# Resistive Sensors for Organic Vapors Based on Nanostructured and Chemically Modified Polyanilines

Silvestre Bongiovanni Abel, Robert Olejnik, Claudia R. Rivarola, Petr Slobodian, Petr Saha, Diego F. Acevedo, and Cesar A. Barbero

***Abstract*— Resistive sensors for organic vapors were made using polyaniline (PANI) and functionalized PANI as thin films or deposits of PANI nanofibers. PANI thin films were synthesized by *in situ* chemical polymerization onto flat polyethylene films. PANI nanofibers were produced by interfacial polymerization. Both polymeric materials were chemically modified through aromatic electrophilic substitution or nucleophili addition and used as active materials in resistive sensors. The analysis of the resistance-time sensor profiles suggested that chemical modification affects strongly the sensor response. Moreover, the magnitude, the sign, and the rate of the sensor response showed differences for active materials with the same chemical structure and different morphologies. It is demonstrated that using only one conducting polymer but creating material diversity by chemical functionalization or morphological changes different sensors responses for the same volatiles can be obtained. This behavior allows a simple way to produce sensors arrays which can be used in electronic noses.**

***Index Terms*— Nanofibers, organic vapors, polyaniline, resistive sensors, thin films.**

## I. INTRODUCTION

AMONG all conducting polymers, polyaniline (PANI) is one of the most investigated macromolecules. Some authors classified PANI as an "adaptive material" because it can switch between different forms (conducting or insulating) with distinctive characteristic [1]–[3]. This polymer presents a simple acid-base doping and de-doping chemistry, a relatively effortless synthesis, high stability, and low monomer cost, allowing numerous uses and applications [4], [5]. These characteristics, make the PANI an excellent material to build technological devices including resistive sensors [6], [7].

Resistive gas sensors are devices that allow to sense different volatiles based on changes in the conductance or resistance of the active material. The resistance changes are due to physicochemical interactions of the conducting sensing material with the volatile compounds [8], [9]. PANI thin films have been used in sensors where the polymer act as a quimioresistor for sensing chemical vapors [10]. PANI thin films has been commonly deposited by *in situ* polymerization. The thin films are compact and the slow diffusion rate of the compounds inside the polymer results in slow response time of the sensor [11]. On other hand, using nanostructured conducting polymers (nanowires, nanoparticles, nanofibers, thin films, and others) it is possible to create open structures with fast diffusion. It has also been demonstrated that the morphology of the nanomaterials generates novel properties [12]–[15].

Sensors based on nanomaterials have been developed [16], [17]. PANI has been synthesized in as particles of nanometric size using several methods: interfacial polymerization, rapid mixing reaction, radiolytic or sonochemical synthesis, and others [4], [18], [19]. Among these methods, one well-known process to synthesize PANI nanofibers is that developed by Kaner and coworkers [20], [21] which produces PANI nanofibers or modified PANI nanofibers avoiding the use of templates or functional dopants. It is known that films of PANI cast from solvents are more compact than those produced by in situ polymerization since in the latter case the nucleation and growth mechanism renders nanostructured films [39], [40]. PANI have been used for sensing hydrochloric acid, ammonia, organic amines, chloroform, methanol, hydrogen sulfide, etc. [22]–[25].Virji *et al.* compared the cast PANI films sensor response with the cast PANI nanofibers sensor response [26]. In that investigation, the response of the PANI sensors towards reactive gases (acids (HCl), bases ($NH_3$), reductants ($N_2H_4$)), and only two nonreactive volatiles ($CHCl_3$, $CH_3OH$) were studied. The authors showed that the casted PANI nanofibers response is faster than the casted PANI films response. Moreover, the casted PANI film did not present any response to hydrazine while the deposited nanofibers showed a clear resistance change. Therefore, the morphology of the PANI strongly affects the sensing mechanism. It has

---

Manuscript received January 5, 2018; revised June 1, 2018; accepted June 3, 2018. Date of publication June 18, 2018; date of current version July 24, 2018. This work was funded by a collaboration project of MCTIP (Argentina)-MEYS (Czech Republic) and the support of CONICET, FONCYT, MinCyT, SeCyT-UNRC and Ministry of Education, Youth and Sports of the Czech Republic-National Sustainability Program NPU (LO1504). The associate editor coordinating the review of this paper and approving it for publication was Dr. Gymama Slaughter. *(Corresponding author: Cesar A. Barbero.)*

S. Bongiovanni Abel, C. R. Rivarola, and C. A. Barbero are with the Instituto de Investigaciones en Tecnologías Energéticas y Materiales Avanzados, Universidad Nacional de Río Cuarto–Consejo Nacional de Investigaciones Científicas y Técnicas, Río Cuarto 5800, Argentina.

R. Olejnik, P. Slobodian, and P. Saha are with the Centre of Polymer Systems, University Institute, Tomas Bata University in Zlín, 760 01 Zlin, Czech Republic.

D. F. Acevedo is with the Instituto de Investigaciones en Tecnologías Energéticas y Materiales Avanzados, Universidad Nacional de Río Cuarto–Consejo Nacional de Investigaciones Científicas y Técnicas, Río Cuarto 5800, Argentina, also with the Departamento de Tecnología Química, Facultad de Ingeniería, Universidad Nacional de Río Cuarto, Río Cuarto 5800, Argentina, and also with the Departamento de Química, Universidad Nacional de Río Cuarto, Río Cuarto 5800, Argentina (e-mail: dacevedo@exa.unrc.edu.ar).

This paper has supplementary downloadable multimedia material available at http://ieeexplore.ieee.org provided by the authors. The Supplementary Material contains experimental details and additional information. This material is 1.63 MB in size.

Digital Object Identifier 10.1109/JSEN.2018.2848843

been suggested that both functional groups attached to the polymer backbone and PANI morphology alter the response rate but also produce clear differences in the sensitivity of the sensor [8], [22], [27]. There are two simple ways to change the chemical structure of the polymer. One of them is by copolymerization and the other is the post-modification of the polymer backbone. It has been shown that the copolymerization affects adversely or even inhibits the polymerization process mainly because of the lower reactivity of the substituted anilines [28], [29]. The post-modification of PANI as thin films, microparticles or nanofibers can be carried out by different methods such as electrophilic or nucleophilic addition [2], [30]–[32],without undue changing the polymer chain length. Our research group has thoroughly studied the chemical functionalization of PANI [11], [29]–[39].

The present study focuses on the synthesis and characterization of PANI thin films, PANI nanofibers, and the subsequent modification of these polymers. Furthermore, it is shown the study of the resistive sensors behavior based on functionalized polyanilines casted by *in situ* polymerization and post-modification or by deposition of preformed nanofibers dispersions at a fixed temperature and humidity. It is demonstrated that the behavior of PANI nanofibers is different with respect to PANI thin films showing faster and responses. Moreover, the PANI modifications allow obtaining different signals against the same analyte.

## II. SYNTHESIS AND FUNCTIONALIZATION

### A. Materials

Aniline (Merck) was distilled under reduced pressure before polymerization. Polyethylene (Goodfellow®) films were previously washed with deionized water. All other reagents and solvents were used as received and were analytical quality. In all aqueous solution, Milli-Q quality water was employed.

### B. Synthetic Process

Polyaniline nanofibers were produced using the method reported by Kaner and coworkers [20]. Aniline (24 mmol) was dissolved in 75 mL of chloroform. A solution containing 6 mmol of ammonium persulfate dissolved in 75 mL of 0.8 M hydrochloric acid was prepared. The two solutions were then carefully transferred to a closed flask generating a liquid-liquid interface. The aniline monomer diffuses into the aqueous phase, where it was oxidized by the persulfate and polymerizes. All the reactions were performed in the dark. After 24 hours, the entire water phase was filled homogeneously with dark-green polyaniline, while the organic layer (chloroform) presented a red-orange color due to oxidation by-products. The aqueous phase was collected and the remaining reactants and low molecular weight by-products were removed by dialysis against water using a cellulose membrane. The morphology of the PANI nanofibers produced in our laboratory was previously characterized using TEM and DLS by Yslas *et al*. [38]. PANI nanofibers were deposited onto interdigitated electrodes by evaporation of a dispersion in ethanol.

In the case of polyaniline thin films, pieces of polyethylene film (Goodfellows®) (5 cm × 5 cm) were superficially oxidized following the procedure described by Acevedo *et al.* [39] to obtain more hydrophilic surfaces. Then, the pieces were immersed in the aniline polymerization solution. The solution consists of 0.1 M anilinium hydrochloride dissolved in 1 M hydrochloric acid solution, with an equimolar amount of ammonium persulfate as the oxidant. The reaction is carried out in a batch reactor at 0 – 0.3 °C (ice bath) under continuous stirring. Under this conditions, polyaniline thin films (c.a. 400 nm) were obtained on the polyethylene substrates [39]. The conditions of the polymerization ensured that the obtained product was polyaniline in emeraldine form. Lastly, the films were thoroughly washed with deionized water to eliminate remaining reactants and by-products and dried in air.

PANI nanofibers and thin films were subsequently modified using two organic reactions: nucleophilic addition and aromatic electrophilic substitution.

*1) Nucleophilic Addition:* The nucleophiles used were thioglycolic acid (TIO), cysteamine (CIA), dodecanethiol (DOT) and 2-aminothiophenol (ATF). The chemical structures of the nucleophiles are shown in **Fig. 1, SI**. In order to perform the reaction, c.a. 0.1 g of polyaniline (dried nanofibers or the equivalent amount of polyaniline film) and 0.025 moles of the nucleophilic reactant dissolved in ethanol were mixed. The mixtures were then heated by refluxing for 4 hours at 70 °C.

*2) Aromatic Electrophilic Substitution:* The reaction was performed by coupling the diazonium salts with the aromatic rings (amine monomer units) in PANI. In order to generate the diazonium salt, the same quantity of the aromatic amine (0.001 moles of 2-chloroaniline, 2-Cl-ANI, etc.) and 0.001 moles of sodium nitrite were mixed with 1 M hydrochloric acid (molar ratio 2:1) at 0 °C and left reacting for 30 minutes. The formed diazonium compounds were then mixed with thin films or nanofibers in a buffered (tris(hydroxymethyl)aminomethane/HCl) media at pH 8 and 0 °C during 15 minutes. The functionalized nanofibers were isolated by filtration and washed with deionized water. The supported thin films were removed from the solution and washed thoroughly with deionized water. The chemical reaction of aromatic electrophilic substitution is represented in the **Fig. 2, SI**.

## III. CHARACTERIZATION TECHNIQUES

### A. UV-Visible Spectroscopy

A Hewlett-Packard 8453 diode array UV-visible spectrophotometer was used to obtain the different spectra of polyaniline dispersions or supported thin films. In all of the cases, blanks were taken using deionized water or ethanol, respectively. The spectra were taken employing quartz cells with 1 cm optical path length.

### B. Microscopies: SEM-EDAX and TEM

Deposits of PANI nanofibers and thin films of PANI were imaged in a high-resolution scanning electron microscope (SEM) VEGA LMU, produced by Tescan Ltd, at 5 kV acceleration voltages in different magnifications. Nanofibers samples were deposited onto a conductive grid and finally dried for analysis. EDAX experiment of thin films was made with the same equipment using liquid $N_2$. TEM micrograph of nanofibers was taken in FEI Tecnai G2 F20 UT microscope operated at 200 kV.

### *C. Contact Angle Measurement*

A computer-controlled microscope Intel QX3 was used for measurement of contact angle by setting flat solid samples on a manually controlled tilt table, illuminating from behind with a white led source and recording with the microscope set in a horizontal position. The shape of water drops (3 $\mu$l) standing still on the surface using a 60X objective was obtained. The pictures were analyzed using Drop Analysis plugin of ImageJ® software [40]. Every contact angle data informed was the average of five measurements.

### *D. Resistance Change Experiments*

Resistance measurements were performed inside a thermostatic cabin (ET619-4, Lovibond, Germany) at 25 °C and 30% of relative humidity (RH) [41]. Maintaining a constant humidity through all experiments is critical towards reproducibility since humidity strongly affect the observed signal [41]. The PANI resistance change–s, upon exposure to volatile organic compounds, depend on the relative humidity values (RH). Positive, negative or nearly zero changes can be obtained depending on the relative humidity value [27]. This means that a defined ambient humidity has to be set to use PANI as volatile compounds sensors. Otherwise, no reproducible values are obtained. Taking this into account, both temperature and humidity (RH) during the measurement were fixed at 25 °C and 30% respectively, for all the experiments. An interdigitated copper electrode of 0.9 cm × 1.5 cm was used to measure the resistance of the nanofibers deposit set over the small gaps (400 $\mu$m of width) between metal fingers **(Fig. 3, SI)**. In the case of thin films, two copper contacts were pressed onto the supported films. The electrical resistance was measured as a time function with a DC multimeter during the absorption and desorption cycles. In all cases, the holder with the sensor was quickly transferred into an airtight Erlenmeyer flask (0.5 L) saturated with vapors of the respective analyte (low molecular weight alcohols and heptane). After six minutes of measurement, the sensor was removed from the flask and for the next six minutes, the measures were taken in a similar flask without the vapor. These cycles were repeated five times in each solvent independently. The sensor was connected to a multimeter, which was controlled by a laptop using the interface program UNI -T 3.0.

## IV. RESULTS AND DISCUSSION

### *A. Materials Optical Properties (UV-Visible Absorption)*

It is known that PANI absorbs strongly in the UV-Visible region and the spectrum bands are related to the electronic transitions between solid state energy levels [27]. Using this spectroscopic technique is possible to confirm the effective functionalization of the polyaniline backbone due to changes in the electronic properties of the polymers. The PANI nanofibers spectra can be appreciated in **Fig. 1a**, using water or ethanol as solvent. The spectrum obtained is similar to other PANI in the emeraldine state reported in the literature [30], [42]–[44]. The band with a maximum at c.a. 420 nm can be attributed to $\pi$-$\pi^*$ transition of the diphenylamine units and the typical conducting band (600–800 nm) [29], assigned to the exciton transition of the quinonimine states (solid state), [45] is showing from c.a. 620 nm. Both bands are present in the spectrum of the PANI nanofibers dispersed. This behavior leads us to conclude that the polymer remains doped in these solvents.

It can be seen that when PANI nanofibers are functionalized, some changes in the absorption spectrum occurs (**Fig. 1b**). On the one hand, those nanofibers in which aromatic rings are incorporated to the backbone during the modification procedure show a significant increase in the near UV absorption due to the additional absorption of the attached ring (PANI-ATF and PANI-2-Cl-ANI). On the another hand, in the case of PANI-TIO, the polaron band (>600 nm) is shifted to lower energy values and decreases in absorbance. This shift would indicate a decrease in $\pi$-$\pi^*$ conjugation and consequently a lower conductivity. The band at c.a. 450 nm assigned to the localized radical cation remains in its position in all the spectra, except for PANI-2-Cl-ANI when it undergoes a shift to c.a. 520 nm. This indicates a decrease in the energy of the transition probably related to the extended conjugation involving the azo group (-N=N-). The chemical modifications seem to decrease the electronic conjugation of PANI. However, the polymer retains its conductivity, which is important if these materials will be used to build the resistive sensors.

### *B. Morphological and Compositional Analysis*

Morphology of deposited PANI nanofibers and thin films were analyzed by Scanning Electron Microscopy (SEM). SEM images of a deposit of unmodified PANI nanofibers and a thin film are shown in **Fig. 2a-d**. In the SEM micrographs is possible to observe that the deposit of nanofibers presents a fibrillary structure after the deposition procedure. **Fig. 2a-c** shows fibrillary shape structures with c.a. 100 micrometers of length and the width ranging from 5 to 10 micrometers. Also, it is possible to observe several nanometric fibers emerging from de each microstructure. These structures were confirmed by transmission microscopy. The TEM image (**Fig. 4, SI**) allows to identify PANI nanofibers as flat structures with micrometric length and c. a. 50 nanometers of width. The data suggest that the micrometric fibers observed in TEM are formed by aggregation of several PANI nanofibers. The SEM image of a PANI thin film is depicted in **Fig. 2d**. The surface presents a smooth profile without any fiber over the whole scanned area. Therefore, the thin films are more compact than the deposits of nanofibers. After the functionalization process, the morphology of deposited nanofibers become different and the surface loses the fibrillary structure (**Fig. 3 a-e**). Evidently, the chemical modification produces a separation of the chains that form the fibrillar structure mainly due to steric effect of the added functional groups.

The presence of new elements from chemical modification reactions was studied by the EDAX technique. The analysis

TABLE I

DISTINCTIVE ELEMENTS DETECTED BY EDAX ANALYSIS OF THE MATERIALS IN FILM FORM

| Film´s material | Differential characteristic |
|---|---|
| PANI-TIO | 4.35 % S |
| PANI-ATF | 30.0 % S |
| PANI-CIA | 1.71 % S |
| PANI-2-Cl-ANI | 4.50 % Cl |

TABLE II

CONTACT ANGLE VALUES FOR DIFFERENT PANI THIN FILMS UNMODIFIED AND AFTER MODIFICATION

| Film´s material | Contact angle |
|---|---|
| PAN I | 58.2° |
| PANI-TIO | 19.0° |
| PANI-DOT | 92.5° |
| PANI-ATF | 76.0° |
| PANI-CIA | 77.0° |
| PANI-2-Cl-ANI | 60.9° |

showed in **Table I** confirms the efficient modification of the PANI films. PANI thin films without any chemical modification show mainly C (62%) and N (26%) as is expected and traces of S (0.28%), probably from the ammonium persulfate used in the polymerization. After the modification process with thiols groups, the ratio of the sulfur to nitrogen increases. The data shown in **Table I** denote that the quantity of sulfur incorporated into the polymer is different before the modification and probably depends on the incorporated molecules reactivity. Moreover, in the polymer modified by reaction with a diazonium salt (PANI-2-Cl-ANI), it is possible to note a clear increment of the chlorine contents compared to the unmodified PANI (4.50% of Cl). As it can be seen, the EDAX analysis suggests that PANI was modified by both procedures in different proportions depending on the reactivity of the modifier molecule and the kind of the reaction.

### C. Material Wettability

Water contact angle technique was used to study the influence of the PANI modifications on the films hydrophilicity/hydrophobicity. Measurements reveal that in all cases, except PANI-TIO, the modified polyanilines are more hydrophobic than pristine PANI film. In **Table II**, the values of contact angle are reported and in **Fig. 5**,**SI** the water-drop images over the sample can be seen. The contact angle measured for PANI surface is c.a. 58.2°. This value is in agreement with previous reports [35], [46]. When PANI is functionalized with ATF, CIA, or 2-Cl-ANI the contact angle value is higher than pristine PANI. Evidently, the alkyl chains and the aromatic rings effect over the polar interactions with water but also even addition of polar groups (PANI-CIA) with short alkyl chains generates a more hydrophobic surface than the pristine PANI [11]. In the case of PANI-TIO, the contact angle value (c.a. 20°) is lower than that of PANI, showing that the modified polymer interaction with water was enhanced after modification probably due to the presence of carboxylic groups attached to the polymer backbone.

### D. Signal Detection

As it was mentioned, the obtained materials were used as resistive sensors. Therefore, a detailed study of the response to volatile compounds was performed. Results show the resistance changes when the sensor is in contact with the different organic vapors such as alcohols (methanol, ethanol, propanol, butanol, pentanol) and heptane. All the data were compared with pure air at the same environmental relative humidity. The equations **(1)** and **(2)** are used to quantify the signal and are named as sensor response (S) and normalized resistance (Sn) respectively:

$$S = (R - Ro) \tag{1}$$

$$Sn = (R - Ro)/R_0 \tag{2}$$

where $R_0$ is the initial resistance and R is the resistance value measured at 6 minutes in contact with the analyte.

In **Fig. 4** are represented the typically normalized response cycles (Sn) where is possible appreciate the resistance changes during time.

### E. Response Rate of Sensors

One of the objectives of this work is the comparison of the response rate of pristine and chemically modified PANI in two different forms: nanofibers deposits and films. It is possible to define the response rate as the differential of the signal (as a function of time). These values were estimated from the mathematical slope of the linear part of the signal (from the time when the analyte was added until the signal is lost linearity) following **(3)**:

$$Response\ Rate = \frac{d\,(Sensor\ \ Response)_{linear\ part}}{dt} \tag{3}$$

In this sense, the response rates were calculated from the typical cycles and are shown in **Fig. 5**. Values of linear regression (R) of the treatment for each sensor can be appreciated in **Table I, SI.**

A comparative study between nanofibers and thin films rate responses show that the materials present different behavior when are exposed to analyte vapors. Unmodified PANI films show faster response rate than unmodified PANI NF when was exposed to methanol and butanol. In general, after modification with TIO, nanofibers present faster response rate than thin films. In particular, it stands out the improvement in butanol, pentanol, and heptane vapors. In the case of PANI-ATF sensors, the response rates reach higher values for thin films against ethanol and propanol vapors. When the modification was performed with CIA, the sensor builds using nanofibers present higher rate than thin film to detect butanol vapors. However, it is possible to observe that the PANI-ATF NF response rate shows a significant improvement for sensing propanol vapors in comparison with pristine PANI film. Finally, PANI-2Cl-ANI NF material sensing displays the best response for ethanol vapors.

Regarding the recovery time of the sensors, it has been evaluated taking into account the time spent by the sensor to reach the initial signal value after the sensor is exposed to pure air **(Fig. 6, SI)**. As it can be seen, the recovery time in all the experiments is shorter than the 360 seconds of the measurement interval. These results ensure that in each cycle the sensor starts from the same $R_0$ value. Besides, it is important to highlight the fact that it is possible to use the same sensor in at least five cycles without response loss. Moreover, the performance of the sensor was tested after 7 months and the sensor is able to show the response, indicating excellent stability.

### *F. Comparative Effect of the Vapor Nature on the Sensing*

All sensors tested were evaluated using the same experimental setup to observe the sensor response value. Analyzing the results depicted in **Fig. 6** is possible to ensure that the sensors behavior versus the same analyte depends not only of the morphology (nanofiber or thin film) but also the chemical structure of the macromolecule. It is notable that both for pristine PANI and functionalized PANI, the responses to the same vapor are different when the sensor is made by PANI films or deposited PANI nanofibers. Since chemical interactions depend on the chemical nature of the groups present, such behavior suggests that the effect of the vapor on resistance obeys a complex mechanism. Previously, we have investigated in detail the effect of humidity and analyte concentration on the total resistance ($\Delta R_T$) using the Eq. 4 [27]. The $\Delta R_{ele}$ represent the resistance changes by intra-chain conductivity of the conducting polymer chains. Both water and the vapour could change this parameter by charge transfer effects. $\Delta R_{hop}$ represent the resistance changes by the hopping of electrons between neighboring chains inside the material. It could be affected by water or the vapor trough swelling (which changes the chain to chain distance). $\Delta R_{med}$ represents the resistance changes by variation of the dielectric media between chains and fibers. Changes in the relative concentration of water and/or organic vapor alter de dielectric constant of the media affecting this term of Equation **(4)**:

$$\Delta R_T = \Delta R_{ele} + \Delta R_{hop} + \Delta R_{med} \tag{4}$$

where:

$\Delta R_{ele}$ is the resistance changes by intrinsic electronic effects,
$\Delta R_{hop}$ represents the resistance changes by the fiber swelling,
$\Delta R_{med}$ considers the resistance changes by modifications in the dielectric medium between the chains.

The ionic conductivity of an electrolyte is directly related to the solvent dielectric constant due to changes in ion stabilization and ion mobility. Therefore, the ionic conductivity contribution, important in doped polyaniline, will increase with an increment of the dielectric constant ($\Delta R_{med}$). While $\Delta R_{ele}$ should be quite similar for PANI as thin film or nanofibers since the chemical nature is the same. Moreover, as the electronic spectra of PANI show small changes when the polymer is dispersed ethanol (See **Fig. 1**). On the other hand, the swelling and dielectric effects could depend strongly on the morphology of the conductive structures. It is noteworthy that a layer built using nanofibers modified with dodecanethiol (PANI-DOT NF) does not show measurable conductivity while a thin film modified with the same reactant is conductive and consequently the resistance is affected by the vapor nature. It is likely that functionalization (by nucleophilic addition) of the external surface of PANI nanofibers with the long chain thiol makes the interfiber contact so poor that the layer is non-conductive while the same reaction on the film only alters the interaction with vapors.

It has to bear in mind that chemical interactions also modulate the swelling and dielectric effect since the amount of vapor adsorbed depend on the interactions strength. This implies that the effect of chemical functionalization and morphology combined to produce different signal profiles for the same analyte. That is, the morphology difference does not simply scale the signals but also influence each response differently. Therefore, the combination of nanostructuring and functionalization allows producing new sensing materials. However, a simple chemical interaction mechanism cannot be used to explain the signal observed neither to guide the design new sensing materials.

Due to the mentioned effect, a detailed analysis of the effect of vapor properties (polarity, hydrogen bonding ability, etc.) as it has been made before, it is not attempted [11]. However, it is clear that the magnitude and sign of the resistance signal changes when the sensors are exposed to different vapors depending not only on the chemical functionalities but also on the morphology of the sensing layer. In that way, new sensing materials can be made by either changing the morphology of the conductive structures (NF or thin films) or the chemical nature of the attached functional groups.

### *G. Evaluation as Sensors. Differential Behavior of the Modified Materials*

Besides the fabrication of better sensors, the ability to produce different sensing materials based on the same polymer backbone and using simple reactions is particularly useful in the fabrication of multiple sensors such as electronic noses or tongues [47]. Therefore, sensors were built and exposed to different vapors. First, single sensors made of each material (a thin film and a NF sensor) were exposed to the set of vapors. In **Fig. 7** is possible to appreciate that the sensors are sensitive to all vapors giving different signals in each case. Moreover, the sensors based on nanofibers, give different signals than those made with films for the same analyte. PANI-ATF and PANI-TIO NF sensors seem to be adequate to detect methanol since the pattern shows a high response to this analyte and the sensor almost do not present any response to other vapors. In order to sense ethanol, PANI-2-Cl-ANI NF is the most active material. The same material is sensitive to non-polar solvent vapors such as heptane. The graphs showing the sensor responses to propanol indicate that PANI-CIA in nanofiber form is the most sensitive for this measurement. However, is an important remark that the footprints for alcohols with a medium-larger alkylic chain as butanol and pentanol are similar, being PANI-ATF and PANI-CIA NF sensors the best option to detect this kind of molecules.

Then, multiple sensors were built with all the materials synthesized as nanofiber layers and tested against different vapors **(Fig. 8)**. As it can be seen, defined patterns can be observed for each vapor allowing fast identification of the vapor from the combined response of thin films and nanofiber deposits [48]. Since the functionalization procedure is simple, the combination allows an easy way to increase the diversity of the PANI active materials with low expense. Such property is quite relevant for application in electronic noses or tongues.

## V. CONCLUSIONS

The post-functionalization of polyaniline in the form of thin films and nanofibers using simple reactions was shown to be effective. Chemical modifications were corroborated using different techniques such as UV-Visible spectroscopy, SEM microscopy, contact angle measurements and EDAX. The materials obtained were employed as sensors to detect different analytes (alcohols and heptane). The observed results depend both on the chemical modification of the polymer backbone and morphology of conductive polymer.

The sensors built in this work present a good performance to detect analytes with short alkyl chains such as methanol, ethanol, and propanol. Also, the results suggest that films and deposits of PANI nanofibers which are modified by chemical reactions present different response rates and signal changes to different analytes. Taking this into account, it is possible to conclude that using nanofibers as the active material the response is faster than when PANI thin film is used. Moreover, the signal response to the same analyte is different for the film and nanofibers deposit for each modified polymer. Therefore, it is possible to generate arrays of functionally diverse materials by changing the morphology and functional group attached. In that way, the fabrication method could be used to produce sensor arrays for electronic noses/tongues.

## ACKNOWLEDGMENTS

S. Bongiovanni Abel thanks CONICET for a graduate research fellowship. C. R. Rivarola, D. F. Acevedo and C. A. Barbero are permanent Research Fellows of CONICET.

## REFERENCES

[1] E. Lahiff, S. Scarmagnani, B. Schazmann, A. Cafolla, and D. Diamond, "Covalent attachment of functional side-groups to polyaniline nanofibres," *Int. J. Nanomanuf.*, vol. 5, nos. 1–2, pp. 88–99, 2010.

[2] E. Lahiff, T. Woods, W. Blau, G. G. Wallace, and D. Diamond, "Synthesis and characterisation of controllably functionalised polyaniline nanofibres," *Synth. Met.*, vol. 159, nos. 7–8, pp. 741–748, 2009.

[3] R. Byrne and D. Diamond, "Chemo/bio-sensor networks," *Nature Mater.*, vol. 5, no. 6, pp. 421–424, Jun. 2006.

[4] Y. Wang *et al.*, "Soluble polyaniline nanofibers prepared via surfactant-free emulsion polymerization," *Synth. Met.*, vol. 198, pp. 293–299, 2014.

[5] B. Adhikari and S. Majumdar, "Polymers in sensor applications," *Prog. Polym. Sci.*, vol. 29, no. 7, pp. 699–766, Jul. 2004.

[6] G. Harsányi, "Polymer films in sensor applications: A review of present uses and future possibilities," *Sensor Rev.*, vol. 20, no. 2, pp. 98–105, 2000.

[7] A. Ramanavičius, A. Ramanavičiené, and A. Malinauskas, "Electrochemical sensors based on conducting polymer–polypyrrole," *Electrochim. Acta*, vol. 51, no. 27, pp. 6025–6037, Aug. 2006.

[8] C. Murugan, E. Subramanian, and D. P. Padiyan, "Enhanced sensor functionality of *in situ* synthesized polyaniline–$SnO_2$ hybrids toward benzene and toluene vapors," *Sens. Actuators B, Chem.*, vol. 205, pp. 74–81, Dec. 2014.

[9] S. Shkirskaya, M. Kolechko, and N. Kononenko, "Sensor properties of materials based on fluoride polymer F-4SF films modified by polyaniline," *Current Appl. Phys.*, vol. 15, no. 12, pp. 1587–1592, 2015.

[10] Y. Wang and X. Jing, "Transparent conductive thin films based on polyaniline nanofibers," *Mater. Sci. Eng. B*, vol. 138, no. 1, pp. 95–100, Mar. 2007.

[11] P. Cavallo *et al.*, "Functionalized polyanilines made by nucleophilic addition reaction, applied in gas sensors field," *Synth. Met.*, vol. 215, pp. 127–133, May 2016.

[12] N.-R. Chiou, C. Lu, J. Guan, L. J. Lee, and A. J. Epstein, "Growth and alignment of polyaniline nanofibres with superhydrophobic, superhydrophilic and other properties," *Nature Nanotechnol.*, vol. 2, no. 6, pp. 354–357, Jun. 2007.

[13] L. E. Ibarra *et al.*, "Assessment of polyaniline nanoparticles toxicity and teratogenicity in aquatic environment using Rhinella arenarum model," *Ecotoxicol. Environ. Saf.*, vol. 114, pp. 84–92, Apr. 2015.

[14] A. Eftekhari, Ed., *Nanostructured Conductive Polymers*. Chichester, U.K.: Wiley, 2010.

[15] U. Lange, N. V. Roznyatovskaya, and V. M. Mirsky, "Conducting polymers in chemical sensors and arrays," *Anal. Chim. Acta*, vol. 614, no. 1, pp. 1–26, 2008.

[16] I. Fratoddi, I. Venditti, C. Cametti, and M. V. Russo, "Chemiresistive polyaniline-based gas sensors: A mini review," *Sens. Actuators B, Chem.*, vol. 220, pp. 534–548, Dec. 2015.

[17] Q. Lin, Y. Li, and M. Yang, "Polyaniline nanofiber humidity sensor prepared by electrospinning," *Sens. Actuators B, Chem.*, vol. 161, no. 1, pp. 967–972, 2012.

[18] S. K. Pillalamarri, F. D. Blum, A. T. Tokuhiro, J. G. Story, and M. F. Bertino, "Radiolytic synthesis of polyaniline nanofibers: A new templateless pathway," *Chem. Mater.*, vol. 17, no. 2, pp. 227–229, Jan. 2005.

[19] X. Jing, Y. Wang, D. Wu, L. She, and Y. Guo, "Polyaniline nanofibers prepared with ultrasonic irradiation," *J. Polym. Sci. A, Polym. Chem.*, vol. 44, no. 2, pp. 1014–1019, Jan. 2006.

[20] J. Huang and R. B. Kaner, "The intrinsic nanofibrillar morphology of polyaniline," *Chem. Commun.*, no. 4, pp. 367–376, Oct. 2006.

[21] H. D. Tran and R. B. Kaner, "A general synthetic route to nanofibers of polyaniline derivatives," *Chem. Commun.*, vol. 40, no. 37, p. 3915–3917, 2006.

[22] M. Matsuguchi and T. Asahi, "Properties and stability of polyaniline nanofiber ammonia sensors fabricated by novel on-substrate method," *Sens. Actuators B, Chem.*, vol. 160, no. 1, pp. 999–1004, Dec. 2011.

[23] S. Abdulla, T. L. Mathew, and B. Pullithadathil, "Highly sensitive, room temperature gas sensor based on polyaniline-multiwalled carbon nanotubes (PANI/MWCNTs) nanocomposite for trace-level ammonia detection," *Sens. Actuators B, Chem.*, vol. 221, pp. 1523–1534, Dec. 2015.

[24] H. Bai, L. Zhao, C. Lu, C. Li, and G. Shi, "Composite nanofibers of conducting polymers and hydrophobic insulating polymers: Preparation and sensing applications," *Polymer*, vol. 50, no. 14, pp. 3292–3301, Jul. 2009.

[25] D. G. Babar, R. Olejnik, P. Slobodian, and J. Matyas, "High sensitivity sensor development for Hexamethylphosphoramide by polyaniline coated polyurethane membrane using resistivity assessment technique," *Measurement*, vol. 89, pp. 72–77, Jul. 2016.

[26] S. Virji, J. Huang, R. B. Kaner, and B. H. Weiller, "Polyaniline nanofiber gas sensors: Examination of response mechanisms," *Nano Lett.*, vol. 4, no. 3, pp. 491–496, Feb. 2004.

[27] P. Cavallo, D. F. Acevedo, M. C. Fuertes, G. J. A. A. Soler-Illia, and C. A. Barbero, "Understanding the sensing mechanism of polyaniline resistive sensors. Effect of humidity on sensing of organic volatiles," *Sens. Actuators B, Chem.*, vol. 210, pp. 574–580, Apr. 2015.

[28] E. Ortega, F. Armijo, I. Jessop, M. A. D. Valle, and F. R. Diaz, "Chemical synthesis and characterization of polyaniline derivatives. Substituent effect on solubility and conductivity," *J. Chilean Chem. Soc.*, vol. 58, no. 4, pp. 1959–1962, 2013.

[29] H. J. Salavagione, D. F. Acevedo, M. C. Miras, A. J. Motheo, and C. A. Barbero, "Comparative study of 2-amino and 3-aminobenzoic acid copolymerization with aniline synthesis and copolymer properties," *J. Polym. Sci. A, Polym. Chem.*, vol. 42, no. 22, pp. 5587–5599, 2004.

[30] D. F. Acevedo, H. J. Salavagione, M. C. Miras, and C. A. Barbero, "Synthesis, properties and aplications of functionalized polyanilines," *J. Brazilian Chem. Soc.*, vol. 16, no. 2, pp. 259–269, 2005.

[31] D. A. Acevedo, A. F. Lasagni, C. A. Barbero, and F. Mücklich, "Simple fabrication method of conductive polymeric arrays by using direct laser interference micro-/nanopatterning," *Adv. Mater.*, vol. 19, no. 9, pp. 1272–1275, 2007.

[32] H. J. Salavagione, M. C. Miras, and C. Barbero, "Chemical lithography of a conductive polymer using a traceless removable group," *J. Amer. Chem. Soc.*, vol. 125, no. 18, pp. 5290–5291, 2003.

[33] H. J. Salavagione, D. F. Acevedo, M. C. Miras, and C. Barbero, "Redox coupled ion exchange in copolymers of aniline with aminobenzoic acids," *Portugaliae Electrochim. Acta*, vol. 21, no. 3, pp. 245–254, 2003.

[34] E. Frontera *et al.*, "Tuning the molecular sensitivity of conductive polymer resistive sensors by chemical functionalization," *Key Eng. Mater.*, vol. 605, pp. 597–600, Apr. 2014.

[35] E. I. Yslas, P. Cavallo, D. F. Acevedo, C. A. Barbero, and V. A. Rivarola, "Cysteine modified polyaniline films improve biocompatibility for two cell lines," *Mater. Sci. Eng. C*, vol. 51, pp. 51–56, Jun. 2015.

[36] C. A. Barbero *et al.*, "Synthesis, properties and applications of conducting polymer nano-objects," *Mol. Cryst. Liq. Cryst.*, vol. 521, no. 1, pp. 214–228, 2010.

[37] D. F. Acevedo, J. Balach, C. R. Rivarola, M. C. Miras, and C. A. Barbero, "Functionalised conjugated materials as building blocks of electronic nanostructures," *Faraday Discuss.*, vol. 131, pp. 235–252, Sep. 2006.

[38] E. I. Yslas, L. E. Ibarra, D. O. Peralta, C. A. Barbero, V. A. Rivarola, and M. L. Bertuzzi, "Polyaniline nanofibers: Acute toxicity and teratogenic effect on Rhinella arenarum embryos," *Chemosphere*, vol. 87, no. 11, pp. 1374–1380, 2012.

[39] D. F. Acevedo, M. C. Miras, and C. A. Barbero, "Solid support for high-throughput screening of conducting polymers," *J. Combinat. Chem.*, vol. 7, no. 4, pp. 513–516, 2005.

[40] M. A. Molina, C. R. Rivarola, M. F. Broglia, D. F. Acevedo, and C. A. Barbero, "Smart surfaces: Reversible switching of a polymeric hydrogel topography," *Soft Matter*, vol. 8, no. 2, pp. 307–310, 2012.

[41] R. Olejnik, Z. Špitalský, M. Prostredný, and P. Slobodian, "Sensing element on the base of graphene/styren-isopren copolymer for VOC detection in idustry," in *Proc. PMA SRC*, 2015, pp. 238–241.

[42] C. Barbero *et al.*, "New methods of polyaniline functionalization," *Synth. Met.*, vol. 101, nos. 1–3, pp. 694–695, 1999.

[43] S. B. Abel, M. A. Molina, C. R. Rivarola, M. J. Kogan, and C. A. Barbero, "Smart polyaniline nanoparticles with thermal and photothermal sensitivity," *Nanotechnology*, vol. 25, no. 49, p. 495602, 2014.

[44] A. Neira-Carrillo *et al.*, "Hybrid biomaterials based on calcium carbonate and polyaniline nanoparticles for application in photothermal therapy," *Colloids Surf. B, Biointerfaces*, vol. 145, pp. 634–642, Sep. 2016.

[45] A. F. Lasagni, D. F. Acevedo, C. A. Barbero, F. Mu, and F. Materials, "Direct patterning of polystyrene–polymethyl methacrylate copolymer by means of laser interference lithography using UV laser irradiation," *Polym. Eng. Sci.*, vol. 48, no. 12, pp. 2367–2372, 2008.

[46] J. Stejskal, J. Prokeš, and M. Trchova, "Reprotonation of polyaniline: A route to various conducting polymer materials," *Reactive Funct. Polym.*, vol. 68, no. 9, pp. 1355–1361, 2008.

[47] H. K. Patel, "Sensor Circuits," in *The Electronic Nose: Artificial Olfaction Technology*. New Dehli, India: Springer, 2014, pp. 181–205.

[48] A. Ortega, S. Marco, T. Šundic, and J. Samitier, "New pattern recognition systems designed for electronic noses," *Sens. Actuators B, Chem.*, vol. 69, no. 3, pp. 302–307, 2000.

**Silvestre Bongiovanni Abel** received the B.Sc. degree in chemistry from the Universidad Nacional de Río Cuarto in 2013 and the Ph.D. degree in chemistry from the Universidad Nacional de Río Cuarto in the subjects of advanced materials based on synergic nanocomposites made of conductive and thermosensitivity polymers in 2018. He currently holds a post-doctoral position at the Research Institute of Materials Science and Technology (UNMdP-CONICET) holding a National Science Council of Argentina (CONICET) Fellowship.

**Robert Olejnik** received the Ph.D. degree from Tomas Bata University, Zlín, Czech Republic, in 2014. He is currently a Researcher, with Tomas Bata University, working with nanomaterials and composites for technological applications.

**Claudia R. Rivarola** received the Ph.D. degree in chemistry from the Universidad Nacional de Río Cuarto in 2003. She is a permanent Research Fellow at CONICET. Her research interests are in the study of polymeric materials for different applications such as sensors/actuators device and biomedicine.

**Petr Slobodian** received the Engineer's degree (M.Sc. equivalent) from the Faculty of Technology, Brno University of Technology, Zlin, in 1994, and the Ph.D. degree in amorphous polymers in 2003. He is currently a Professor and a Researcher with Tomas Bata University in Zlín, Zlin, Czech Republic. He published more than 70 manuscripts, two chapter books, and also patents.

**Petr Saha** is currently an Ing. Professor with Tomas Bata University in Zlín, Zlin, Czech Republic. He was a Researcher and a Professor in Brno, Czech Republic, and with the Chalmers University of Technology, Gothenburg, Sweden. He has been with Tomas Bata University in Zlín since 2001. Since 2010, he is a Rector of Tomas Bata University in Zlín, Czech Republic. He is a member of a number of scientific boards and higher education institutions. He published numerous articles in international journals and has more than 3000 citations in the Web of Science database.

**Diego F. Acevedo** received the Degree in chemical engineering in 2000 and the Ph.D. degree in chemistry from the Universidad Nacional de Río Cuarto in 2006. He is currently a Research Professor with the Department of Chemical Engineering, Universidad Nacional de Río Cuarto, and a permanent Researcher at CONICET. His research interests focus on the development of advanced and functional materials.

**Cesar A. Barbero** received the B.Sc. and Ph.D. degrees in chemistry from the Universidad Nacional de Río Cuarto (UNRC), in 1984 and 1988, respectively. He was a Post-Doctoral Researcher with the Paul Scherer Institute, Switzerland, from 1988 to 1994. He is currently a Full Professor with UNRC and a Superior Researcher at CONICET. He is the Director of the Advanced Materials Group, UNRC. He published more than 170 manuscripts (2290 citations, h=32) and produced 11 patents. His research interest is in advanced materials (conducting polymers, carbon, and hydrogels) for technological applications, especially nano and mesomaterials. He is an IUPAC Fellow. He received the Tajima Prize of ISE in 1997 and the Guggenheim Fellowship in 2007.