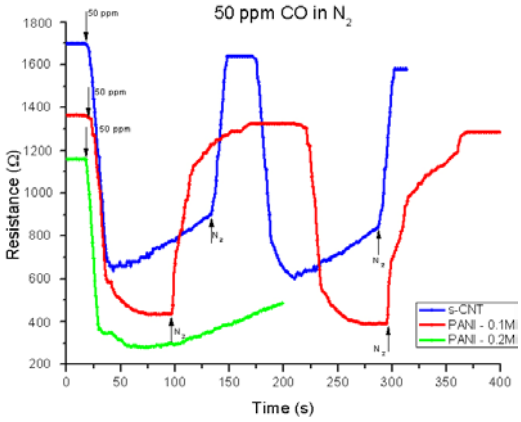


*Fig. 6. Resistance evolution of sensors for 50 ppm CO in N2 calibrated gas sample*

In the case of carbon nanotubes (CNTs)/Polyaniline (PANi) active layer, the resistance evolution indicates that the electrical conductivity of PANi improves, by orders of magnitude, through increasing the doping level of the relative carbon content with emeraldine base in equimolar proportion.

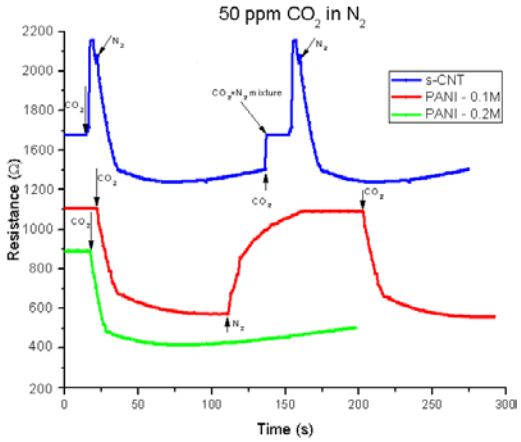


*Fig. 7. Resistance evolution of sensors for 50 ppm $CO_2$ in N2 calibrated gas sample*

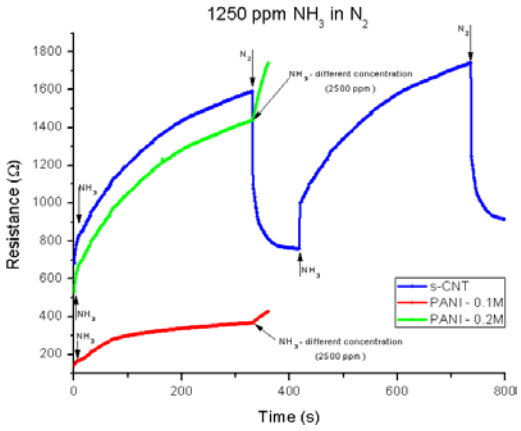


*Fig. 8. Resistance evolution of sensors for 1250 ppm $NH_3$ in N2 calibrated gas sample*

## V. CONCLUSIONS

In conclusion, linear output, low power requirements and good resolution has been obtained for both developed s-CNTs and PANi/CNTs based sensors. Once calibrated to a known concentration, the sensors have provided accurate reading of the target gases and proved the repeatability in measurements. This technology can support the development of portable sensor systems that should allow detection and screening of multiple chemical analytes. Designed for measurements and detection of air pollutants like CO, $CO_2$, $NH_3$, at room-temperature the sensors represent a viable solution for innumerable applications in environmental protection and monitoring. An electrochemical sensor usually has a shelf life of six months to one year, depending on the analyte to be detected and the environment in which it is used. For the presented sensors, the lifetime has passed over one year, with very low decrease in characteristics.

Sensor market prospects indicate that the convenience of small and hearty sensors will always be of use for personal gas detection devices especially for environmental issues and human safety.

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