

Accepted Manuscript

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PII: S0925-4005(16)30710-9
DOI: <http://dx.doi.org/doi:10.1016/j.snb.2016.05.034>
Reference: SNB 20193

To appear in: *Sensors and Actuators B*

Received date: 19-1-2016
Revised date: 28-4-2016
Accepted date: 6-5-2016

Please cite this article as: Alireza Akbarinejad, Arash Ghoorchian, Mahdie Kamalabadi, Naader Alizadeh, Electrospun soluble conductive polypyrrole nanoparticles for fabrication of highly selective n-butylamine gas sensor, *Sensors and Actuators B: Chemical* <http://dx.doi.org/10.1016/j.snb.2016.05.034>

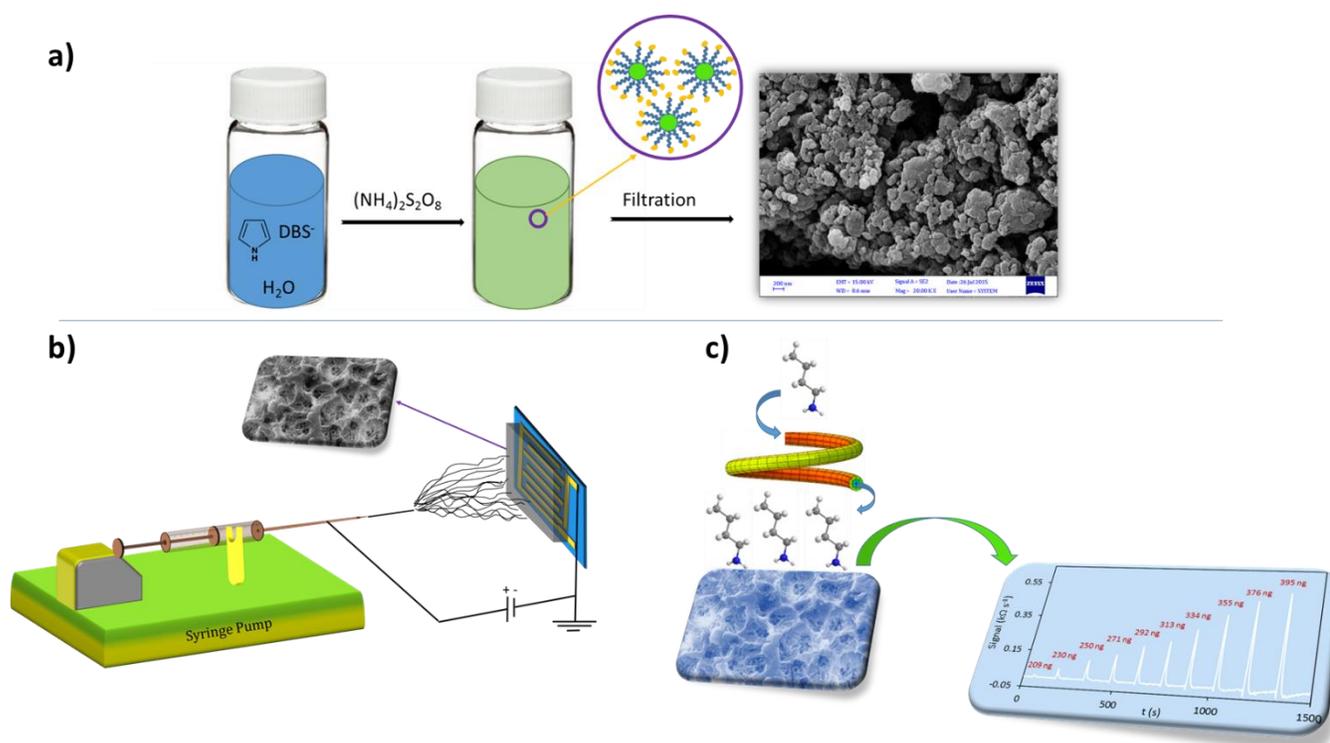
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Electrospun soluble conductive polypyrrole nanoparticles for fabrication of highly selective n-butylamine gas sensor

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Graphical abstract:



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Highlights

- Soluble polypyrrole nanoparticles (SPNs) were chemically synthesized.
- SPNs stabilized electrostatically based on dodecylbenzenesulfonate DBS⁻.
- SPNs were coated onto Cu-IDEs using electrospinning (ES) technique.
- The ES polypyrrole film is highly selective and sensitive to n-butylamine.

ABSTRACT

A three-dimensional and highly porous polypyrrole (PPy) film was successfully coated onto a copper interdigital electrode (Cu-IDE) surface by electrospinning of soluble PPy nanoparticles. The chemical composition of PPy nanoparticles was analyzed using X-ray photoelectron spectroscopy (XPS) and fourier transform infrared spectroscopy (FT-IR). The Brunauer–Emmett–Teller (BET) analysis confirmed the porous nature of PPy nanoparticles. The field emission scanning electron microscopy (FE-SEM) images of polymer coated Cu-IDE revealed that PPy nanoparticles were assembled by electrical forces to form an outstanding honeycomb-like architecture. As a proof-of-concept demonstration of the functional properties of the electrospun PPy (Es-PPy) film, the polymer coated Cu-IDE was investigated as a sensing device for gas sensor. The as-prepared Es-PPy film proved to be a viable aliphatic amines sensing material with large response, low detection limit, fast response and good repeatability at a low operating temperature of 150°C. Moreover, the sensor demonstrated an extremely high sensitivity and selectivity to n-butylamine. The calibration sensitivity to n-butylamine is up to three orders of magnitude higher than that of other common aliphatic amines. The detection limit and linear range for determination of n-butylamine were 0.42 ppm and 10.54-21.08 ppm, respectively. Es-PPy gas sensor exhibited

good repeatability with $RSD \leq 8\%$ at temperature ranges 90-200°C. The response of the Es-PPy sensor to n-butylamine was compared with electrochemically and drop coated sensors and found that it has an extremely higher response. Finally, the Es-PPy gas sensor was successfully applied to real well water sample analysis.

Key words: Polypyrrole nanoparticles, Soluble conducting polymer, Electrospinning, Gas sensor, Aliphatic amines.

1. Introduction

Chemiresistor gas sensors are in great demand for their potential in determination of harmful agents [1-3]. Metal-oxide semiconductors have been widely used as active materials for construction of chemiresistor gas sensors [4]. However, poor selectivity and high operating temperatures are two significant drawbacks of metal-oxide based gas sensors. To improve the performance, scientists have developed gas sensors based on other sensing materials such as metal–organic frameworks [5, 6], carbon materials [7], polymer compounds [8, 9], zeolites [6, 10], ionic liquids [11] as well as mixed systems [12-14]. Conductive polymers are a class of macromolecules, known by high electrical conductivity along their polymeric chains [15, 16]. In the recent years there have been increasing interest on the applications of conductive polymers as sensing materials for the preparation of gas sensors [17-19]. This class of conducting materials offer many advantages including: low cost, easy preparation, ready modulation of their sensing properties by varying their chemical structure, and being able to operate at low temperatures [20]. Polypyrrole (PPy) is a heterocyclic conductive polymer which has considerable potential to be used as a gas sensor material due to its high conductivity and environmental stability [21]. Moreover pyrrole monomer could be polymerized into highly porous PPy films by a number of

various methods. The high porosity of these polymeric films provide an extremely high sensing surface, giving rise to improved performance in sensing applications. Both chemical and electrochemical polymerization routes have been applied to deposit porous films of PPy on gas sensor substrates. Single PPy nanowires have been synthesized by chemical polymerization inside SiO₂ coated alumina membranes [22]. The template directed PPy nanowires were used to selectively detect gaseous ammonia at a concentration level as low as 40 ppm. In the other work PPy nanotubes have been chemically fabricated in sodium bis(2-ethylhexyl) sulfosuccinate reverse microemulsions [23]. It has been shown that the electrical response of PPy nanotubes to NH₃ vapor depends on nanotubes diameters. Electrochemical polymerization could be used to prepare PPy nanostructures without utilizing any templates. In our previous work, a 3-dimensional network of PPy with honeycomb-like shape was fabricated by constant current electrodeposition on Au interdigital electrodes in the presence of anionic dopants [24]. The nano-structured PPy gas sensor was applied for selective determination of methanol in the biodiesel samples. Al-Mashat et al reported fabrication of PPy nanowires through template-free electropolymerization in the presence of Na₂HPO₄, and LiClO₄ and applied it as a hydrogen gas sensor [25]. It has been proposed that O₂ nano bubbles formed at the electrode surface prevent the PPy overoxidation by hydroxyl radicals and allows the electropolymerization of pyrrole monomer into polymer nanowires [26, 27]. In the all aforementioned methods the structure formation of PPy occurs along with polymerization process.

Electrospinning is a long-known technique which employs polymeric solutions or molten polymers to form nanostructured materials [28]. The strong electrical field generated by a high-voltage power supply produces electrically charged jets from polymer fluid streams. As the electrified jet of polymer travels toward the collector, it undergoes stretching and drying processes,

leading to formation of highly porous polymeric films. Electrospinning has attracted a lot of interest for its capability to produce nanostructured materials from a wide range of polymers [29, 30]. Although electrospinning has successfully applied to many types of polymer materials, it remains a great challenge to apply electrospinning to the most conducting polymers such as PPy due to their poor solubility. Most of the reports about electrospinning of PPy use other spinnable polymers as fiber forming materials [31, 32].

Several analytical methods have been developed to determine aliphatic amines. Common methods are chromatography [33] and spectroscopic [34] methods. These methods suffer from disadvantages such as lack of specificity, sensitivity and time consuming (in the case of GC and HPLC methods). Although some modifications such as derivatization have been developed to increase the sensitivity and specially deactivation of column, but these steps increases the time consumption and this drawback is still remained [35]. The gas sensors based on conducting polymers are one of the distinguished candidates (sensitive, fast and low-cost) for aliphatic amines determination [36].

Herein, we have synthesized soluble PPy nanoparticles and used them to coat homogeneous films of PPy on the surface of Cu-IDE via electrospinning method. The electrospun PPy film was used for sensing of aliphatic amines in gas phase. The synthesis, coating and gas sensing application of PPy nanoparticles are presented in Scheme 1a-c. The developed gas sensor shows remarkable sensitivity, very good selectivity, fast response and good repeatability toward n-butylamine vapors at a low operating temperature. Finally, the Es-PPy gas sensor was applied to real well water sample by using dispersive liquid-liquid micro extraction (DLLME) technique.

Scheme 1

2. Experimental

2.1. Reagents

Pyrrole (Fluka, Switzerland) was distilled and stored in a refrigerator in dark prior to use. Allylamine, diallylamine, triethylamine, diethylamine, n-butylamine, dibutylamine, tributylamine, chloroform, acetone, n-hexane, nitromethane, acetonitrile, THF, ethylacetate, toluene, dichloromethane, 2-propanol, 1-propanol, ethanol, methanol, calcium chloride dehydrate, ammonium persulfate, sodium dodecylbenzenesulfonate and sodium hydroxide were purchased from Merck or Fluka. All chemicals (except for pyrrole) were of analytical reagent grade and used without purification.

2.2. Synthesis of soluble PPy nanoparticles

Soluble PPy nanoparticles were prepared as described by our previous work [37]. The detailed synthesis process was as follows. First, SDBS (2.9 mmol) was added to 35 mL of distilled water and stirred magnetically at 3°C. Freshly distilled pyrrole monomer (2.9 mmol) was then added to the above solution dropwise and the obtained mixture was stirred for 5 min. The polymerization reaction was initiated by dropwise adding of a precooled aqueous solution of APS (2.9 mmol in 5 mL distilled water) into the above mixture under magnetic stirring. The stirring was continued for 5 h at 3°C. Then the reaction mixture was mixed with 5 mL methanol to terminate the polymerization reaction. The resulting polymeric particles were then filtered and purified by washing with distilled water several times. Finally, the black-colored PPy particles were dried for 24 h prior to further analysis.

2.3. Fabrication of gas sensor by electrospinning

In order to prepare electrospinning solution 80 mg of the black polymer powder was added to 20 mL chloroform, sonicated for 10 min and then filtered to separate aggregated insoluble particles. Then, solvent was evaporated to give a final volume of 0.5 mL. The concentrated PPy solution was loaded into a 2.5 mL syringe equipped with a metal needle. The syringe was then located in a syringe pump, providing a steady flow rate of 1 mL h⁻¹. A Cu-IDE was connected to ground potential and used as the collector. The Cu-IDE collector was placed perpendicular to the syringe needle at a distance of 8 cm. The electrospinning deposition of PPy film was performed by applying a 5 kV positive potential to the syringe needle for 15 min. Video 1 in the Supporting Information shows step-by-step deposition of PPy film on the Cu-IDE surface. The reproducibility of electrospinning coating was tested with the measuring mass loading of polymer on surface of IDEs by weighting 10 IDEs before and after coating in the same experimental conditions and found that average of the mass loading is 1.69 ± 0.13 mg PPy on its surface (RSD < 8%)

2.4. Gas sensing measurements

The Es-PPy gas sensor was put in an aluminum chamber with dimensions of 40 × 60 × 30 mm. Gas sensing properties of Es-PPy film toward aliphatic amines were studied using a test station system (Shimadzu GC-4C). The target materials were evaporated in the injection port and transferred into the sensing chamber through a steel tube (without coating, 2 mm i.d, 100 cm length) by using nitrogen carrier gas at a flow rate of 40 mL min⁻¹. A sensor was directly connected

to the outlet of the steel tube. The injector and sensor temperatures were both set at 150°C during the measurements. The first derivation of resistogram was plotted (dR/dt) and peak height was measured as signal of the gas sensor. The stock solutions of each amine were prepared by dissolving or diluting the standards in n-hexane. The stock solutions were repeatedly diluted to prepare different concentration levels.

2.5. Characterization

X-ray photoelectron spectroscopy (XPS) analysis was performed on PPy nanoparticles using an ESCA Lab220I-XL spectrometer with Al K α X-ray radiation source ($h\nu=1486.6$ eV), operating at a vacuum $< 10^{-7}$ Pa. FT-IR spectrum of PPy nanoparticles was obtained in the 4000–400 cm^{-1} range using a Nicolet 100 FT-IR spectrometer. The BET surface area, total pore volume and average pore diameter were obtained using a BELSORP-mini 2 (BEL Japan). The surface morphology of the polymer coated Cu-IDEs were investigated on a Hitachi FE-SEM system model S-4160.

3. Results and discussion

3.1. Chemical composition and morphology analysis

The chemical composition of the synthesized PPy nanoparticles was studied using XPS and FT-IR spectroscopies. Fig. 1a displays a survey photoelectron spectrum, indicating the elemental composition. The N1s peak at binding energy of 402.0 eV is attributed to the nitrogen of pyrrole.

It can be decomposed into three components occurring at binding energies of 400.5, 402.5 and 403.5 eV which are assigned to neutral NH (amine) in the pyrrole ring and two positively charged amine species in the form of polarons and bipolarons, respectively (Fig. 1b) [38]. The incorporation of dodecyl benzene sulphonate (DBS⁻) anions into the PPy backbone is evident from the S2p peak at 170.0 eV. This peak has been deconvoluted into two components centered at 168.5 eV and 170.2 eV (Fig. 1c). The peak at 168.5 eV is assigned to the SO₃⁻ group of DBS⁻ anion while the peak at 170.2 eV is attributed to an oxidized form of SO₃⁻ [39, 40]. The C1s and O1s lines at binding energies of 285.0 and 533.0 eV originate from both polymer and surfactant molecules. The high resolution C1s spectrum exhibits the presence of four distinct peaks attributed to aromatic carbon atoms of DBS⁻ (283.5 eV), aliphatic carbons of DBS⁻ and β-carbons of pyrrole ring (285.0 eV), α-carbons of the pyrrole ring (286.1 eV) and the C-O or C=O bonds in the PPy structure (287.9 eV), respectively (Fig. 1d) [39]. The O1s spectrum has two components (Fig. 1e). The component at 532.0 eV derives from SO₃⁻ group of DBS⁻ and the other component at 533.7 eV corresponds to C-O species, respectively.

The FT-IR spectrum of PPy nanoparticles confirms the XPS results (Fig. S1). The peaks at 1555 and 1637 cm⁻¹ correspond to the fundamental symmetric and antisymmetric ring-stretching modes, respectively [41]. The peaks at 1039 and 1323 cm⁻¹ are attributed to the C-H and C-N in-plane deformation vibrations, respectively [42]. The broad band occurring at 3000-3700 cm⁻¹ is assigned to N-H and C-H stretching vibrations [43]. The peak at 1177 cm⁻¹ is representative of a S=O stretching vibration of sulfonate anion [44], confirming that surfactant molecules enter the polymer structure during synthesis process and compensate the positive charges of the PPy chains.

Fig. 1

Analysis of the porosity of PPy nanoparticles showed a type IV isotherm with a BET surface area of $114.80 \text{ m}^2 \text{ g}^{-1}$ which confirms the mesoporous structure of nanoparticles (Fig. 2). The total pore volume and average pore diameter of the PPy nanoparticles were calculated from Barrett–Joyner–Halender (BJH) method and found to be: $0.39 \text{ cm}^3 \text{ g}^{-1}$ and 2.31 nm , respectively, indicating the porous nature of polymer nanoparticles.

Fig. 2

The surface morphology of the gas sensor prepared via electrospinning was studied using FE-SEM, as shown in Fig. 3. The gas sensor consists of a three-dimensional network of Es-PPy with honeycomb-like shape which provides a highly porous microstructure. The highly porous structure of PPy film provides a large surface area which allows ready access of the analytes to the sensing surface.

Fig. 3

3.2. Response behaviour of Es-PPy film

We tested the response behaviour of Es-PPy gas sensor to the presence of different volatile aliphatic amines, and examined the corresponding selectivity of the response of the sensor to the given compounds. When the vapors of amines were introduced into the test station system the sensor resistance increased fast and a plateau response was achieved (Fig. S2). The first derivation of the resistogram (dR/dt vs. the time) was plotted and peak height was measured as the gas sensor signal (Fig. 4). As it can be seen well-defined peaks for all aliphatic amines were obtained by applying derivation on the resistogram.

To investigate if the vapors of other volatile organic compounds (VOCs) can alter the sensor resistance, we examined the response of the sensor to a wide variety of VOCs. Fig. S3 compares

the response of the Es-PPy gas sensor to 15.80 ppm of n-butylamine, 2630 ppm of other aliphatic amines and 10520 ppm of each VOCs. As the results show, the response of the gas sensor to the tested compounds is different. No significant change in the sensor resistance was obtained upon injection of large amounts of each VOCs. Moreover, of all the aliphatic amines tested the Es-PPy gas sensor gives the most sensitive response to n-butylamine, indicating that the sensor has a remarkable potential for the selective detection of this compound.

Fig. 4

The response of Es-PPy gas sensor to different amounts of n-butylamine and the corresponding calibration curve are shown in Fig. 5a and 5b. The calibration curve of Es-PPy gas sensor to different concentrations of seven aliphatic amines has been shown in Fig. 5c on a logarithmic mass scale. The detection limit (DL), linear range (LR), calibration sensitivity (CS) and correlation coefficient (R^2) of Es-PPy gas sensor to aliphatic amines are summarized in Table 1. The detection limit of the Es-PPy sensor, which was calculated as the amount gives a reading equal to three times the standard deviation of background signals, $3\sigma_{blank}$, was estimated as follows:

$$DL = \frac{3\sigma_{blank}}{CS} \quad (1)$$

Where the calibration sensitivity (CS) is the slope of the calibration curve. The detection limit of PPy sensor was found to decrease in the following order: diallylamine > allylamine \approx tributylamine > dibutylamine > triethylamine > diethylamine \gg n-butylamine. It is obvious that the Es-PPy sensor exhibits the lowest detection limit to n-butylamine (0.42 ppm). The calibration graph for n-butylamine is linear in the range of 10.54-21.08 ppm with $R^2 \geq 0.99$. The selectivity coefficient of Es-PPy gas sensor to the aliphatic amines (S_{Es-PPy}) was calculated from equation (2):

$$S_{Es-PPy} = \frac{CS_{RNH_2}}{CS_{n-butylamine}} \quad (2)$$

The value of S_{Es-PPy} is greater for n-butylamine which indicates that the Es-PPy gas sensor has higher selectivity for n-butylamine compared to the other aliphatic amines.

Fig. 5

The repeatability of the response of Es-PPy gas sensor was investigated with a series of 9 repetitive injections for 13.17 ppm, 14.23 and 16.49 ppm of n-butylamine (Fig. S4). The response to 13.17 ppm, 14.23 and 16.49 ppm of n-butylamine exhibited good repeatability with relative standard deviations of 8%, 6% and 6%, respectively. The repeatability of Es-PPy gas sensor toward n-butylamine was also examined at injector and sensing temperatures of 90°C, 150°C and 200°C with 14.23 ppm of n-butylamine (Fig. 6). The results show that Es-PPy gas sensor offers good relative standard deviations of 7%, 6% and 7% at injector and sensing temperatures of 90°C, 150°C and 200°C, respectively.

Fig. 6

Table 1

We evaluated the possible application of air as the carries gas. We observed a significant decrease in the calibration sensitivity when air was applied as the carrier gas, which is consistent with our previous work [24]. The calibration curve for n-butylamine in air is linear in the range of 13.17-21.08 ppm with detection limit of 1.63 ppm. Fig. 7 indicates the response behaviour of Es-PPy gas sensor to n-butylamine vapors using air as the carrier gas.

Table 2 illustrates detection limits obtained from other gas sensors used for determination of n-butylamine. As the results show, the detection limit of Es-PPy sensor is comparable and in most cases even better than the other sensors developed for determination of n-butylamine [47-52].

Fig. 7

Table 2

3.3. Comparing the morphology and response of Es-PPy with drop coated and electrochemically prepared PPy gas sensors

The morphology and sensing behaviour of PPy depends on the deposition method. The FE-SEM images in Fig. 8 compare the morphology of Es-PPy sensor with drop and electrochemically coated sensors. The calibration sensitivities for Es-PPy, drop coated and electrochemically deposited sensors are 2.7756, 0.0040 and 0.0006 ($\text{k}\Omega \text{ s}^{-1} \mu\text{g}^{-1}$), respectively. The calibration sensitivity of Es-PPy sensor is about three times of magnitude higher than that of drop coated and electrochemically deposited sensors. The larger response of Es-PPy sensor presumably arises from the higher surface area of the electrospun PPy film. Besides the higher sensitivity, electrospinning offers other advantages over drop coating and electrochemical deposition methods. While electrospinning could be used to coat polymers onto both conducting and insulating surfaces, the substrate needs to be conducting and electrochemically inactive in electrochemical deposition method. Due to this limitation of electrochemical deposition method, usually noble metals such as Au and Pt are used as electrode or a passivation process is performed when using active metals such as Cu as electrode. On the other hand, the coatings obtained by drop coating method are not homogeneous enough and also have a weak adhesion to the surface.

Fig. 8

3.4. Sensing mechanism

The active sensing material of the gas sensor interacts with the analyte and causes the electrical resistance changes of the conducting polymer film. The interactions which lead to response in gas

sensors could be multiform, depending on the type of analytes and active materials. The first mechanism is the interaction of analyte with the charge carriers which may affect the sensor resistance through altering the mobility of polarons and bipolarons, changing the number of polarons and bipolarons by oxidizing or reducing the polymer structure and modifying the potential barrier for the hopping process of charge carriers between the polymer chains. The other mechanisms include the interaction of analyte with dopant molecules and inducing a change in the morphology of polymer film by the analyte [45].

In the present study, the most possible sensing mechanism is suggested to be a donor-acceptor process in which electron-donating amine molecules attach to the positively charged positions in the polymer structure according to the equation (3) and Fig. S5.



The interaction of amine molecules with the PPy film leads to a change in electrical state of polymer. This triggers a decrease in the number of charge-carriers and a subsequent rise in the resistance of the polymer.

3.5. Application of Es-PPy gas sensor to real sample analysis

The particular response of the Es-PPy gas sensor to n-butylamine makes it a favorable candidate for gas sensor applications to determine n-butylamine in real samples. To evaluate the applicability of the developed gas sensor toward real water sample analysis, experiments were performed on a well water sample (Tehran, Iran). DLLME method was applied for extraction and pre-

concentration of n-butylamine from aqueous solutions. Analysis was carried out under optimum conditions used in our previous work [46]. The optimum conditions were as follow: the sample pH: 13, chloroform and acetone as the extraction solvent and the disperser solvent, respectively, extraction solvent volume: 50 μL , disperser solvent volume: 1.5 mL.

A 5 mL of the sample solution adjusted to pH 13 was placed in a 10 mL screw cap glass tube with conical bottom. Then, a mixed solution of 50 μL chloroform (as the extraction solvent) and 1.5 mL acetone (as the disperser solvent) was rapidly injected into the sample and a cloudy solution was formed. In this step, n-butylamine was extracted into the fine droplets of chloroform. Then, the cloudy solution was centrifuged at 5000 rpm for 2 min and the upper aqueous phase was removed by a syringe. In order to remove the trace water residues, the sedimented phase was dried using calcium chloride. After this process, 2 μL of this sedimented phase was introduced to the sensor. By a standard addition method at concentration levels of 600 ng g^{-1} and 900 ng g^{-1} , n-butylamine was detected in the real sample and the content was found to be 195 ng g^{-1} . Satisfactory relative recoveries of 98% and 92% were achieved at the concentration levels of 600 ng g^{-1} and 900 ng g^{-1} , respectively.

4. Conclusions

In conclusion, we demonstrated a facile, cost effective and conventional electrospinning method for coating PPy nanoparticles onto Cu-IDE surface. FE-SEM analysis confirmed the deposition of a porous and three dimensional film of PPy with honeycomb-like morphology on the Cu-IDE surface. The potential application of Es-PPy film as a gas sensor material for different volatile aliphatic amines was investigated. The Es-PPy gas sensor exhibited a high sensitive, selective and

fast response with good repeatability to n-butylamine vapors at a low operating temperature of 150°C. The response behavior of Es-PPy sensor toward n-butylamine was also studied in air and found that it works well but with some reduction in sensor response. The response of Es-PPy sensor toward n-butylamine vapors was compared with drop coated and electrochemically deposited sensors and found that it has a response which is about three times of magnitude larger than that of other sensors. Furthermore, the applied electrospinning technique for the coating of PPy nanoparticles presents other advantages including: polymer nanoparticles could be easily coated onto IDEs made from active metals such as Cu without performing a passivation step, something that couldn't be achieved by electrochemical deposition method. Moreover, polymer films obtained by electrospinning have better homogeneity and more powerful adhesion to the surface than the ones obtained by drop coating method. Finally, the developed Es-PPy gas sensor was successfully applied to the analysis of a well water sample using DLLME method.

Acknowledgements

This work has been supported by grants from the Tarbiat Modares University Research Council and the Iran National Science Foundation (INSF) which are gratefully acknowledged.

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Biography



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Figure captions:

Fig. 1. XPS spectra of PPy nanoparticles: (a) Survey spectrum; (b) N1s spectrum; (c) S2p spectrum; (d) C1s spectrum; (e) O1s spectrum.

Fig. 2. N₂ adsorption isotherm of soluble PPy nanoparticles at 77 K. Inset: The BJH pore size distribution plot.

Fig. 3. FE-SEM images of Es-PPy film with different magnifications (a) 600; (b) 2500; (c) 30000.

Fig. 4. Response behaviour of Es-PPy gas sensor to 2630 ppm of different aliphatic amines and 15.80 ppm of n-butylamine. Conditions: carrier gas: N₂ with a flow rate of 40 mL min⁻¹, injector and sensing temperatures of 150°C.

Fig. 5. (a) Response transients of Es-PPy gas sensor to different concentrations of n-butylamine using N₂ as the carrier gas; (b) The changes in Es-PPy sensor response in terms of n-butylamine concentration; (c) The changes in Es-PPy gas sensor response in terms of log (ppm) of seven aliphatic amines.

Fig. 6. Repeatability of Es-PPy gas sensor upon exposure to 14.23 ppm n-butylamine at injector and sensing temperatures of a) 90°C, b) 150°C and c) 200°C using N₂ as the carrier gas.

Fig. 7. (a) Response transients of Es-PPy gas sensor to different concentrations of n-butylamine using air as the carrier gas; (b) The changes in Es-PPy gas sensor response in terms of n-butylamine concentration in gas phase.

Fig. 8. FE-SEM images of (a) Drop-coated sensor; (b) Electrochemically coated sensor [36]; (c) Es-PPy sensor.

Scheme. 1. (a) Synthesis procedure for the preparation of PPy nanoparticles; (b) Fabrication of gas sensor by coating PPy nanoparticles on the Cu-IDE surface using electrospinning method; (c) Application of electrospun PPy film as aliphatic amines gas sensor.

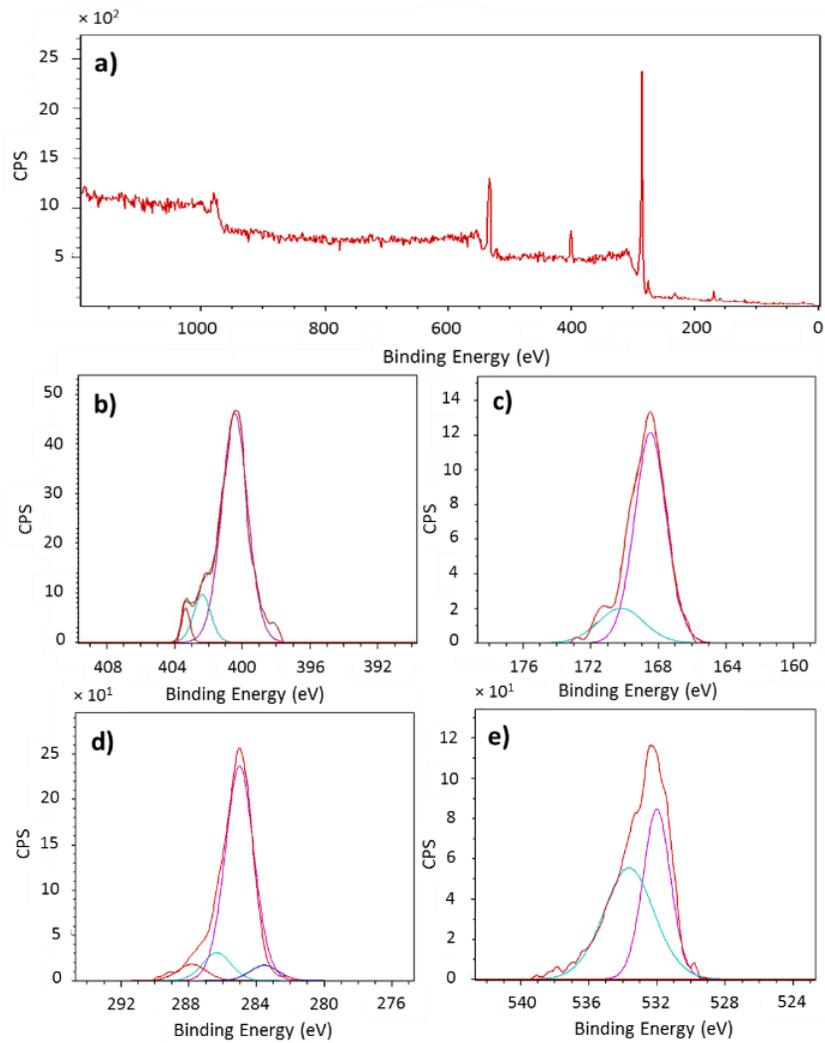


Fig. 1

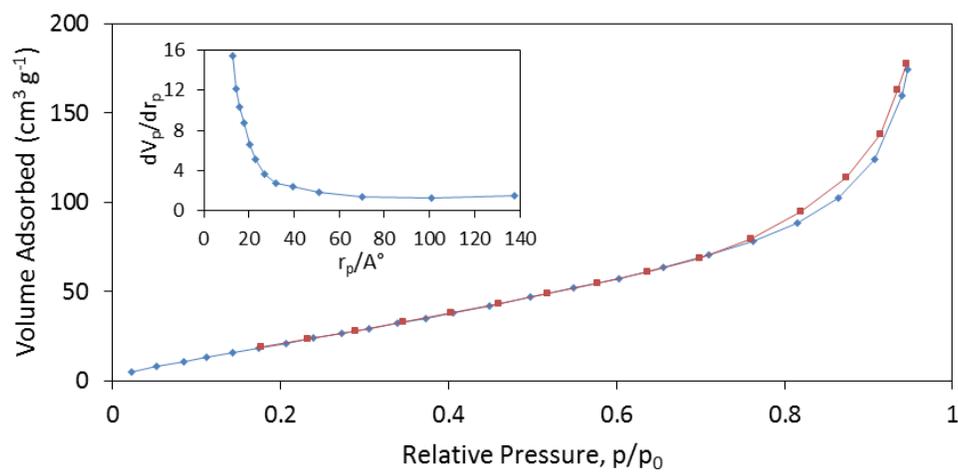


Fig. 2

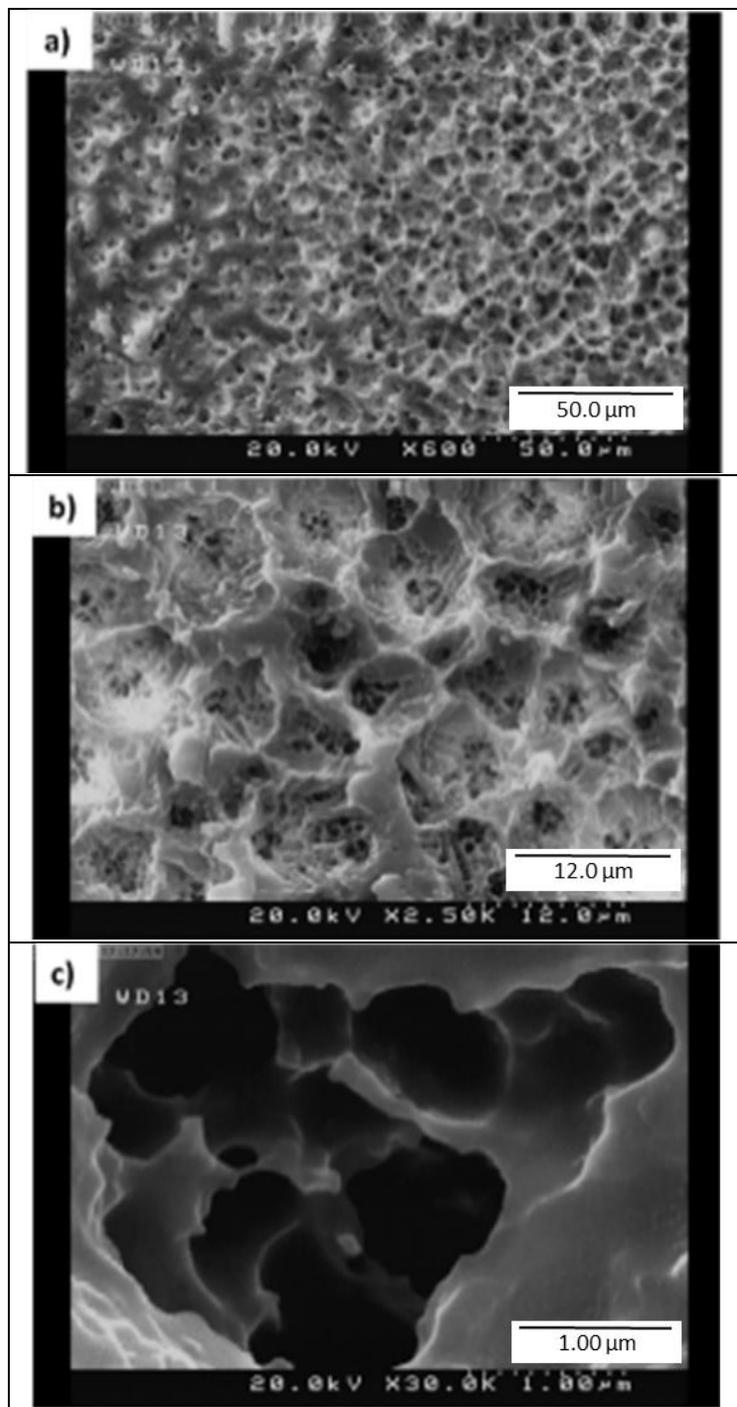


Fig. 3

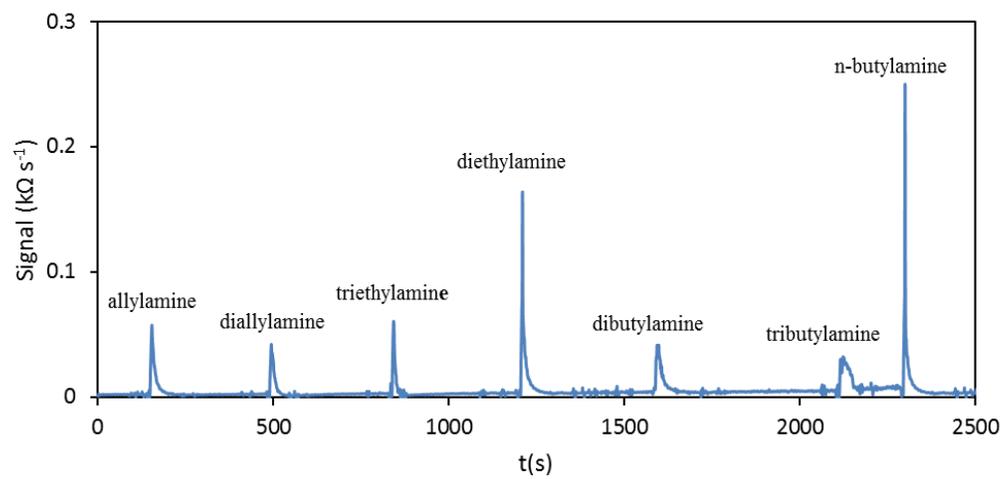


Fig. 4

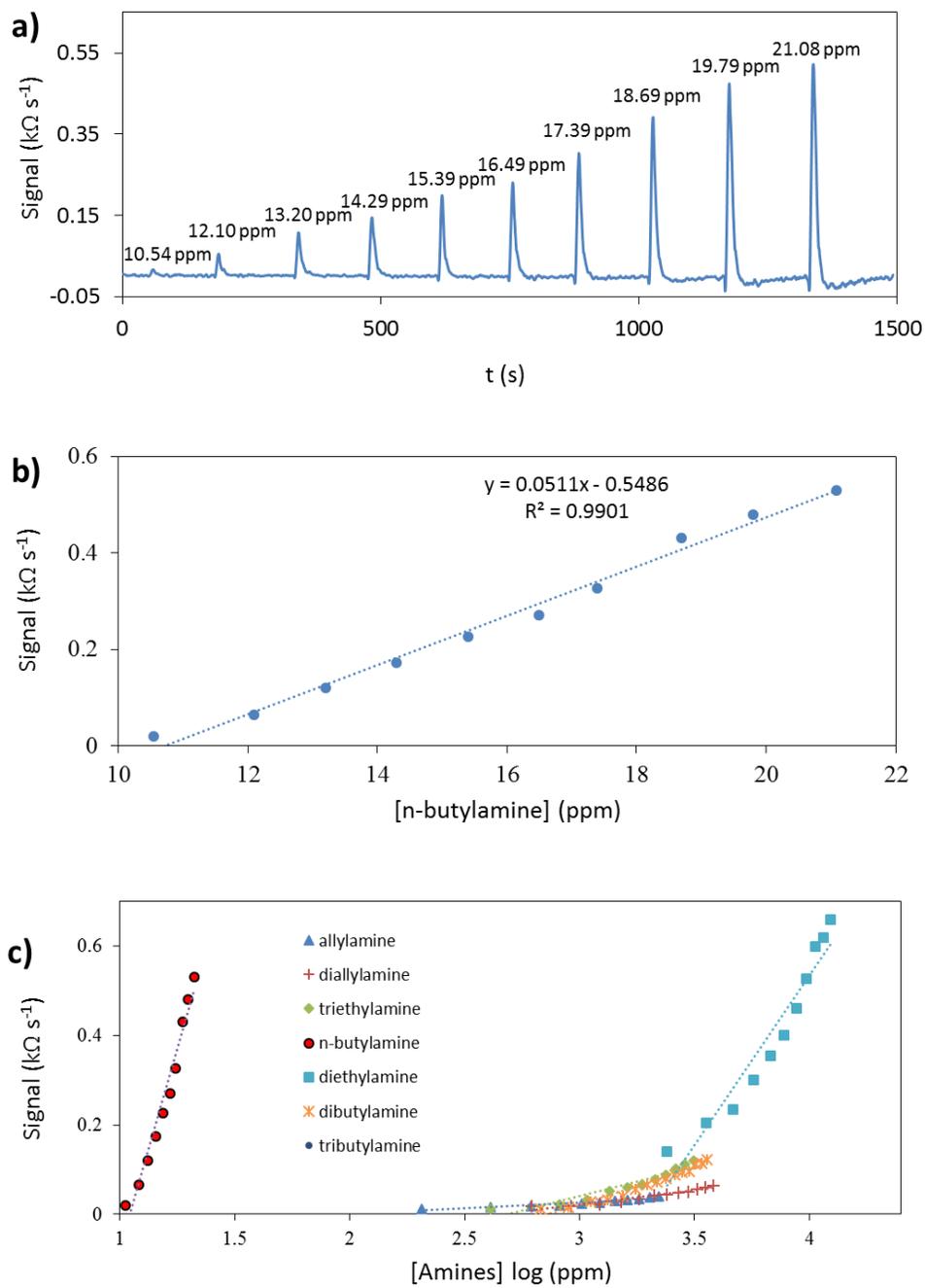


Fig. 5

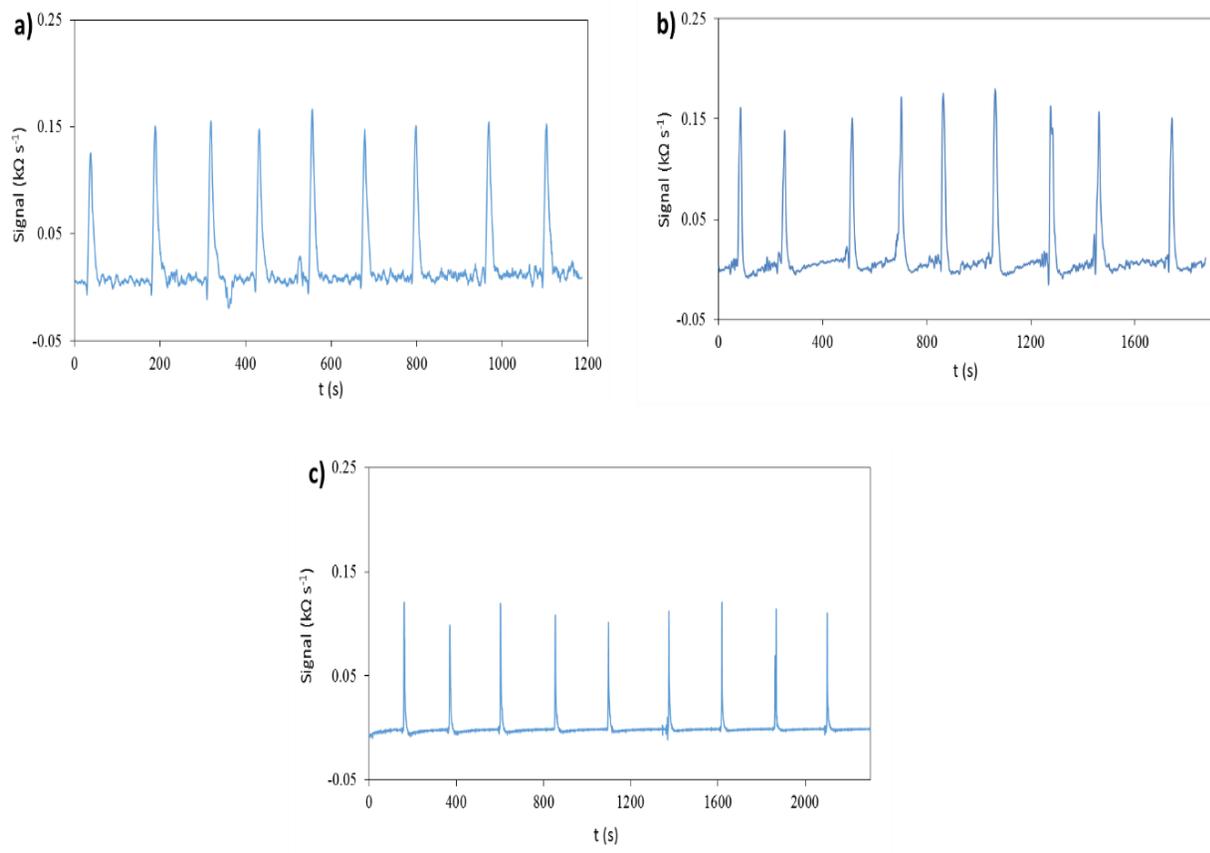


Fig. 6

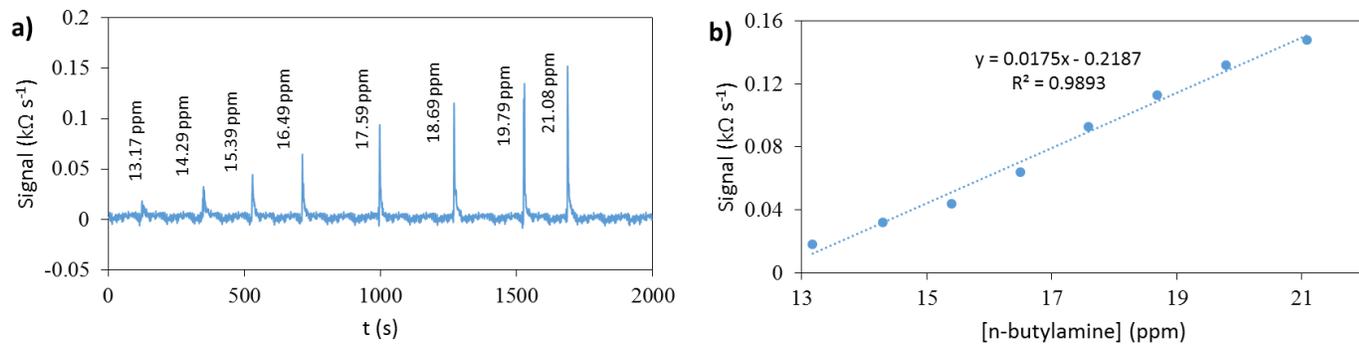


Fig. 7

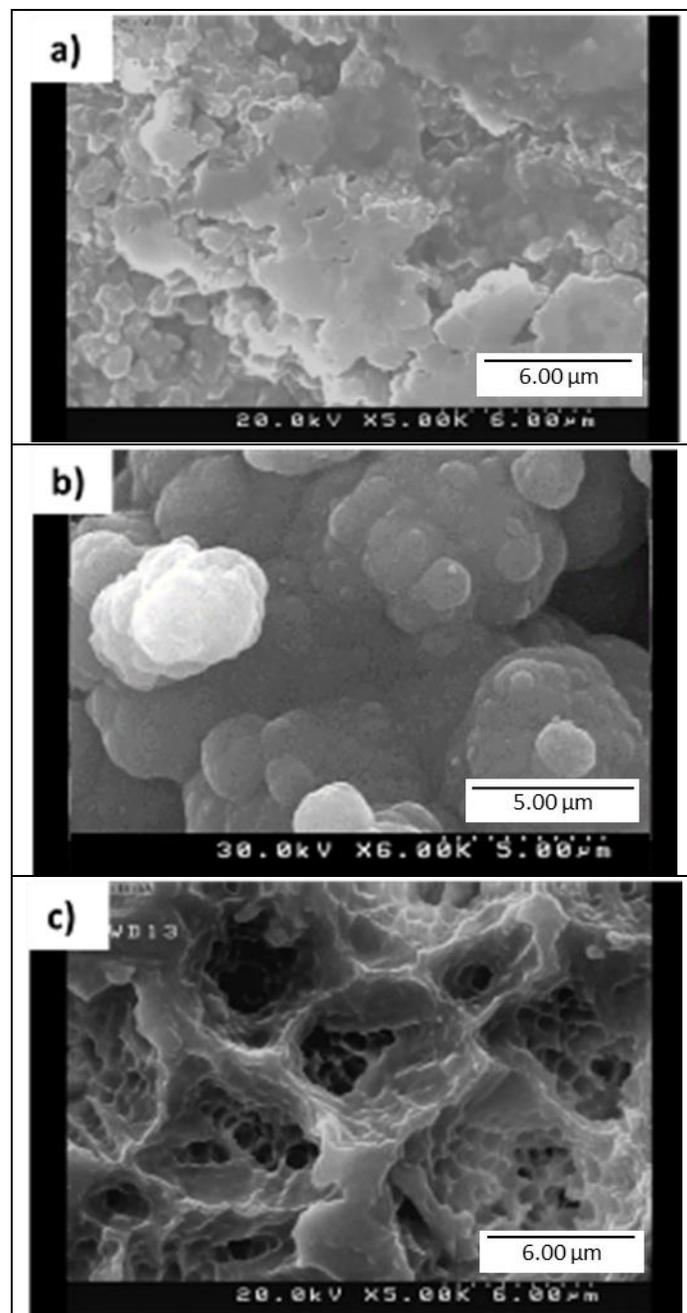
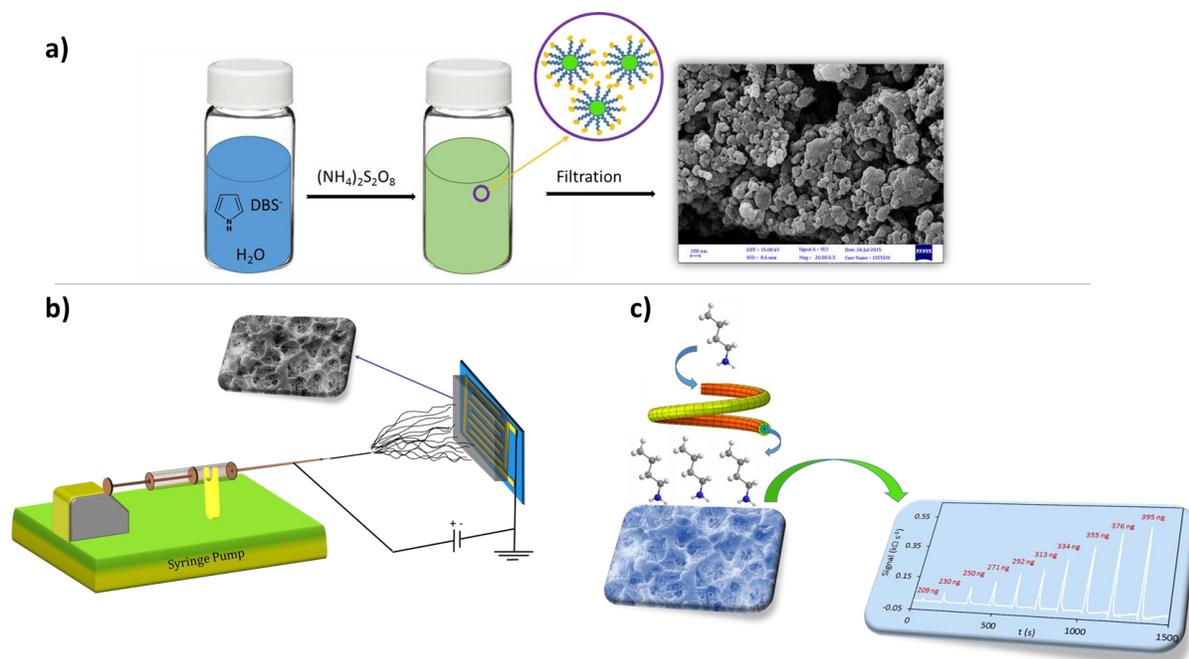


Fig. 8



Scheme. 1

Table 1 Figure of merits of Es-PPy gas sensor to n-butylamine at sensing temperature of 150°C.

Aliphatic amines	CS k Ω /s. μ g	DL ^a (ppm)	LR (ppm)	Selectivity ^b
n-butylamine	2.7756	0.42	10.54-21.08	1
diethylamine	0.0028	423.44	2402.82-12425.12	0.001
triethylamine	0.0016	535.61	815.06-3126.92	0.0006
allylamine	0.0009	1687.39	411.72-2213.86	0.0003
diallylamine	0.0006	1487.49	924.23-3811.95	0.0002
dibutylamine	0.0012	559.12	894.59-3578.35	0.0004
tributylamine	0.0009	519.80	478.22-3077.21	0.0003

^a DL was calculated from equation (1) for gas phase concentration. ^b Selectivity was calculated from equation (2).

Table 2 Detection limits obtained for determination of n-butylamine using the developed Es-PPy gas sensor and other sensors.

	Sensing Material	DL (ppm)	Ref
Chemiresistor	V ₂ O ₅ nanofibres	0.03	[47]
Chemiresistor	Polypyrrole modified with crown ethers	13.17	[48]
Optical sensor	Dimer-monomer equilibrium of indium(III) octaethylporphyrin in a polymeric film	0.10	[49]
Fluorescence sensor	Two-component gels	3.40	[50]
Fluorescence sensor	Fibrous film of a two-component organogel	1.16	[51]
Liquid crystal-based optical sensor	5CB doped with 0.1 wt% lauric aldehyde	10.00	[52]
Chemiresistor	Electrospun PPy film	0.42	This work