Departamento de Física e Ciências Materiais - IFSC/FCM   Artigos e Materiais de Revistas Científicas - IFSC/FCI

2011-12

Nanostructured polyaniline thin films as pH sensing membranes in FET-based devices

Nanostructured polyaniline thin films as pH sensing membranes in FET-based devices

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ARTICLE INFO

ABSTRACT

Polyaniline (PANI) has become an important conducting polymer for sensing due to its morphological and electrical properties. However, the processing of polyaniline in the form of nanostructured thin films is often limited by the low solubility of the polymer in water. We synthesized nanostructured polyaniline (N-PANI) aimed at improving its solubility to form layer-by-layer (LbL) thin films in conjunction with poly(vinyl sulfonic acid) (PVS) as counter ion. N-PANI was characterized via spectroscopic measurements and SEM images. After assembled as LbL thin films onto gold (Au) substrates, the PVS/N-PANI were employed as separative extended gate pH sensing membrane in FET-based devices presenting pH sensitivity around 58 mV/pH with small voltage drift. The results suggest that N-PANI can be easily processed to form suitable thin films for pH sensing and can be combined with biomolecules to be applied in FET-based biosensors.

1. Introduction

Polyaniline (PANI) is a well-known semiconductor polymer that has attracted attention in the scientific and engineering fields especially for application in chemical sensors [1], light emitting diode [2] and biosensors [3] due to its chemical environmental stability, facile synthesis, low cost, and possibility of control over electrical properties upon reversible doping of the polymer backbone [4]. One of the most exciting applications of the polyaniline lies in the application as active material for sensing devices [5–7].

Polymeric thin films can be self-assembled using layer-by-layer (LbL) technique, which has been considered a powerful tool for developing nanostructured multilayered composites with control and organization of structure at molecular level [8]. The LbL technique is based on the alternating adsorption of molecular layers with opposite charges upon immersion of a solid substrate into the cationic and anionic polyelectrolyte solutions, followed by cleaning and drying steps. LbL thin films exhibit potential applications in biosensor devices, since many enzymes can be charged in aqueous solutions and immobilized via electrostatic interactions on specific platforms [9,10]. The main advantages of the LbL technique are the simple methodology and low cost, ideal for industrial applications. However, due to the poor solubility of the semiconductor polymers, their use in LbL thin films is limited. Recent studies have

suggested that the nanofibrilar morphology can enhance the solubility of semiconductor polymers [11,12]. Therefore, the synthesis, characterization and application of water soluble/dispersion PANI nanostructures (N-PANI) are attractive for processing PANI via LbL technique.

Our group has focused researches in new gate materials for applications as pH sensors based on field effect transistor (FET) devices [13]. These devices are a modified version of conventional ion sensitive field effect transistors (ISFETs) [14] by connecting a pH sensitive membrane into the input (or gate) of a high-impedance FET device forming a separative extended gate field effect transistors (SEGFETs) [13]. According to the literature, some insulating materials that were applied as sensing material in conventional ISFETs have failed in SEGFETs [15]. Aiming to solve this problem, conducting materials, specifically oxides, have been successfully used presenting Nernstian sensitivity [15,16]. In addition, synthetic metal thin films such as N-PANI, which show very good control of physicochemical properties, seem to be ideal for such application.

In this study we used a simple chemical route to obtain a water solution/dispersion of PANI nanostructures produced by interfacial polymerization. The N-PANI was further used in modified electrodes produced via LbL methodology for pH sensors applications. The N-PANI showed a higher solubility as compared to polymers synthesized by conventional synthetic routes and their properties were investigated by Scan Electron Microscopy (SEM), FTIR and UV–Vis spectroscopy. The LbL PVS/N-PANI films assembled onto Au were applied as sensing membranes in SEGFET pH sensor showing sensitivity close to the expected Nernstian theorical value.

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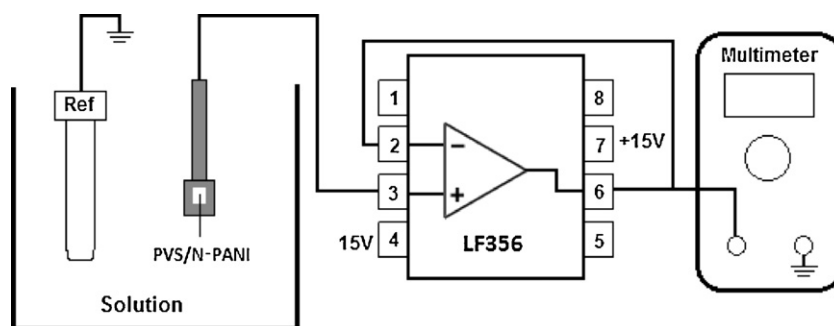*E-mail address:* nirton@ursa.ifsc.usp.br (N.C.S. Vieira).

Fig. 1. SEGFET measurement system showing the pin connections (top view) of the single J-FET operational amplifier LF356.

2. Experimental

2.1. N-PANI synthesis and characterization

Aniline monomers were purchased from Sigma Aldrich and distilled twice under vacuum and stored at low temperature (5 °C) protected from light. All other chemicals (Sigma Aldrich) were of analytical grade and used as received. Protonated polyaniline nanostructures were synthesized by interfacial polymerization. The method involved the reaction of the aniline monomer (1 mL) dissolved in an organic phase (chloroform, 50 mL), to which an aqueous phase containing solution of ammonium peroxydisulfate (2.85 g) dissolved in HCl (50 mL, 1 M) was added gently. The HCl solution forms the upper aqueous phase (using ammonium peroxydisulfate as oxidant agent) and the aniline/chloroform solution forms the lower organic phase. After 3 h, the entire aqueous phase was filled homogeneously with dark green PANI. The N-PANI formed was filtered and washed with HCl (1 M) and acetone to remove the unreacted chemicals and aniline oligomers. Finally, the obtained N-PANI cakes were dried in a vacuum oven at 40 °C for 24 h. N-PANI were characterized by field emission scanning microscopy (SEM, Zeiss® DSM 940A), infra-red (FTIR, Nicolet 470 Nexus) and UV–Vis (Hitachi U3000) spectroscopies. Thickness measurements of the films were performed with a Veeco Dektak 150 surface profilometer.

2.2. PVS/N-PANI multilayer assembly

Quartz slides for the PVS/N-PANI deposition were previously treated according to the RCA method (caution: Piranha solution is very oxidant), followed by rinsing in ultra-pure water (Milli-Q water, 18.3 MΩ cm). BK7 glasses (previously coated with 20 nm of chromium) were covered with Au by evaporation (150 nm) and were cleaned in a mixture of HNO_3:HCl:H_2O (1:3:20) for 30 s. Multilayer deposition was carried out as follows: the substrates were immersed in the polycationic N-PANI solution (1.0 mg mL^{-1}, 5 min) for the adsorption of the polymer and washed in a solution at the same pH for a few seconds. After rinsing, the substrates were gently dried by N_2 flow. After that, the substrates were immersed in the polyanionic PVS solution (1.0 mg mL^{-1}, 5 min), following the same steps described to the N-PANI deposition. The pH of the solutions and water rinse were fixed at 5 addicting HCl (1 M) and relevant parameters of the films preparation were previously examined and optimized. The N-PANI solution was prepared by dissolving the polymer in N,N-dimethylformamide (DMF) by sonication (5 min) and vigorous stirring overnight. Subsequently, the DMF solution containing N-PANI was diluted in water under stirring to a final ratio 2:8 (DMF:water, v/v). UV–Vis spectroscopy was used to monitor the deposition process.

2.3. pH sensing measurements

SEGFET device was constructed based on the concept introduced by Van der Spiegelt et al. [17]. A pH sensitive membrane formed by PVS/N-PANI bilayers was connected in the input pin of readout circuit based on high input impedance J-FET operational amplifier, used here as unity gain buffer. The films were immersed in different pH buffer solutions for 3 min and measurements of the output voltage versus time using a reference electrode (Ag/AgCl) were recorded by a Keithley multimeter (195 A) to determine the PVS/N-PANI pH sensitivity. Fig. 1 displays the SEGFET measurement system.
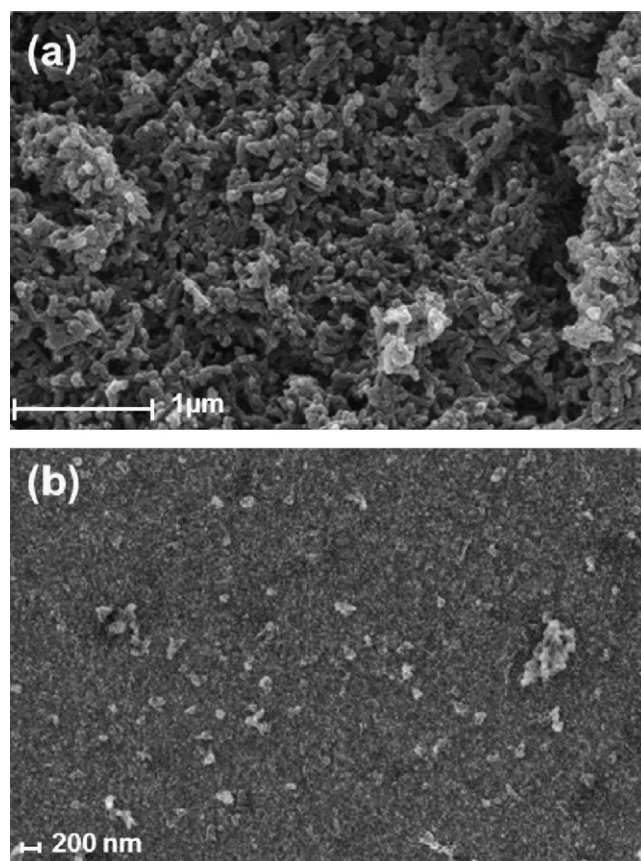

Fig. 2. SEM image of PANI nanostructures synthesized by interfacial polymerization (a) and LbL (PVS/N-PANI)$_3$ film (b).
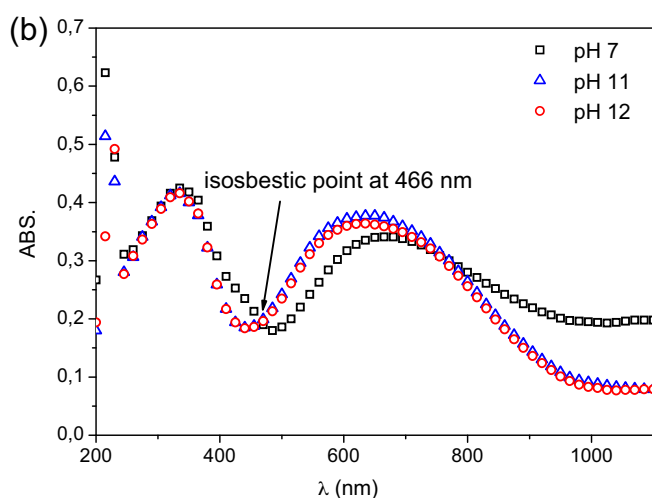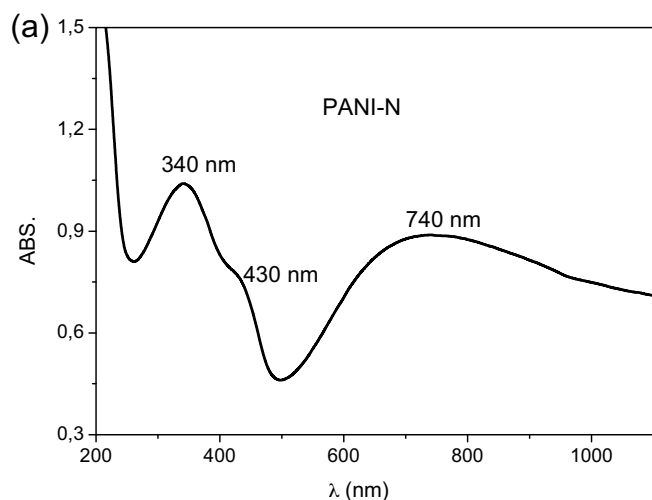
(a)

Fig. 5. Relationship between the film absorbance at 800 nm and the number of PVS/N-PANI bilayers. The inset shows the UV–Vis absorption spectra of PVS/N-PANI multilayer films with different numbers of layers. Thickness of 5-bilayers PVS/N-PANI film: 70 ± 2 nm.

(b)

Fig. 3. UV–Vis spectra of N-PANI in aqueous solutions. Characteristic bands of the emeraldine form of the N-PANI ($0.3\,g\,L^{-1}$) (a) and the isosbestic point of the N-PANI ($0.02\,g\,L^{-1}$) at 466 nm (b).

3. Results and discussion

3.1. Characterization of the synthesized N-PANI

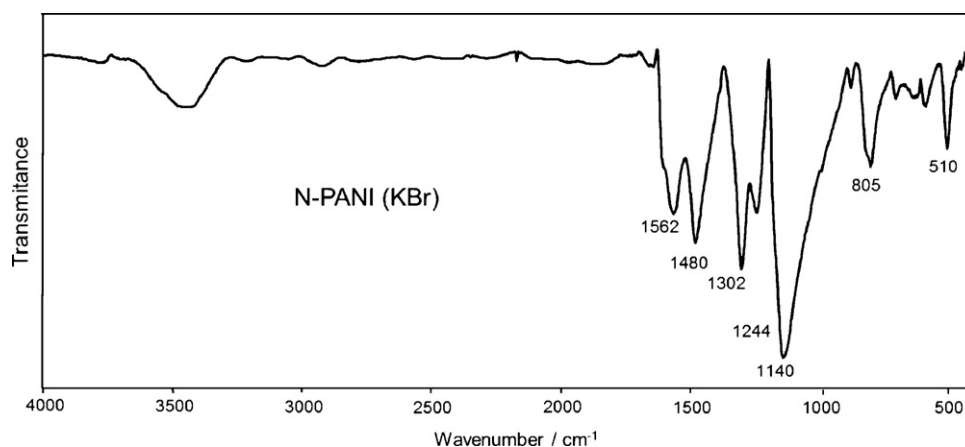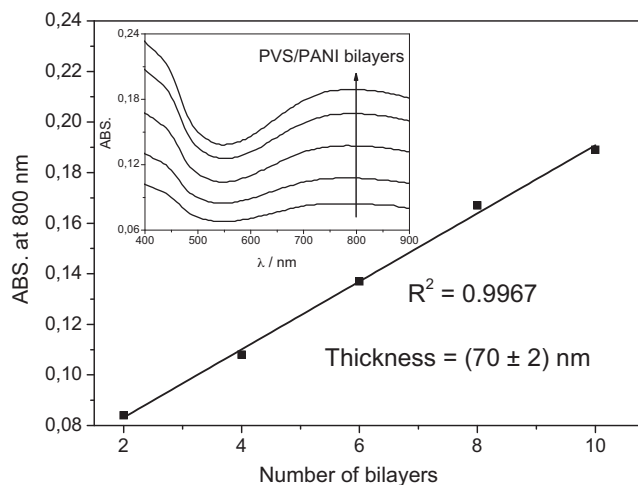The synthesized conducting N-PANI can be easily diluted in water without significant sedimentation for hours (depending on the solution concentration), but we can enhance the stability even more to create highly water stable N-PANI solution/dispersion, without sedimentation for several days, with a DMF (N,N-dimethylformamide)/water solution (as described in Section 2). Fig. 2 shows the morphology of the synthesized powder of N-PANI (a) and PVS/N-PANI in the form of LbL film (b) obtained by SEM microscopy. The average diameter of the nanostructures was about 50–90 nm in powder form, while the PVS/N-PANI in the form of LbL film shows a homogeneous distribution of the nanostructures with some aggregates. This may be explained by the fact that smaller structures tend to adsorb easier than larger ones. The low aggregation of the larger structures may be due to the drying process in LbL assembling.

UV–Vis spectra of N-PANI water solution is presented in Fig. 3 and show the absorption bands that confirm the polymer in its conducting form of emeraldine salt (ES). N-PANI exhibited a strong absorption band at 740 nm due to the polaron band characteristic of doped polyaniline [18]. The band at 340 nm is ascribed to the π–π^* transitions of the benzenoid rings and the band at 430 nm can be assigned to the partial oxidation state of the PANI (ES) [4,19]. UV–Vis spectra collected for solutions of N-PANI in different pH values reveal the characteristic isosbestic point (i.p.) at 466 nm (Fig. 3b), similar to that observed by Braga et al. [20].
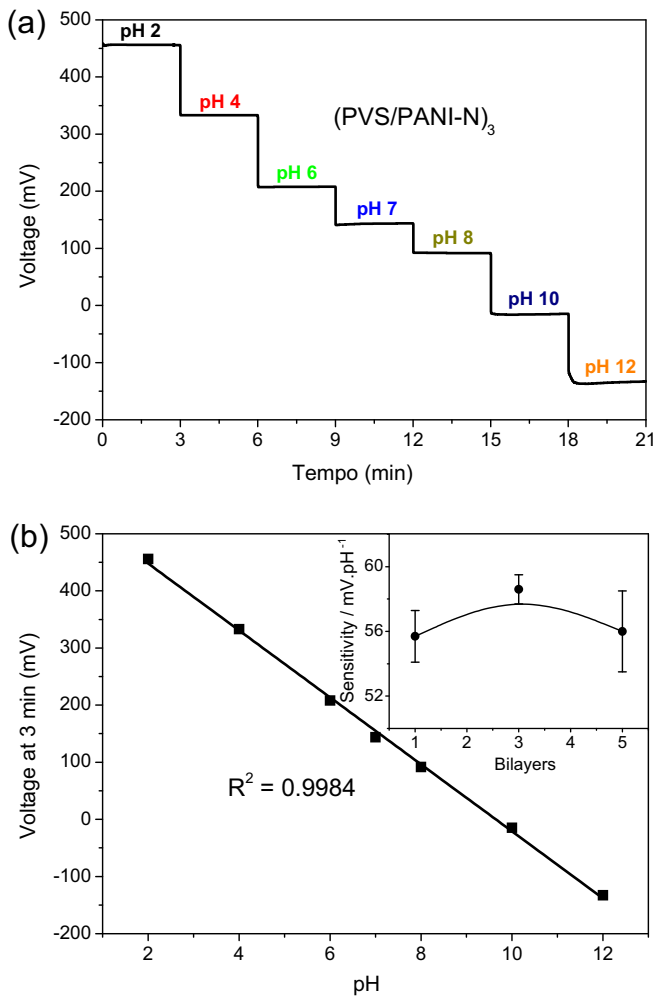

Fig. 4. FTIR spectrum of the PANI nanostructures.

Fig. 6. Dynamic response of (PVS/N-PANI)₃ sensing membrane in different pH buffer solutions (a). (PVS/N-PANI)₃ pH sensitivity obtained when the voltage was read at 3 min (b). Inset: pH sensitivity as function of PVS/N-PANI bilayers.

Fig. 7. Hysteresis characteristics of (PVS/PANI-N)₃ sensing membrane in a loop of pH buffer solutions (a). Drift in the output voltage along the time for (PVS/N-PANI)₃ sensing membrane measure in pH 7 buffer solution (b).

The structural characteristics of N-PANI can be confirmed by FTIR spectroscopy [21]. All the main characteristic peaks could be observed in the FTIR spectrum, as shown in Fig. 4. FTIR bands were assigned as stretching vibration of the C=C of quinoid ring at $1562\,cm^{-1}$ and the benzenoid ring at $1480\,cm^{-1}$. The bands at $1302\,cm^{-1}$ and $1244\,cm^{-1}$ were related to the C–N stretching vibration of the secondary aromatic amine and C–N$^{+\bullet}$ stretching vibration in the polaron structure, respectively. The band at $805\,cm^{-1}$ is assigned to C–H out-plane bending of benzenoid rings [12,19,21,22]. An estimative of the PANI oxidation degree (y) can be obtained by the ratio of the areas of the FTIR bands at ca $1590\,cm^{-1}$ and ca. $1500\,cm^{-1}$, resulting in 0.49 for the synthetized N-PANI [23].

UV–Vis absorption spectroscopy was employed to monitor the deposition process of the multilayer films. The build-up bilayers of PVS/N-PANI are displayed in the inset of Fig. 5. The polaronic band from 600 to 900 nm was used to follow the growth of the LbL films from doped polyaniline. It can be seen that the amount of adsorbed N-PANI is the same in each deposition step once the absorbance increased linearly with the number of bilayers (Fig. 5). The thickness of 5 bilayers of PVS/N-PANI films taken using a surface profilometer was 70 nm, i.e., approximately 14 nm per bilayer. It is important to notice that the polaronic band of N-PANI shifts to ca. 800 nm in the LbL films when compared to N-PANI in solution. This is related to protonation of immobilized PANI, and the absence of
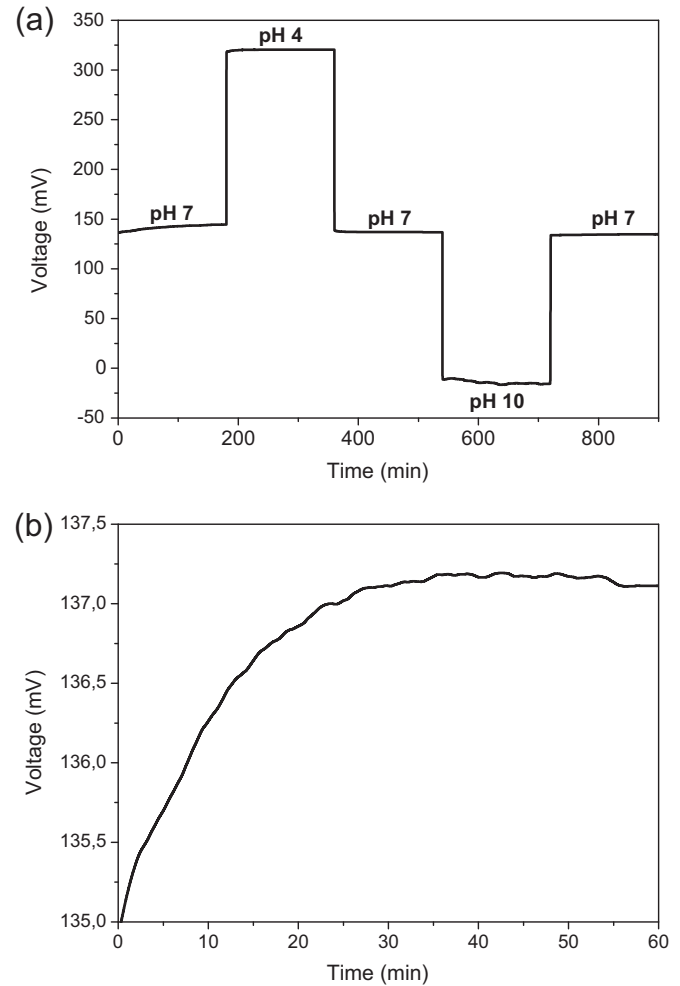
the interaction between the polymer and the solvent. Assembly of the N-PANI layers in the films may be driven by both electrostatic interactions and H-bonding, since N-PANI is slightly protonated at ca. pH 5 [20].

3.2. PVS/N-PANI as FET-based pH sensor

PVS/N-PANI LbL films were employed as pH sensing membranes in SEGFET devices. Fig. 6a shows the dynamic response of 3 bilayers of PVS/N-PANI deposited on Au substrates. Sensitivity values around 58 mV/pH were obtained for these membranes estimated at a time of 3 min in the pH range between 2 and 12, near the Nernstian limit value of 59.15 mV/pH (Fig. 6b). Similar results were obtained in the same range for optical PANI pH-sensor [24]. This sensitivity is in agreement with the results of Ge et al. [25] who studied the pH-sensing properties of 2-bilayers LbL films of PANI self-assembled with poly-(acrylic acid) (PAA) on ITO. These layers presented potentiometric response of 59 mV/pH over pH 3–9. Potentiometric sensors composed of electropolymerized polyaniline and polypyrrole (PPy) exhibit sensitivity of 59 mV/pH and 48 mV/pH, respectively, with a deviation from linearity in the former [26]. The high surface-to-volume ratio, characteristic of nanomaterials, improves the device performance, as presented here.

The sensitivities for 1, 3 and 5 PVS/N-PANI bilayers are shown in the inset of Fig. 6b. The sensitivity observed for PVS/N-PANI

system is in good agreement with the expected value for pH sensing membranes, suggesting that the substrates are totally covered with N-PANI (see Fig. 2b). In addition, the adsorption of N-PANI increases the surface roughness, which in turn increases the effective area of the electrode, explaining the good pH sensitivity of the films.

The capacity of recovery is an important characteristic in pH sensors. Some organic and inorganic membranes present instability in extreme acid or alkaline pH values [27]. To evaluate this possibility a hysteresis study was performed on a 3 bilayers PVS/N-PANI LbL film, immersing the membrane in the following buffer solutions: pH 7, pH 4, pH 7, pH 10 and pH 7. As shown in Fig. 7a, PVS/N-PANI sensing membrane presented a hysteresis of around 10 mV in the cycle with good agreement with inorganic sensing membranes [16,28]. This result confirms the film stability, i.e., no material desorption, as the voltage is recovered to the same pH value.

Another characteristic of FET-based pH sensors is the drift in the output voltage over time as a result of redox reactions in the sensing membrane interface [29]. ENREF_28 To evaluate this feature, PVS/N-PANI membranes were immersed in pH 7 buffer solutions for 60 min, after which a small drift of 2.2 mV can be observed, as shown in Fig. 7b. Conventional membranes of hydrated metal oxides take part in redox reactions due to their amphoteric nature. In our case, polymeric membranes present the same effect, but smaller, probably because the redox reaction is less favorable and it is not reversible in contrast with conventional metal oxide membranes.

4. Conclusions

PANI nanostructures were prepared by an interfacial polymerization method that enables the easy manipulation of polymer at molecular level by LbL technique. Self-assembled films of N-PANI doped with HCl alternated with PVS were successfully produced, characterized and applied as pH sensing membrane in SEGFET devices. PVS/N-PANI exhibited a Nernstian behavior in the pH range from 2 to 12, (sensitivity of ca. 58 mV pH^{-1} with small voltage drift), suggesting that nanostructured multilayer films could be a useful platform for pH sensing. Further applications comprise enzyme immobilization in PVS/N-PANI LbL films to be applied as potentiometric FET based biosensors.

Acknowledgements

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Biographies

Nirton C.S. Vieira received his degree in Physics (2003) from University of Formiga (UNIFOR-Brazil) and his MSc in Materials Science (2006) from Federal University of Itajubá (UNIFEI-Brazil). He is now a PhD student at University of São Paulo (USP-Brazil) since 2007, under supervision of prof. Francisco E.G. Guimarães. His thesis focuses the development of nanostructured platforms forsensing based on extended gate FET configuration.

Edson G. R. Fernandes studied at Federal University of Itajubá (UNIFEI) where he obtained his Bachelor in Electrical Engineering (Electronic) in 2003 and the MSc in Materials Science for Engineering in 2005. Now, he is a PhD student at University of São Paulo (USP) in Materials Science and Engineering. He has experience in Electrical

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V. Zucolotto is a PhD in Materials Science and Engineering. Coordinator of the Laboratory of Nanomedicine and Nanotoxicology at University of São Paulo, Brazil. Primary interests are focused on Nanomedicine, a research line including experimental and theoretical investigation on the interactions between biomolecules and nanomaterials for application in Medicine, more specifically the development of hybrid nanocomposites for Cancer diagnosis and therapy, and the development of highly sensitive biosensors for diagnosis of tropical diseases.

Francisco E.G. Guimarães has a professor position at the University of São Paulo. He graduated in Physics at the Federal University of Minas Gerais where he also got the MSc in Physics. Subsequently he obtained a PhD degree at the University of Duisburg in Germany studying the growth of semiconductor heterotructures. He worked at the Max Planck Institute in Stuttgart and as post-doc at the University of Aachen in Germany working on optical characterization on III–V and II–VI semiconductor films and heterostructures. His recent research activity is focused on the study of emission properties of conjugated organic molecules and inorganic semiconductor structures. Particular attention is devoted to photophysic properties.