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Electrospun PVC-nickel phthalocyanine composite nanofiber based conductometric methanol microsensor

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Abstract

A conductometric microsensor for measuring methanol vapor was conceived, based on electrospun composite nanofibers of polyvinyl chloride (PVC) doped with nickel phthalocyanine (NiPc) deposited on interdigitated electrodes (IDEs) as transducers. The nanofiber's shape, structure, percent atomic content and thermal properties were studied. The methanol sensor showed good sensitivity ($505\mu\text{S}\cdot\text{cm}^{-1}\cdot(\text{v/v})^{-1}$), low limit of detection (LOD = 15 ppm), short response time (13 s), and short recovery time (25 s). The sensor was 4 times more sensitive to methanol than to ethanol and 19 times more sensitive to methanol than to acetone. Furthermore, the sensor response was unaffected by the interfering water vapor, making it more suitable for volatile organic compound (VOC) sensing in the presence of humidity. The sensor was applied for conductometric detection of methanol in rubbing alcohol.

Keywords: Electrospinning; PVC; Nickel Phthalocyanines; Methanol; Conductivity; Nanofiber.

I. Introduction

Methanol is commonly utilized in laboratories and industries as solvents or cleaning agents [1]. Methanol is a frequent feedstock for a variety of critical compounds and a possible energy carrier alternative to hydrogen [2]. Inhaling significant amounts of methanol vapor can result in headache, tiredness, nausea, impaired vision, convulsion, and even blindness, tumors, and

cancer [1]. The wide range of applications for MeOH, as well as its toxic effects and the desire to fine-tune its synthesis under extreme conditions, all of these factors point to the necessity for reliable and selective methanol sensors. The American Conference of Governmental Industrial Hygienists (ACGIH) recommends a released threshold for methanol vapor concentration of 200 ppm for repeated exposure without severe health effects during the working day (8 h). Originally, non-invasive analytical pieces of equipment such as PTR-MS (Proton Transfer Reaction/Mass Spectrometry), GC-MS (Gas Chromatography/Mass Spectrometry), and chemiluminescence gas analyzers were known for methanol detection and measurements for early diagnostic techniques [3]. With these techniques, conventional VOC analysis becomes time-consuming, expensive, and unsuited for extensive screening [4]. Sensors are good candidates for the low cost detection of VOCs. Chemical species interact with the sensitive layer of the sensor, changing its electrical conductivity as a result. The change in resistance/conductivity of a sensitive layer because of processes (adsorption, chemical reactions, diffusion, catalysis, charge transfer) occurring on the surface of the sensing area is the base of conductometric sensor functioning [5]. So far, sensor scientists have carried out numerous studies to develop amazingly gas sensors capable of detecting NH₃, H₂S, CO, and others [6]. Nickel-phthalocyanines are a class of coordination compounds that can act as a chemically reactive and sensitive film due to the enormous physical properties of interactions with a wide range of volatile organic compounds (VOCs) [7-12]. Compared to pure phthalocyanines, polymers-phthalocyanines mixed materials are less crystalline, and have high electrical conductivity, and are more effective in gas sensing properties [13]. This opens the door to the meticulous manufacture and design of a thin film with high sensitivity, selectivity, and stability (3S) [14]. A conductometric based on a chitosan/nickel phthalocyanine (NiPc) composited was recently developed for the detection of methanol [15]. A detection limit of 700 ppm was obtained at ambient temperature and a low sensitivity for water was obtained, due to

a differential measurement. In order to increase the surface area of the polymer/NiPc composite, for a better interaction with methanol, it is here proposed to prepare this composite as nanofibers.

Electrospinning is a low-cost, effective technique for creating ultra-thin polymer and composite fibers having diameters ranging from a few nanometers to a few micrometers [16]. It requires utilizing a high voltage to polymer solutions or melts ejected from microsyringe pumps through electrostatic stretching [17]. Over the last two decades, this technique has gained significant attention. It was used to actively spin more than a hundred polymers into ultra-fine fibers [18]. Electrospun fibers with several properties, fine structure, tunable membrane, thickness, and an attractive large specific surface area are indicators of the best prospects for a sensing application's configuration [19].

In this study, we investigate the activities for VOC sensing of the electrospun polyvinyl chloride doped with the NiPc deposited on interdigitated electrodes. The ideal conditions for nanofiber manufacturing were explored using characterization techniques like scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA). Analytical performance of the obtained conductometric sensor was determined for methanol detection.

II. Experimental

Chemicals and reagents together with the fabrication and cleaning process and binding of micro conductometric chips was demonstrated in the first section of the supplementary materials.

Electrospinning Process was done by dissolving 4.12 g of PVC powder in 15 mL of DMF/THF mixture (volume ratio of 1/1), at a temperature of 50°C and under a stirring speed of 500 rpm, a clear solution of the polymer was obtained after 3 h mixing. To eliminate air bubbles and stabilize the solution, it was kept at room temperature for 1 h. In parallel, a suspension of NiPc was prepared by dissolving blueish NiPc 1mg/mL in THF for overnight stirring. The solution of PVC polymer and the NiPc suspension were mixed in a volume ratio of 4:1 respectively for further electrospinning processes.

The electrospinning operation was carried out using a spray base kit. A spray base syringe pump module (PLS000004) was used to pump the polymer solution, and a spray base 20 kV, 1bar electro spraying controller (PLS00047) was used to control the voltage. An XYX belt-driven stage (CAT000108) was utilized to manage the tip-to-collector distance. A point grey Chameleon (USB powered) 1/3 monochrome CCD camera (CMLM-13S2M-CS) was employed as the imaging system.

The prepared PVC polymer gel (reference sensor) and PVC-NiPc polymer gel (working sensor) were introduced into a 5 mL disposable plastic syringe fitted with a Spray Base pump system and pumped at a flow rate of from 0.2 mL/min to 2.0 mL/min. The distance between the needle's aperture and the stainless-steel flat plate collector was fixed 15 cm. The blunt steel needle was 22 gauge in size. The applied voltage was from 8.35 kV to 17.5 kV. The PVC nanofibers were deposited during about 2-3 min on both sensors (reference and working sensors respectively). The electrospinning process was carried out under standard conditions RT for all studies.

5. Instrumentation

The surface morphology study and energy dispersive X-ray (EDX) analysis of the bare chips, and of PVC nanofibers doped with NiPc deposited on chips were carried out using scanning electron microscopy (SEM) (COXEM EM-30AX⁺). The functional groups of nanofiber array were investigated using Fourier transform infrared spectral data acquired with a NEXUS spectrophotometer ((Nicolet-Thermo Fisher, UK). Thermogravimetric analysis (TGA) using a thermal gravimetric analyzer (TA Instruments Q50) was employed at a flow rate of 90 mL/min under air, to determine the thermal properties of the samples.

Fixing a significant amplitude of sinusoidal potential difference of (10 mV peak to peak at 0V) to each pair of the interdigitated electrode (microelectrode) with an optimized frequency of 10 kHz produced by a limited frequency waveform generator allowed conductometric detection of volatile organic compounds. These parameter values were fixed to diminish faradaic activity, double-layer charging, and concentration polarization at the microelectrode surface. To

generate the differential output signal between the working sensor (conductometric chip covered with PVC nanofibers doped with NiPc) and the reference sensor (conductometric chip covered with PVC nanofibers), the Standard Research System Lock-in Amplifier SR510 was used. The detection was performed in the gas phase above the aqueous phase and the recovery was obtained by taking off the sensors to the ambient air condition ($T = 298 \text{ K}$, Pressure = 1 atm) ($\Delta G = 0$).

6. VOC generation of gas samples

Gaseous samples of acetone, ethanol, and methanol were measured through the headspace above aqueous solutions of known concentrations between 0-100 v/v%.

The concentrations of the solvents as mentioned above in the gas phase and in the aqueous solution depended on Henry's law constants of the given analytes in water. They were converted from Henry's law from Sander's third version equation reported at (25°C) in 1999 [20].

$$kH^{\circ} = C_a/P_g \quad (1)$$

Here, C_a being the concentration of a species in the aqueous phase and P_g being the partial pressure of that species in the gas phase. Where H° refers to Henry's law constants for the standard condition.

For the listed solvents above at (25°C), i.e., methanol, ethanol, and acetone, Henry's law constants value of $2.2 \times 10^2 \text{ M/atm}$, $1.9 \times 10^2 \text{ M/atm}$, and $0.2 \times 10^2 \text{ M/atm}$ were considered respectively [21] (Table 1).

Table 1. Equilibrium gaseous phase concentrations above aqueous methanol, ethanol, and acetone solution at 25°C per Henry's law constants reported by Sender et al. [20].

S/N	% Volumetric concentration	The concentration of methanol in the gaseous phase (%v/v)	The concentration of ethanol in the gaseous phase (%v/v)	The concentration of acetone in the gaseous phase (%v/v)
1	0%	0	0	0
2	10%	1.13	0.9	5.63
3	20%	2.25	1.79	11.26
4	40%	4.5	3.58	22.52
5	60%	6.75	5.37	33.78
6	80%	9	7.16	45.04
7	100%	11.25	8.95	56.03

III. Results and Discussion

III.1. Optimization of the electrospinning process

Electrospinning of a 15% and 11% w/v PVC solution in a 1:1 v/v DMF/THF solution proved relatively easy and is suggested that electrospinning of PVC in the THF/DMF solution is more favorable [22]. Four parameters were explored to investigate the electrospinning process and generate smooth nanofibers. Polymer concentration, applied voltage, and flow rate are critical parameters that have a direct impact on nanofiber shape [23]. Thus, we produced 15% and 11% PVC solutions and then varied flow rates and voltages. Nanofibers were placed on the substrate's surface to determine the best electrospinning settings. The collection period was 3 min, which resulted in dense polymer deposition and allowed the experiment to be completed in a fair amount of time. Experiments that determine Taylor cone, stability of jet, and fabrication of nanofibers are summarised in Table S1.

The parameters of the electrospinning technique for the formation of PVC nanofibers on the interdigitated gold electrode substrate were successfully optimized. We observed that 15% wt. polymer content in DMF/THF solution, flow rate of 1.5mL/h, and 15 cm between the needle

and the collector and 17.74 kV as applied voltage, are the most impressive parameters for fabricating consistent bead free nanofibers.

III.2.Characterization of electrospun PVC-NiPc nanofibers

III.2.1. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) scans of electrospun 15% PVC nanofibers and that of PVC-NiPc nanofibers are shown in Figure 1.

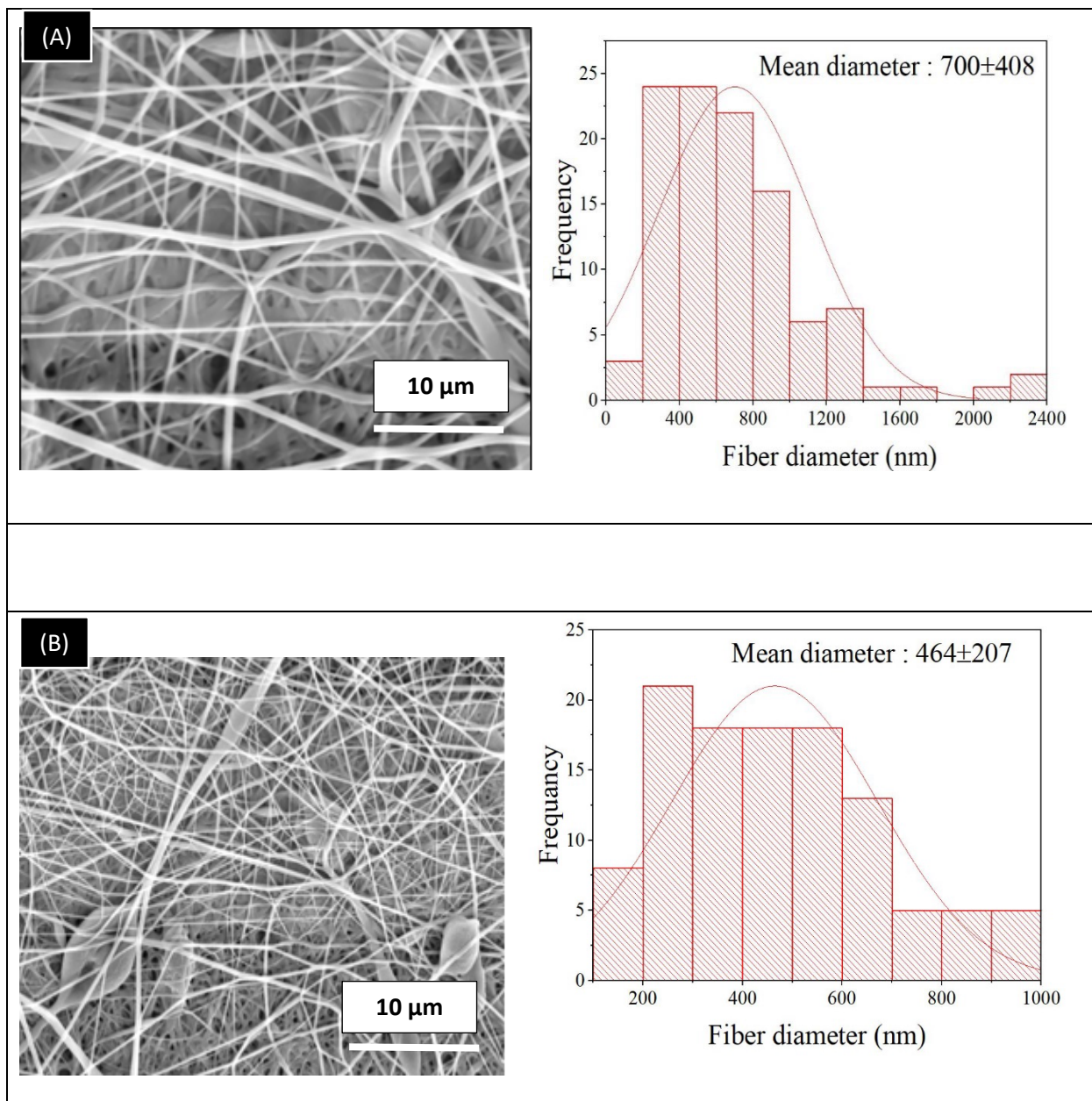


Figure 1. SEM scans and diameter distribution histograms of fibrous mats (A) PVC nanofibers (B) PVC-NiPc nanofibers electrospun at 1.5 mL/h, applied voltage 17.74 kV, 15 cm between the needle and the collector. The polymer concentration in DMF/THF solution was 1.5 %wt.

The morphological surface of the produced nanofibers is presented in Figure 1. Figure 1A depicts fibrous mats obtained from the electrospinning of PVC on interdigitated electrodes. In agreement with the histogram of PVC nanofiber size distribution, PVC nanofibers (NFs) present an average diameter within the range of 700 ± 408 nm. PVC-NiPc nanofibers were found to be dark at the first glance, because of the bluish color of NiPc. The size distribution of PVC NFs average diameter had reduced within the range of 464 ± 207 nm. This size reduction might be due to the reduced viscosity and increased conductivity of the PVC-NiPc solution (see Figure 1B). These conditions of deposition giving the more regular nanofibers were chosen for the fabrication of all the conductometric sensors.

III.2.2. *Thermal Gravimetric Analysis (TGA) and FTIR Analysis*

Presented in Supplementary Material

III.3. VOC differential measurements

The VOC differential detection performance of PVC/NiPc fibrous mats on the interdigitated electrode as working sensor and using only PVC nanofiber as the reference sensor is shown in Figure 2a. The difference in conductivity (ΔG) of the working and reference sensors, is obtained from the conductimetric differential measurement using lock-in amplifier. Sensor operated at optimum conditions ($T = 298$ K, Pressure = 1 atm). The analytical measurement of methanol begins by accounting for the essential sensor parameters, which are response and recovery time of the device, as shown in Figure S6. The response time is 13 s and the recovery time is 25 s.

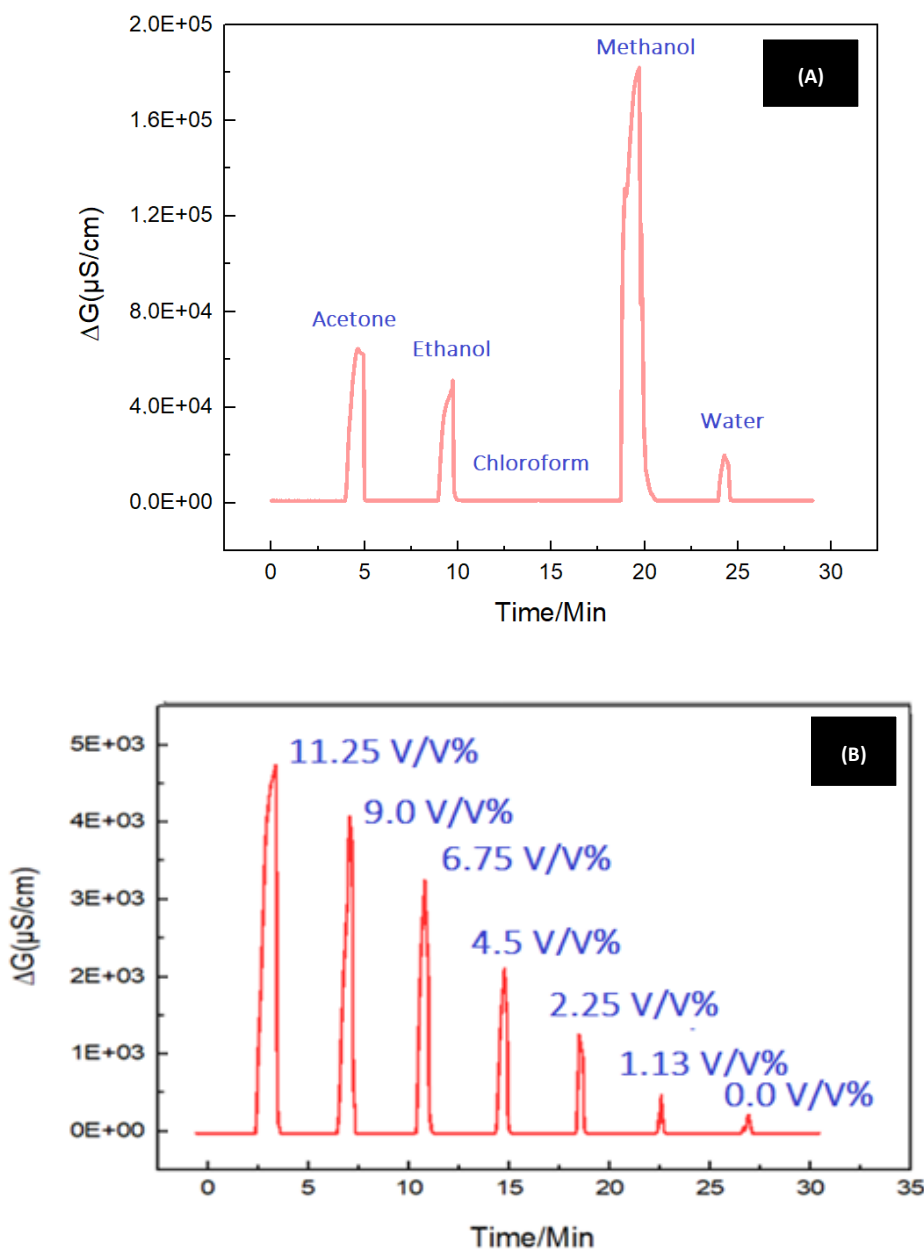


Figure 2: (a) VOCs' detection kinetics (b) gaseous phase of methanol detection kinetics. Electrospinning conditions: electrospun NiPc/PVC-NiPc nanofibers electrospun at 1.5 mL/h, 17.74 kV. Conductometric measurements: differential measurements between the reference sensor (electrospun PVC nanofibers) and the working sensor (electrospun PVC-NiPC nanofibers). Amplitude of the sinusoidal potential: 10 mV – frequency 10 kHz. (T = 298K, Pressure = 1 atm).

The sensor response of five different VOCs was tested initially, as shown in Figure 2a. The sensor response towards methanol is much higher than for ethanol, acetone, and water, with no response when exposed to chloroform. The sensing mechanism should be related to the

rearrangement of the electrical dipole in the bulk thin film due to the interaction of phthalocyanine and analytes (alcohols and acetone), in other words, the interaction generates modulation in the electronic levels for π - π^* transitions of the phthalocyanine ring [24]. After testing the sensor's selectivity of the VOCs as depicted in Figure 2a, the sensor was exposed to successive decreasing concentrations of methanol (Figure 2b). When the concentration of methanol was 0%, the sensor was exposed to pure water and the measured conductivity, corresponding to 100% of humidity, is then 4.4×10^2 $\mu\text{S}/\text{cm}$. This low value is due to the hydrophobicity of the PVC matrix and to the differential measurement system. When the concentration of methanol was 11.25%, the measured signal was 5×10^3 $\mu\text{S}/\text{cm}$, the contribution of 89% of humidity is less than 10% of this signal, which is in the range of the experimental error in this range of concentration. The sensors were exposed to different concentrations of acetone, ethanol, and methanol to ascertain the sensitivity of each of the three VOCs accordingly. The linearity of the methanol calibration curve was verified in the range of 0v/v% to 11.25v/v%. The sensor has a sensitivity of $505 \mu\text{S}/\text{cm} (\text{v}/\text{v})^{-1}$ and a limit of detection of 15 ppm, as demonstrated in the calibration curve in Figure 3. The sensor was 4 times more sensitive to methanol than to ethanol and 19 times more sensitive to methanol than to acetone.

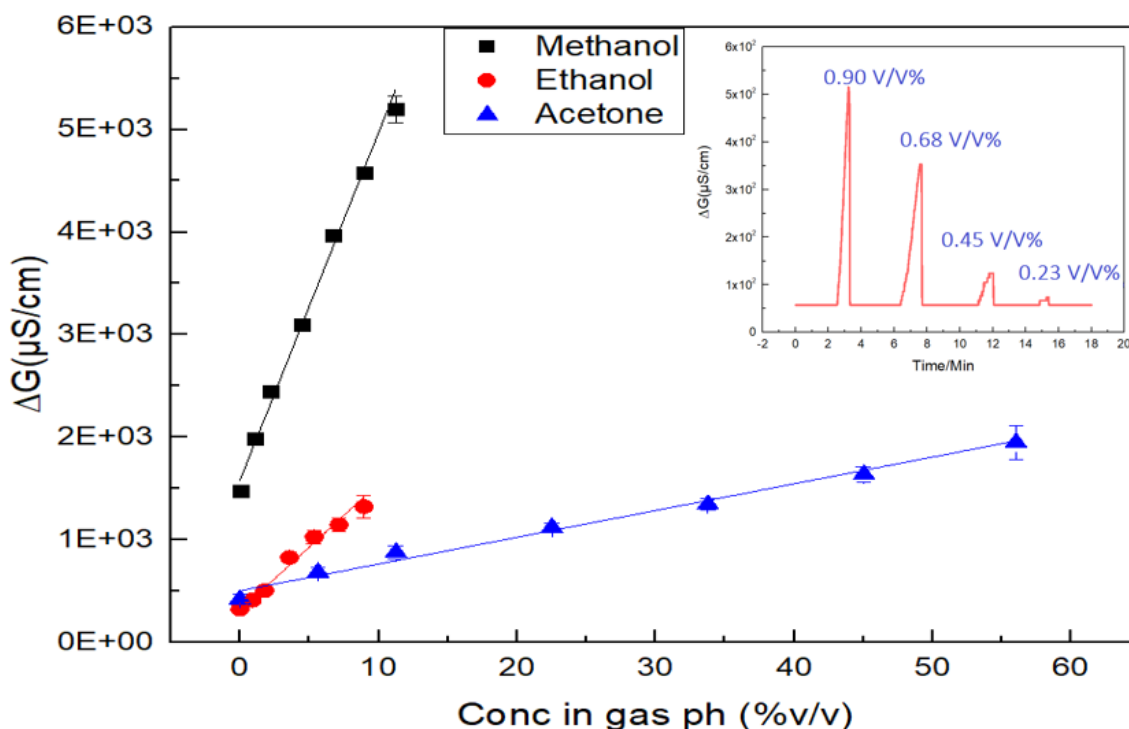


Figure 3. Calibration curves of the gaseous phase of VOCs sensitivities.

Electrospinning conditions: electrospun NiPc PVC-NiPc nanofibers electrospun at 1.5 mL/h, 17.74 kV. Conductometric measurements: differential measurements between the reference sensor (electrospun PVC nanofibers) and the working sensor (electrospun PVC-NiPC nanofibers) Amplitude of the sinusoidal potential: 10 mV – frequency 10 kHz. (T = 298K, Pressure = 1 atm).

For the same methanol sensor, the repeatability was studied over ten determinations. The obtained relative standard deviation ranges from 5% all concentrations. The reproducibility was studied using 5 different methanol sensors. The obtained relative standard deviation was 10%. The sensor retains 94% of its initial response after two weeks, 89% of its initial response after two weeks and 80% of the initial response after seven weeks, when every four days, methanol was tested.

The effect of the presence of 1/10 of acetone and 1/10 of ethanol on the methanol peak is 2 times higher than the measurement error for pure methanol.

Due to the low sensitivity of the methanol sensor for the determination of ethanol and acetone, the repeatability for them was worse. The relative standard deviation was 7% for ethanol determination and 10% for acetone determination.

Table 2. Comparison of the analytical performances of conductometric methanol sensors based on different materials

Sensitive materials	Working Temperature	Response time (s)	Dynamic range (ppm)	Detection limit (ppm)	Ref
Graphene oxide/polyindole	26°C±1°C	7	1.14 – 11.36	0.15	[25]
Pt doped SnO ₂ nanoparticles	22°C	10	0.13 - 5	0.13	[26]
TiO ₂ nanotubes	Ambient temperature	30	100 - 300	100	[27]
Tin dioxide doped cadmium sulfide	360°C	—	0 - 6	0.9	[28]
Chitosan-NiPc film	25°C	31	700 - 10 ⁵	700	[15]
PVC-NiPc nanofibers	25°C	13	15 – 1.1x10 ⁵	15	This work

In our previous work, using a film of chitosan doped with NiPc [15], the obtained detection limit is 700 ppm whereas the use of PVC-NiPc fibrous mats leads to a very lower detection limit (15 ppm). Compared to other nanomaterials presented in Table 2, the advantages of PVC-NiPc fibrous mats is the measurement at room temperature, short response time and large dynamic range.

III.4. Application of methanol sensor

Commercial rubbing alcohol is a product made from methanol and is used as a liquid onto barbecues or fireplaces or as solvent or antifreeze. In addition, if used at home, it is a powerful cleaner for stubborn dirt.

The standard addition method was used for the detection of methanol in the headspace of commercial rubbing alcohol. From the experimental points the calibration curve was found to be : $10^{-5}y = 0.0140 \pm 0.0005 x + 1.32 \pm 0.01$ where y is the conductivity and x the percentage of methanol in water. From this equation, the determined concentration of methanol rubbing alcohol is 94.3 ± 4 % in compliance with the concentration specified by the provider, 95%.

IV. Conclusion

The current research proposes a one-step elaboration of electrospun nanofibrous mats and optimization of the electrospinning parameters to generate PVC electrospun nanofibers doped with NiPc. According to our research, the most optimal parameters for fabricating continuous non-beaded nanofibers were 15 weight percent PVC polymer, 1.5 mL/h flow rate, and 12 cm distance between needle and collector.

The findings revealed that nanofiber morphology is greatly influenced by the applied voltage, flow rate, and polymer concentration in solution and the adhesion and stability of nanofiber deposition on the substrate surface. PVC/NiPc-NFs, synthesized electrospun nanofibers, were employed to make the VOC conductometric sensor. Sensor demonstrated good sensing performance for methanol. In the future, to fabricate an efficient gas sensor for biomedical, industrial, and environmental applications, we wish to couple our sensor with a LCU and GC-MS to enable detection at a much lower concentration.

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