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A new easy method for preparation of high sensitive nanopolypyrrole chemical sensor using ultrasonic spray technique

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ABSTRACT

In this paper we describe an easy method to deposit thin films from soluble Polypyrrole (Ppy) synthesized by chemical polymerization using SDBS as surfactant. Ultrasonic spray technique was adopted to deposit these films, using a commercial domestic humidifier, on alumina substrates coated with two interdigitated electrodes, to be used as chemiresistor sensor. The obtained films were characterized by FTIR, X-ray diffraction, scanning electron microscope (SEM), and four point probe techniques. We also investigated the effect of polymerization time, molar ratios of Pyrrole monomer to the oxidant (FeCl_3) [Mo] / [Ox] on sensing property. X-ray diffraction pattern of Ppy with SDBS showed a shift of diffraction peak angle of about ($2\theta = 11.46^\circ$), relatively to pure Ppy, indicating that SDBS acted as a spacer between the conducting polymer chains, and induced a very high d-spacing comparing to the pure one. This has a positive impact on sensor sensitivity, as it makes more easily for analyte molecules to penetrate inside the films. Small peaks shifts were also observed between Ppy prepared with different molar ratios [Mo] / [Ox], indicating that the higher the molar ratio, the higher the space between chains is. Conductivity measurements were made for the selected molar ratios. The best conductivity was 0.62(S/cm) corresponding to a molar ratio of 3. Finally, sensors showed a good sensitivity towards methanol and ethanol which could be explained by the high specific surface area and porosity as demonstrated by SEM images.

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KEYWORDS

(SDBS) Sodium dodecylbenzenesulfonate;
Polypyrrole;
Ultrasonic spray deposition;
XRD;
Conductive polymers;
Conductivity;
Sensors.

INTRODUCTION

Semiconducting properties of organic materials are not new, but the availability of film-forming semiconducting polymers is very recent. There is a high level of interest in the potential that these structures might have for use in large-area thin-film electronics, because of

the prospect for low-cost fabrication of devices with very acceptable performance. Over the last three decades, conducting polymers such as Polypyrrole, Polythiophene, and Polyaniline have attracted a great deal of research interest because of the great promise of their electrical, electrochemical and optical properties for commercial applications such as sensors, light-

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emitting diodes, rechargeable batteries, electrochromic display devices, etc. In these applications, conducting polymers are normally used as films or coatings, with different thicknesses, depending on the requirements of the application. Key hurdles to the use of these polymers in commercial products have been the lack of facile synthetic methods for producing useful quantities as well as simple approaches for processing bulk polymer into useful forms. In addition, the stability, including mechanical, thermal, conductivity (with time and at high temperature) and overoxidation, has been a concern. The limitations in postsynthesis processability are due to the chain stiffness and interchain interactions that render these materials insoluble in common solvents. For example, polymers can become crosslinked, highly branched, or electrostatically crosslinked due to polaron/bipolaron charge interactions. The chemical or ionic crosslinking renders the polymer intractable^[1]. As a result, these conjugated polymers are difficult to process into thin films on flexible substrates using traditional methods such as spin coating^[2]. Polypyrrole is one of the more promising conducting polymers. It is prepared by oxidation of Pyrrole either by chemical or electrochemical means^[3]. Chemically prepared Ppy is in the form of brittle powders that are insoluble and infusible, and have poor processability, the poor processability of Ppy has been clarified by the existence of strong interchain interactions. Polymerization conditions affect the properties of Ppy such as monomer to oxidant molar ratio, presence of surfactant, reaction time and temperature^[4]. Depositing a sensitive film on a substrate is a crucial point when looking for reproducibility and stability of sensor response. There are several methods for depositing sensitive films on a substrate such as casting, spray, spin coating, self-assembly, sputtering, evaporation, and Langmuir-Blodgett. Among the simple methods for depositing sensing films, those obtained by self-assembly have the best uniformity. However, the thickness of the film is limited by the self-assembly chemical process and usually is reduced to a monolayer or some tens of nanometers. On the other hand, with the casting method it is possible to deposit a thicker film, but there is a poor control on the amount of material deposited. Furthermore, the structure, thickness and uniformity of the film change from one run to another. Although spray and spin coating

methods have better controllability, they have a lack of the sensor response reproducibility, which is dependent on the uniformity, structure and thickness of the sensitive film. Such reproducibility is required, for instance, when replacing sensors without calibration steps or in systems where two or more sensors with similar characteristics are required^[5]. In the present work, a novel method for depositing Polypyrrole films based on an ultrasonic atomizer was developed. Although ultrasonic atomization has been widely investigated and used for a variety of applications, up to our knowledge it has not been used for depositing Polypyrrole films used as sensors, so far. Polypyrrole sensitive films were deposited on alumina substrates coated with two interdigitated electrodes, for their use as chemical sensors. The obtained films were characterized by FTIR, X-ray diffraction, scanning electron microscope (SEM) and four point probe techniques. We also investigated the effect of polymerization time, molar ratios of Pyrrole monomer to the oxidant (FeCl_3) $[\text{Mo}]/[\text{Ox}]$ on sensing property.

EXPERIMENTAL

Materials

Materials used for the chemical synthesis were Pyrrole monomer (Py) purchased from (Merck), Sodium dodecylbenzenesulfonate (SDBS) (Aldrich) ($M_w = 348.48 \text{ g/mol}$), hexahydrate ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), Ethanol (Aldrich), Methanol (Merck), Acetone (Panreac), Deionized water (DI), all materials used in this research were analytical grade.

Polypyrrole synthesis

Polypyrrole was chemically synthesized with five different molar ratios (3, 5, 6, 8, and 10) of monomer to oxidant $[\text{Mo}] / [\text{Ox}]$. The oxidant solution was prepared by dissolving 1 mmol of hexahydrate ferric chloride in 25 mL of DI water under stirring for 10 min. The monomer solution was prepared by dissolving the appropriate moles of Pyrrole in 100 mL of DI water by stirring for 10 min, the flask was put in an ice bath to maintain the temperature between $(0^\circ\text{C} - 5^\circ\text{C})$ ^[6], then 5 mmol of SDBS was added under stirring for 30 min. Then a drop wise of oxidant solution was added to the cold mixture of Py and SDBS during one hour, the mixtures

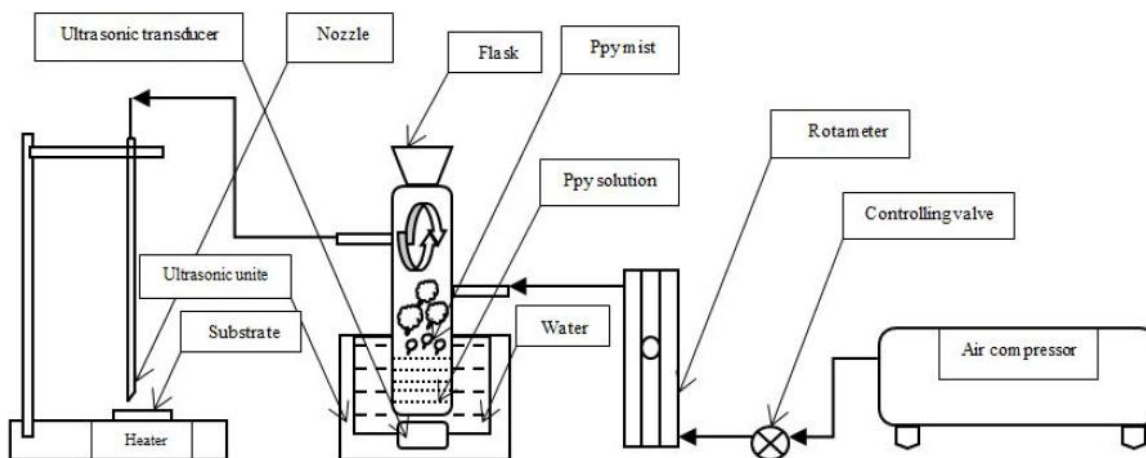


Figure 1 : Schematic view for ultrasonic spray deposition technique

were gently stirred until the termination of the polymerization reaction by pouring excess amount of methanol into the black mixture. Three polymerization times (1, 24, 45) h were chosen for each molar ratio. Finally, solutions were filtered, and the resulted black Ppy precipitates were washed with DI water, methanol, ethanol, and acetone, sequentially followed by drying in vacuum oven at 30°C for 24 hours.

Ultrasonic spray deposition system

The deposition system consists of four main parts: mist generator (from LAICA) equipped with piezoelectric ultrasonic transducer, air compressor, heater, and nozzle, as shown in Figure 1. A controlling valve was used to control air flow rate which was measured with a rotameter^[5,7].

Preparation of sensors substrates

Figure 2 shows alumina substrate with two interdigitated electrodes used in this work^[8]. The cleanliness of substrates is of prime importance to have good adherent films. So, we followed a multistep cleaning procedure, consisting of soaking the alumina substrates in distilled water, methanol, distilled water, acetone, and distilled water, successively, in an ultrasonic bath for 10 minutes. Then, substrates were dried in oven at 70°C for one hour.

Sensors fabrication by ultrasonic spray deposition

About 50 mL from the prepared Ppy solutions were put in the pulverization flask, which is in turn placed in the ultrasonic bath, just above the transducer (see Figure 1). Compressed air, with 500 cc/min flow rate, en-

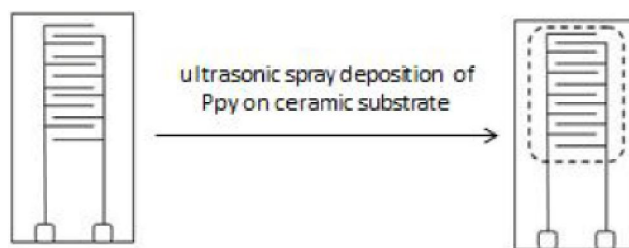


Figure 2 : Schematic view of the interdigitated sensors substrates

ters the flask inlet, carries the generated Polypyrrole mist and exits from the outlet of the flask into the glass nozzle, and finally to the heated substrate. A temperature of about 100°C was found to give the best results. The deposition time was fixed at 15 min for all sensors. In the following, we will denote each sensor by (Sx-y) where x indicates the molar ratio, and y the polymerization time.

Characterization and gas sensitivity measurement

Electrical conductivity measurement of Ppy powder pellets was done by using standard four probe method (SIGNATONE) equipped with (KEITHLEY 617 programmable electrometer), and (KEITHLEY 220 programmable current source). Thin pellets were prepared from Ppy powder using a stainless steel mold with 1 cm diameter and 10 tons pressure.

The structural characterization of Ppy with SDBS was obtained by using (Philips, X'pert), X-ray powder diffractometer XRD with Cu K α emission ($\lambda = 1.54187$ Å). Diffraction patterns were collected between 10° and 70° in 2 θ . FTIR spectra were obtained by (Bruker, Vector 22 spectrometer) in transmission mode, by scraping a little amount from the deposited Ppy film (af-

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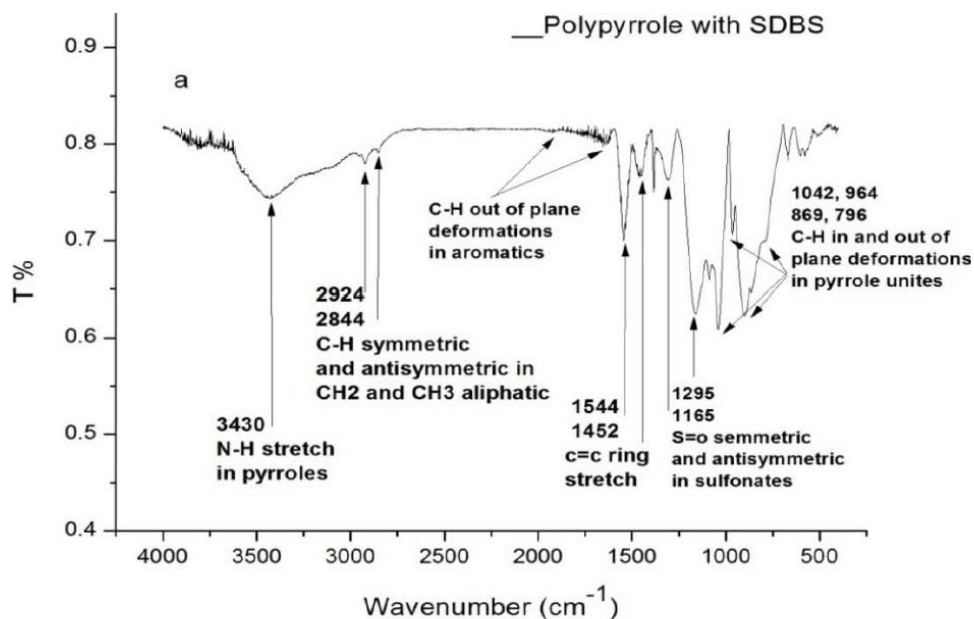


Figure 3 : Infrared transmission spectrum (FTIR) of Polypyrrole with SDBS

ter washing in DI water ethanol, and methanol successively) and mixing with KBr (Merck), the mixture was crushed and mixed in a mortar, and compressed into pellet. Morphology measurement was obtained by SEM (Scanning Electron Microscope) (VEGAI TESCAN) with (LVSTD) detector. Gas sensitivity measurements at different concentrations of methanol, and ethanol for each sensor were made in a known volume chamber equipped with a measurement system consisting of dual display multimeter (FLUKE 45) connected to a computer for measuring sensor resistance^[9].

RESULTS AND DISCUSSIONS

FTIR spectrum

IR spectrum of prepared Ppy in transmission mode was recorded between (500-4000) cm^{-1} , and shown in Figure 3. The peak at 3430 cm^{-1} belongs to N-H stretching vibration, two small peaks at 2924 cm^{-1} and 2844 cm^{-1} refer to the C-H symmetric and antisymmetric in both CH₂, and CH₃ aliphatic, C-H out of plane deformations were observed approximately at the region between 1600 cm^{-1} , and 2100 cm^{-1} , followed by 1544 cm^{-1} , and 1452 cm^{-1} assigned to the C=C ring stretching that is responsible of the conductivity of the material. Peaks at 1295 cm^{-1} , and 1165 cm^{-1} refer to S=O symmetric and antisymmetric in sulfonates which confirms the SDBS presence. The four peaks at

(1042, 964, 869, and 796) cm^{-1} indicate the C-H in plane, and out of plane deformations in Pyrrole units. This spectrum is in well agreement with published results^[10,11,12].

Electrical conductivity

Variation of synthesized Polypyrrole conductivity with molar ratios shown in Figure 4. A linear relation is observed in the studied range; the conductivity had its highest value (0.62 S/cm) at [Mo]/[ox] = 3, and decrease gradually by the increment of molar ratio until reaching the lowest value (0.035 S/cm) at [Mo]/[ox] = 10. This could be related to the decrease of the polymer doping level, as FeCl₃ acts as a dopant through Cl⁻, in addition to its oxidant role^[13].

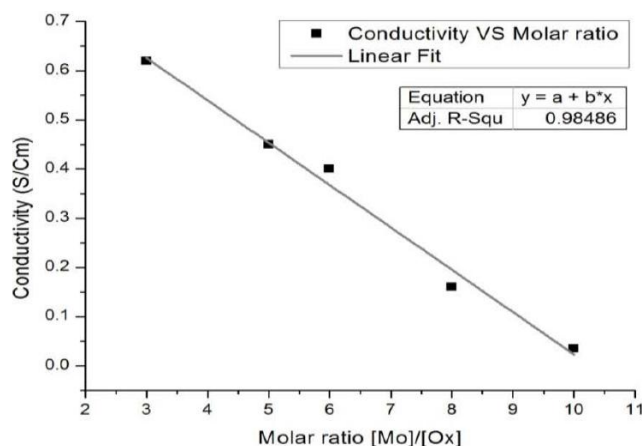


Figure 4 : Conductivity of polypyrrole with SDBS at different [Mo]/[Ox]

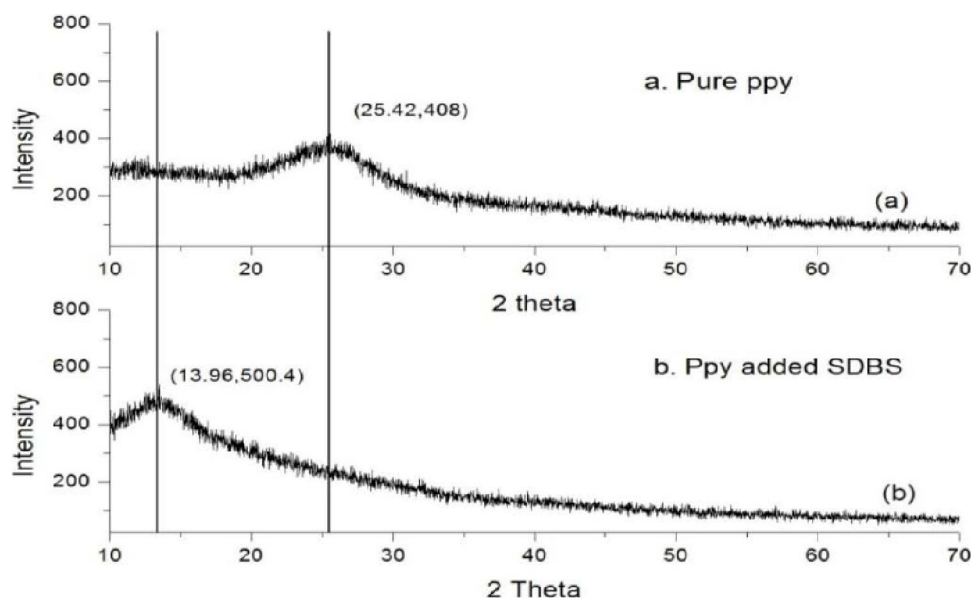


Figure 5 : XRD diffraction patterns of Polypyrrole: a. pure Ppy, b. Ppy with SDBS, [Mo]/[ox] = 6

TABLE 1 : Comparison of d-spacing between the pure and added SDBS one, [Mo]/[ox] = 6

Polypyrrole	2θ (Rad)	d-spacing (Å°)
Pure Ppy	25.42	3.504
Ppy /SDBS	13.96	6.344

XRD

X-ray diffraction patterns for pure Polypyrrole and that with SDBS, [Mo]/[ox] = 6 in both cases, are shown in Figure 5. We observe a shift of diffraction peak angle of Ppy with SDBS of about ($2\theta = 11.46^\circ$), relatively to pure Ppy^[14], indicating that SDBS acted as a spacer between the conducting polymer chains (interlayer spacing), and induced a very high d-spacing comparing to the pure one. The d-spacing was calculated from Bragg's equation (1)^[4], and the results are shown in TABLE 1.

$$n \cdot \lambda = 2d \cdot \sin \theta \quad (1)$$

This difference of d-spacing highlights the impact of the surfactant, and explains in part the great increment of solubility, due to its high steric effects between the chains during their formation.

Peaks positions and d-spacings for each molar ratio [Mo]/[Ox] were calculated and plotted in Figure 6. We observed a decrease of d-spacings with the increment of the oxidant (decrease of monomer/oxidant ratio). This could be explained by the increase of the oxidation intensity of polymerization reaction, which de-

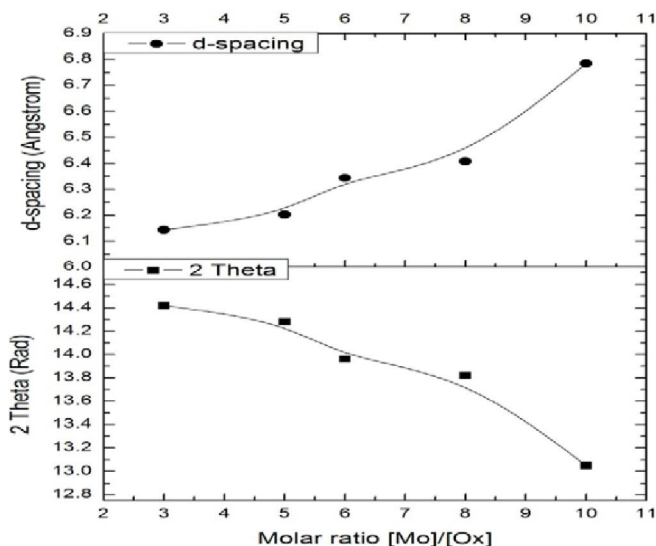


Figure 6 : Effect of molar ratio on XRD diffraction peaks positions and d-spacings

TABLE 2 : Experimental conditions used in fabrication of tested sensors

sensor	[Mo]/[Ox]	Polymerization time
S3-1	3	1
S3-24	3	24
S3-45	3	45
S5-1	5	1
S5-24	5	24
S5-45	5	45
S6-1	6	1
S6-24	6	24
S6-45	6	45

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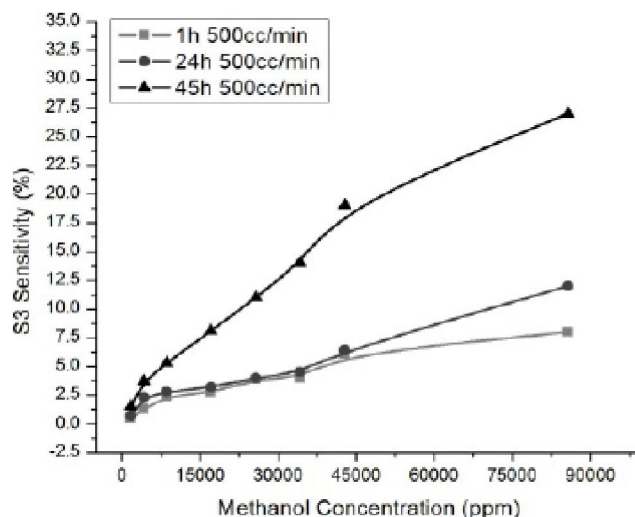
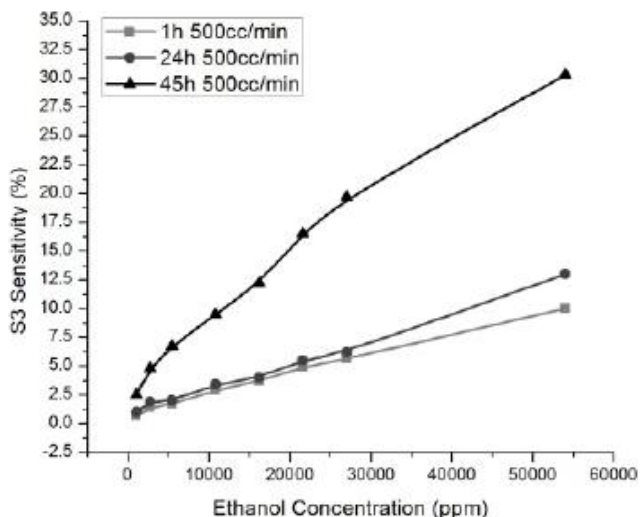


Figure 7 : Sensitivities of sensors S3, seriestowards ethanol, and methanol

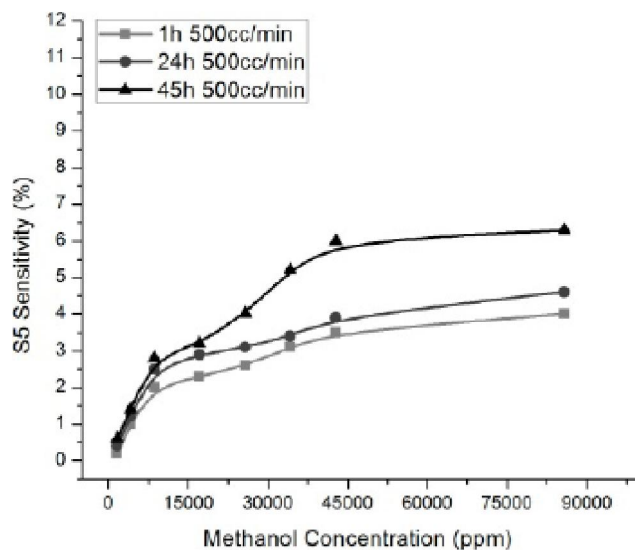
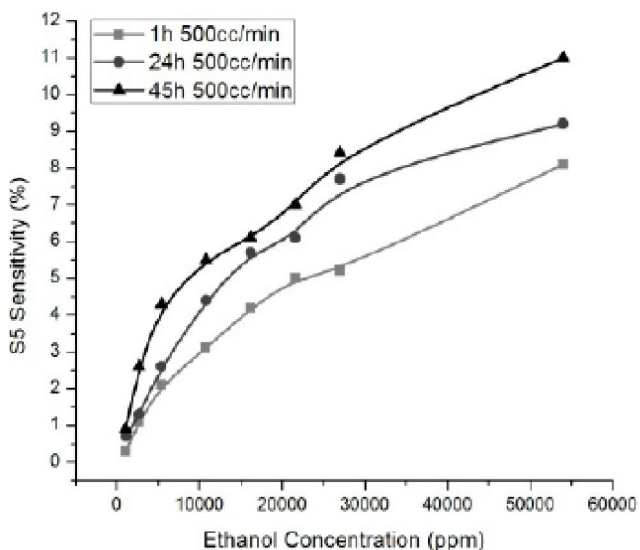


Figure 8 : Sensitivities of sensors S5 seriestowards ethanol, and methanol

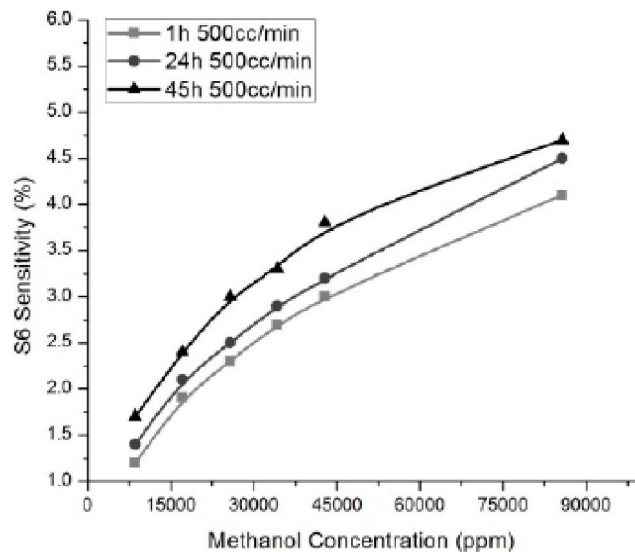
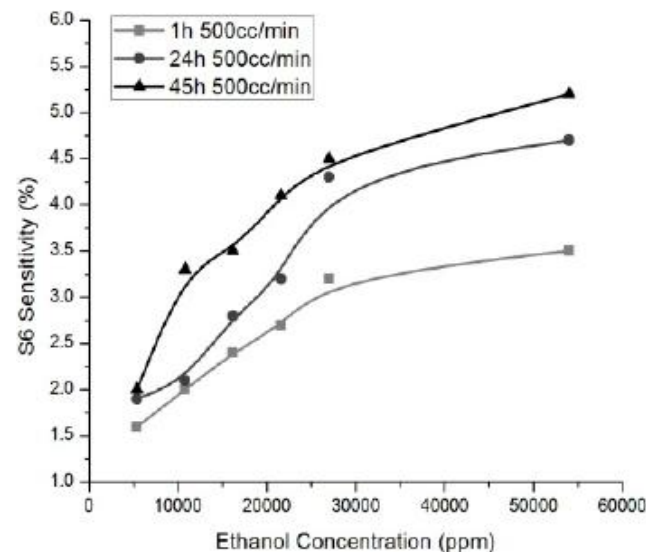


Figure 9 : Sensitivities of sensors S6 seriestowards ethanol, and methanol

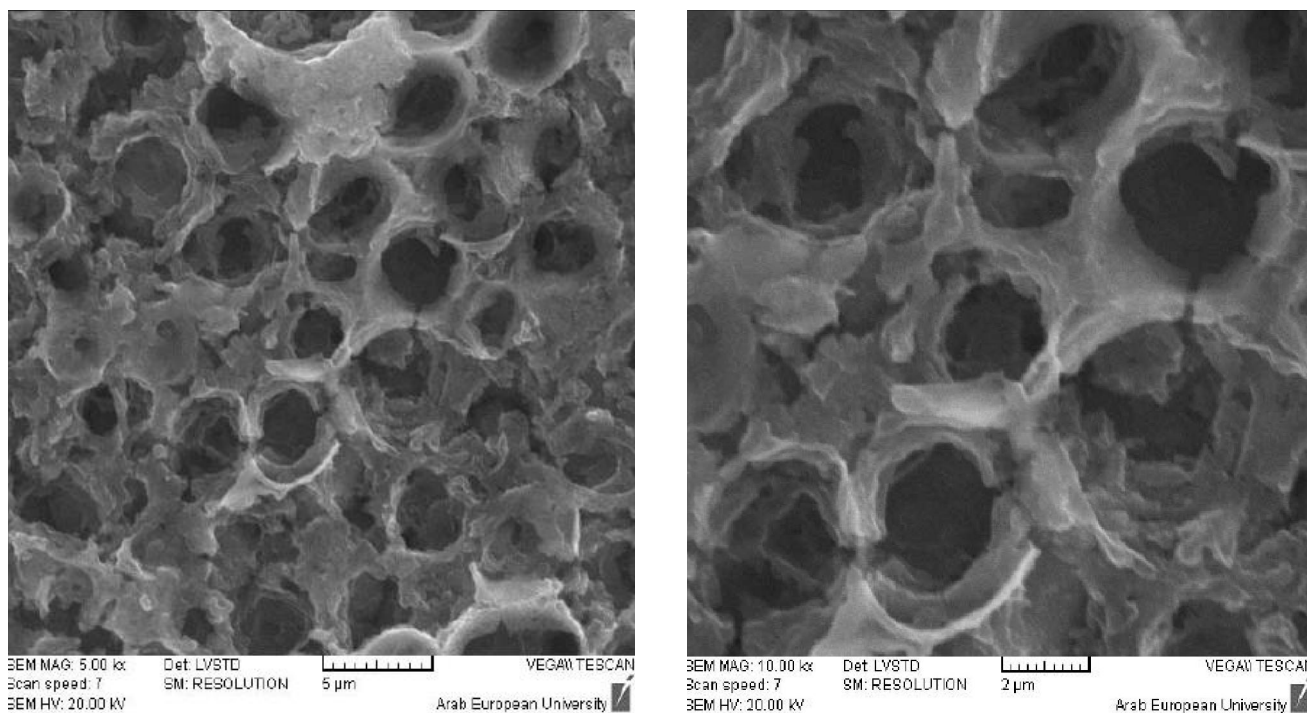


Figure 10 : SEM morphology of Ppyfilm deposited by ultrasonic spray technique after 1 h polymerization time (S3-1)

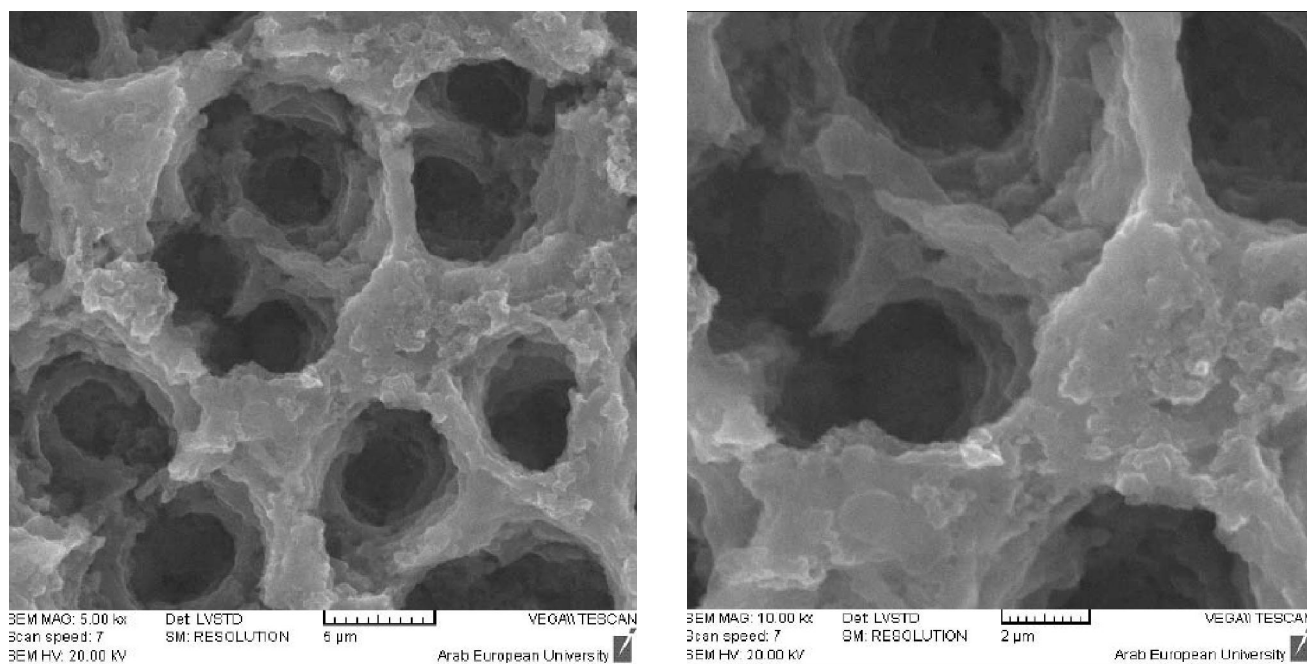


Figure 11 : SEM morphology of Ppyfilm deposited by ultrasonic spray technique after 24 h polymerization time (S3-24)

feats the effect of spacer and reduces the distance between chains.

Gas sensitivity

The percentagesensitivity S of Ppy sensors upon exposure to methanol, and ethanol vapors was calculated from relation (2):

$$S(\%) = [(R_v - R_0)/R_0] * 100 \quad (2)$$

Where R_0 is the initial sensor resistance, R_v is the sensor resistance after exposing to the target vapor^[15]. Three series of sensors (S3, S5 and S6) were studied, each corresponds to a predefined monomer to oxidant ratio namely 3, 5 and 6. Sensors of high molar ratios S8 and S10 were excluded, because of their sensitivity

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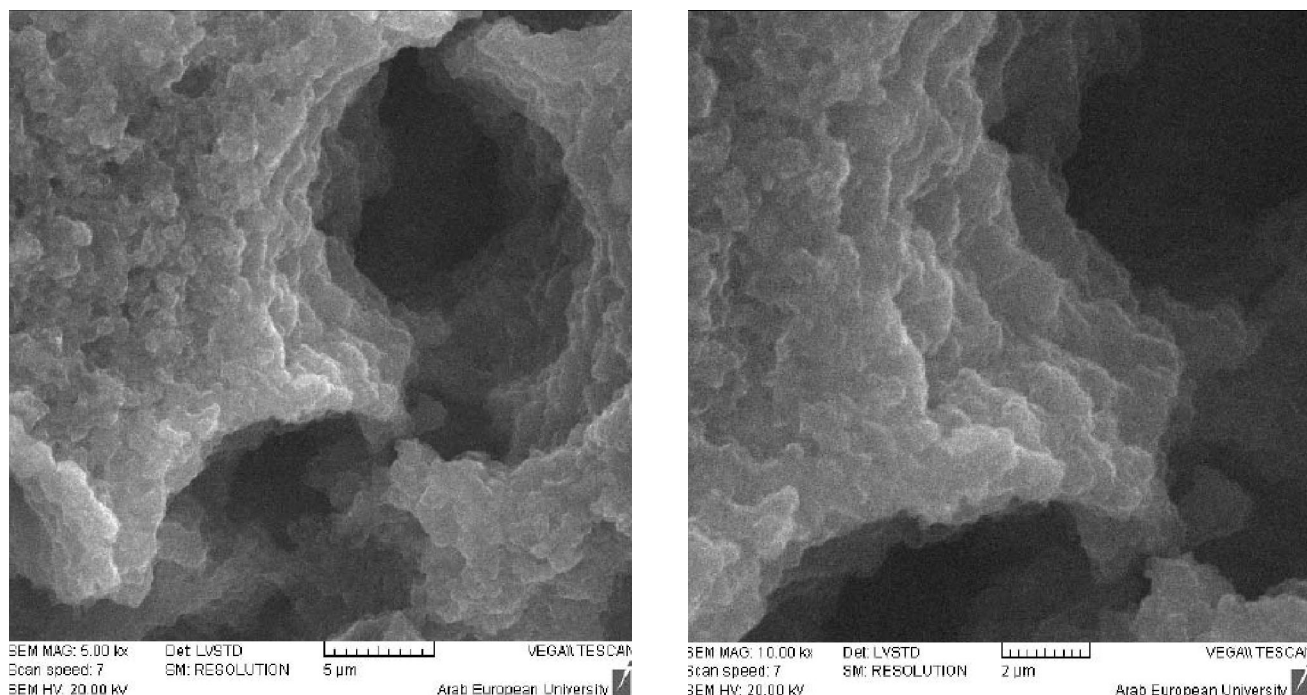


Figure 12 : SEM morphology of Ppyfilm deposited by ultrasonic spray technique after 45 h polymerization time (S3-45)

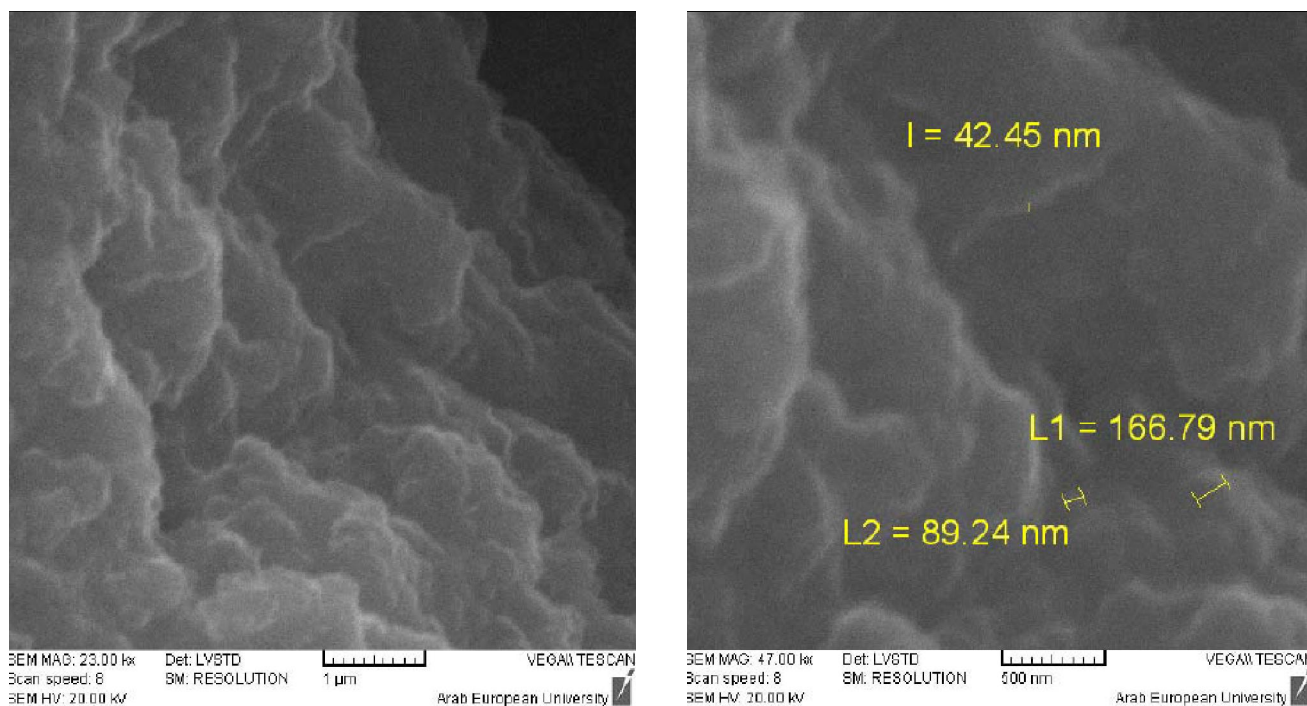


Figure 13 : SEM morphology of Ppy nano-flakes located at the internal surfaces of the tubular pores for 45 h reaction time (S3-45)

instability, may be due to their low conductivity. Each series include three different polymerization times, namely 1h, 24h and 45h. TABLE 2 summarizes the experimental conditions used in fabrication of tested sensors.

Figures (7-9) show sensitivities of these sensors as

a function of methanol and ethanol concentrations. In all sensors, the sensitivity increases with analyte concentration, with a trend to saturation. Moreover, sensitivity to methanol and ethanol increased steadily with the increasing of molar ratio, and also with the increasing of polymerization time. The S3 series sensors

showed the highest sensitivity, and among them S3-45 (45 h polymerization time) had the highest one. Changes in sensitivity with the polymerization times were attributed to morphological factors related to surface area, and porosity, as will be discussed in the next paragraph. Also, for all sensors the sensitivity toward ethanol is higher than methanol, this could be attributed to the higher volatility of methanol, leading to a lower concentration in the polymer^[16].

SEM

Morphology of Ppy films prepared with different polymerization times were examined by (SEM); for S3 series sensors ([Mo]/[Ox]=3), the results are shown in Figures (10-13). All films possess high porosity, with pores diameter of about 2 μm , which enhance sensor sensitivity, as it increases the specific area of the interaction surface. Stratified layers inside the tubular pores are observed, which are similar to thin flakes with nano dimensions of about 42 nm, and granules of about 90 nm. This leads to an increase of area-to-volume ratio, and could explain sensitivity improvement with polymerization times increase.

CONCLUSIONS

We have demonstrated the feasibility of nanostructure films by a homemade ultrasonic spray setup, from soluble Polypyrrole with SDBS surfactant, and synthesized by chemical oxidation polymerization. It's showed that addition of SDBS leads to an increase of the interchain spacing, so enhancing Polypyrrole solubility. Impact of molar ratio of Pyrrole monomer to FeCl_3 oxidant, and polymerization time on sensitivity toward methanol and ethanol were studied. Improvement of sensitivity was correlated with the morphology of the obtained films, as demonstrated by SEM. Best results were obtained for sensors made from a molar ratio of 3, and 45 h polymerization time.

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