Electrochemical Studies Based on Local Interfacial pH Changes of Gold Nanoparticles Immobilized on Polystyrene Brushes

Tamara R.T.A. Antonio[1], Caroline R. Basso[1], Murilo F. Cabral [2], Valber A. Pedrosa[1,]*

[1] Institute of Bioscience, Department of Chemistry and Biochemistry, UNESP, Botucatu, SP – Brazil
[2] Institute of Biology, Department of Genetics, Evolution and Bioagents, UNICAMP, Campinas, SP – Brazil.
[*]E-mail: vpedrosa@ibb.unesp.br

The electrochemical behavior of polystyrene modified with gold nanoparticle (Au NPs) was investigated in terms of pH-responsive polymer brush. A pH-responsive of modified polymer brush from tethered polystyrene was prepared and used for selective gating transport of anions and cations across the thin-film. An ITO-coated glass electrode was used as substrate and applied to study the switchable permeability of the polymer brush triggered by changes in pH of the aqueous environment. The pH-sensitive behavior of the polymer brush interface has been demonstrated by means of cyclic voltammetry (CV) and Localized Surface Plasmon Resonance (LSPR). CV experiments showed at ph values of 4 and 8 induces swelling and shrinking of the grafted polymer brushes, respectively, and this behavior is fast and reversible. LSPR measurements showed a blue shift of 33 nm in the surface resonance band changes by local pH. The paper brings an easy methodology to fabrication a variety of nanosensors based on the polymer brushes−nanoparticle assemblies.

Keywords: Polymer brushes; Local pH change; gold nanoparticle; stimuli-responsive materials

1. INTRODUCTION

Polymer brushes have emerged as new class of building blocks with switchable properties. They have a high flexibility of the polymer chains and are enabled of reorganization by changing the surrounding environment. External signal-responsive such as solvent [1,2], temperature [3,4], pH [5,6], ionic strength [7], or light [8] have been explored by different application. The discovery of switchable properties has offered exciting and novel possibilities for the fabrication of adaptive or responsive surfaces. The fabrication of patterned polymer brushes with controlled shape, feature dimension, grafting density and spacing has recently received considerable interest, and presents exciting

opportunities for micro- and nanotechnology applications [9], biosensing [10], biofuel cells [11], drug delivers [12] and electrochemical systems processing information [13].

Few papers have reported signal-responsive interface with switchable/tunable redox properties based on a pH-responsive polymer brush. Recently, Katz and co-workers[14] grafted Poly(4-vinyl pyridine) functionalized with Os-complex redox to an indium tin oxide (ITO). The modified electrode surface was sensitive to the changes of the pH value of the electrolyte solution: at acidic the redox polymer film demonstrated the reversible electrochemical process; while at neutral the polymer was not electrochemically active. They suggested that quasi-diffusional mechanism of the electron transfer provided by the flexible polymer chains as being in the swollen state. Harris and Bruening [15] demonstrated that the pH-induced swelling of multilayers prepared from poly(allylamine hydrochloride) and poly(styrenesulfonate sodium salt) bilayers affected the permeability of the film for diffusive ionic redox species. The swelling of the multilayer in basic solutions was accompanied by a 10-fold increase in the film permeability. Hydrogel thin films with reversible pH-switchable selectivity for both cations (pH 10) and anions (pH 3) were reported by Advincula and co-workers [16]. The responsive multilayers were assembled from benzophenone-modified poly(acrylic acid) and poly(allylamine) under pH conditions in which the polymers were partially ionized, resulting in a large fraction of loops and tails that contain free carboxyl and amino groups (i.e., not involved in the formation of the polyelectrolyte complex). The pH-dependent ionization and protonation of these groups, which enabled switching of the net ionic charge of the multilayer between negative and positive values, were responsible for the observed bipolar ion permselective properties of the photo-cross-linked PAH/PAA films.

Recently, the use of (LSPR) in metal nanoparticles associated with polymer brushes have been used to probe swelling-shrinking transitions. Yameen et al. [18] described the ionic current switching characteristics displayed by the nanochannels resemble the typical behavior observed in many biological channels that fulfill key pH-dependent transport functions in living organisms, that is, the nanochannel can be switched from an "off" state to an "on" state in response to a pH drop. The construction of such a chemical nanoarchitecture required the integration of stable and ductile macromolecular building blocks constituted of pH-responsive poly(4-vinyl pyridine) brushes into solid state nanopores that could act as gate-keepers managing and constraining the flow of ionic species through the confined environment. Tokarev et al. [19] reported a stimuli-responsive polymer/noble metal nanoparticle composite thin film based on poly(*N*,*N*′-dimethylaminoethyl methacrylate) brush and the LSPR in metal nanoparticles to enable the transduction of changes in the solution pH in the near-physiological range into a pronounced optical signal.

In this paper, we further integrated of environmental stimuli-responsive polystyrene brush modified with gold nanoparticle on ITO. These brushes into solid-state nanochannels would lead to the creation of robust signal-responsive that can be switched from an "off" state to an "on" state in response to a pH drop. The electrochemical properties on the local interfacial pH changes were studied by means of cyclic voltammetry and LSPR based on the gold nanoparticle response that resides in the thin film.

2. EXPERIEMENTAL PROCEDURE

2.1 Chemicals and Reagents

Carboxyl group-terminated poly(styrene) (PSCOOH) (P-7546, Mw = 42000 g mol^{-1}, Polymer Source), 3-glycidyloxypropyl-trimethoxysilane (GPS, Sigma-Aldrich), Sodium borohydride (NaBH$_4$), trisodium citrate dehydrate, toluene, ferrocene monocarboxylic acid (FMCA) (Sigma-Aldrich), hydrogen tetrachloroaurate(III) (HAuCl$_4$·3H$_2$O), and other chemicals and solvents were used as supplied without any further purification. Indium tin oxide (ITO)-coated glass (60 Ω/sq surface resistivity, Sigma-Aldrich) served as the working electrode, platinum wire was employed as a counter electrode and the reference electrode was a Ag/AgCl (3.0 mol L^{-1}) for electrochemical measurements. Ultrapure water from a Milli-Q (Millipore Inc.) purification system was used in all the experiments.

2.2 Modification of electrodes

The ITO electrodes were chemically modified with PSCOOH brushes using the "grafting-to" method [19] according to the following procedure. ITO-coated glass slides were cut into 30 mm × 8 mm strips. They were cleaned with ethanol in an ultrasonic bath for 15 min and dried in a stream of nitrogen. The cleaning step was repeated using methylene chloride as a solvent. The initial cleaning steps were followed by immersing the strips into a cleaning solution (heated to 60 °C in a water bath) composed of NH$_4$OH, H$_2$O$_2$, and H$_2$O in a ratio of 1:1:1 (v/v/v) for 30 min. Subsequently, the glass strips were rinsed several times with water and then dried under nitrogen flow. The freshly cleaned ITO strips were reacted with 0.1% v/v GPS in dry toluene for 20 min. The silanized ITO was rinsed with several aliquots of toluene and dried under nitrogen. Then 60 μL of a 1% wt PSCOOH solution in methylene chloride was applied to the surface of each ITO glass strip, dried to form a polymer coating, and left to react in a vacuum oven at 140 °C overnight. The final cleaning step to remove the unbound polymer consisted of soaking the samples in ethanol for 10 min. Modified electrodes were stored under water.

2.3 Preparation of Gold Nanoparticles

HAuCl$_4$·3H$_2$O (60 mg, 0.15 mmol) and trisodium citrate dehydrate (44 mg, 0.15 mM) were dissolved in 200 mL of Ultrapure water (Milli-Q system). After 1 h of stirring, ice−NaBH$_4$ aqueous solution (3.0 mL, 0.9 mmol) was added and the solution immediately turned red. The solution was allowed to stir for 5 h. Gold nanoparticles were attached on the PSCOOH polymer brushes from a 1 mM solution in toluene by incubating the samples overnight. Then the electrode was rinsed by several times with toluene to removed unbound gold nanoparticles.

2.4 Equipments

Electrochemical measurements were performed with an ECO Chemie Autolab Microautolab III/FRA2 with an electrochemical analyzer and the GPES 4.9 (General Purpose Electrochemical

System) software package. Cyclic voltammograms were recorded in the presence of 0.5 mM FcMA. Peak currents for each measurement were obtained from a second scan. Before each experiment, a stream of nitrogen was bubbled through the solution for *ca.* 10 min.

A series of UV−vis spectra of the PSCOOH-Au plasmonic platform in an unbuffered aqueous medium was obtained by titration with a base from pH 4 to pH 9 using a Biochrom Libra S11 spectrophtometer.

3. RESULTS AND DISCUSSION

3.1. Effect of scan rate on the peak currents of FcMA

Cyclic voltammetry were used to study the electrochemical properties polymer brush-modified electrode. It was carried out in order to investigate the kinetics of the electrode reactions and verify whether diffusion is the only controlling factor for mass transport or not. Figure 1A shows cyclic voltammograms of the PSCOOH-Au modified electrode at different potential scan rates in the presence of 0.5 FcMA in 10 mM PBS buffer. The cyclic voltammograms demonstrate the oxidation and reduction peaks occur at 0.22V and 0.18V, respectively. The results obtained shows that with the increase of scan rate, the redox peak current also increase gradually. The correlation of the redox peak currents with the scan rate are shown in Figure 1B. In the range from 20 to 250 mV/s the peak currents were proportional to the square root of the scan rate ($v^{1/2}$), which indicates that the determining step of reaction is mass transport to the PSCOOH-Au surface. The peaks on the cyclic voltammograms were stable and reproducible after many potential cycles and after the electrode washing, thus confirming that the electrochemical process originates from the surface-confined redox species. One would expect that the peak current value, I_p, should linearly increase with the elevated potential scan rate as it is theoretically predicted for a surface-confined electrochemical process [21]. However, we found that I_p is proportional to the square-root of the potential scan rate as predicted by the Randles−Sevcik equation for the peak current corresponds to a electrochemical process (i.e. mass transport) dependent on electrode potential and diffusion [22]. In our case, the electroactive species have to reach the electrode surface by diffusion to occur the electron transfer. It means that the electron transfer is controlled by mass transport although the whole process is governed by diffusion. This behavior does not allow the quantitative treatment of the electrochemical data to derive the diffusional parameters of the flexible chains. However, Katz and coworkes [14] found the same behaviour using Poly(4-vinyl pyridine) functionalized with Os-complex redox units grafting at ITO. They suggested the charge transfer between the conductive support and the redox centers bound to the polymer brush proceeds upon the quasi-diffusional translocation of the polymer chains requiring their flexibility, and the distances between the redox centers are too long for the electron hopping between them.
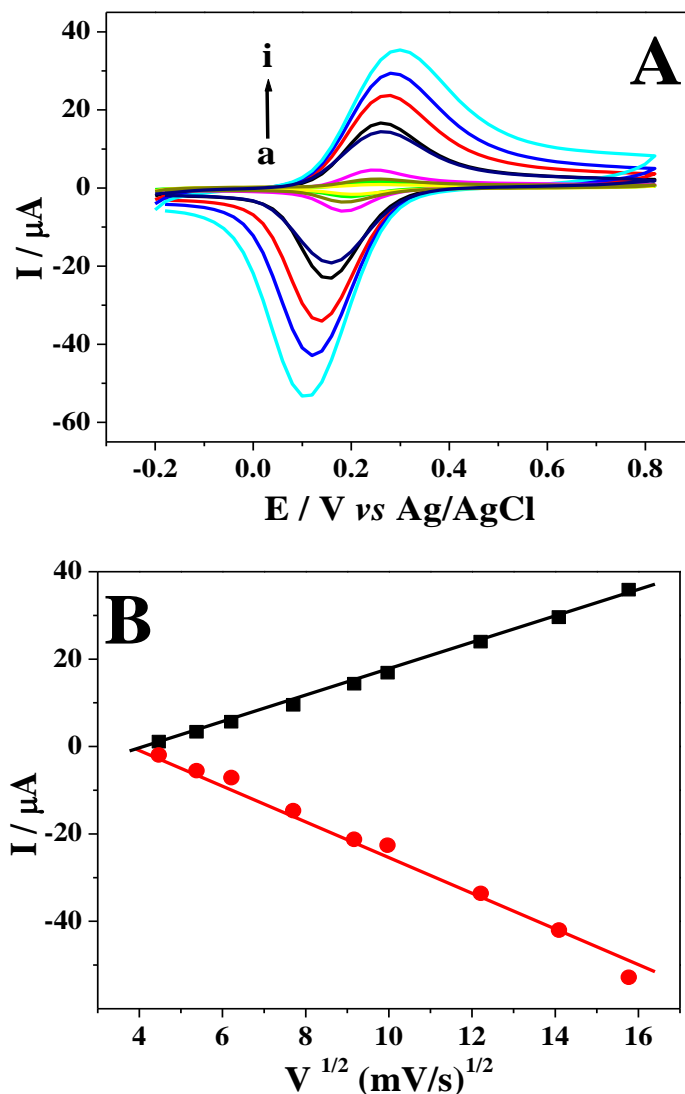
Figure 1. (a) Cyclic voltammograms of the PSCOOH-Au modified electrode at different scan rates (a–i: 20, 30, 50, 60, 90, 100, 150, 200, and 250 mV/s) in 10 mM PBS (pH 4.0) + 10 mM FcMA, and (b) is the plot of the redox peak current versus the square root of scan rate.

To better understand the reaction mechanism, it was analyzed the peak potential versus increasing of the scan rate. Separation of peak-to-peak (ΔE_p) remains nearly constant up to 50 mV, which suggested an electrochemical process reversibly confined surface [21]. It should be noted that the elevated potential scan rate resulted in the deviation of the electrochemical process from the reversibility yielding the increasing ΔE_p values, resulting in the similar anodic and cathodic electron transfer coefficients, and reflecting similar activation energies for the anodic and cathodic processes. From the dependence of the peak potentials on the potential scan rate, the heterogeneous electron-transfer rate constants k_s, for the redox process corresponding to PSCOOH-Au modified electrode, were estimated 12 s^{-1} (n=1) using the Laviron's equation [21]. Laviron's plot can be obtained by measuring deltaE (defined as deltaEp −E$_0$; Ep is the peak potential value for the anodic or cathodic wave, and deltaE$_0$ is the formal potential) as function of log of the potential scan rate. Following the theory, alpha and k_s can be calculated using Eqs. (1) and (2): [23]

$$\frac{a}{1-a} = \frac{v_a}{v_b} \tag{1}$$

$$k_s = \frac{nF\partial v_c}{RT} = \frac{(1-a)nFv_a}{RT} \tag{2}$$
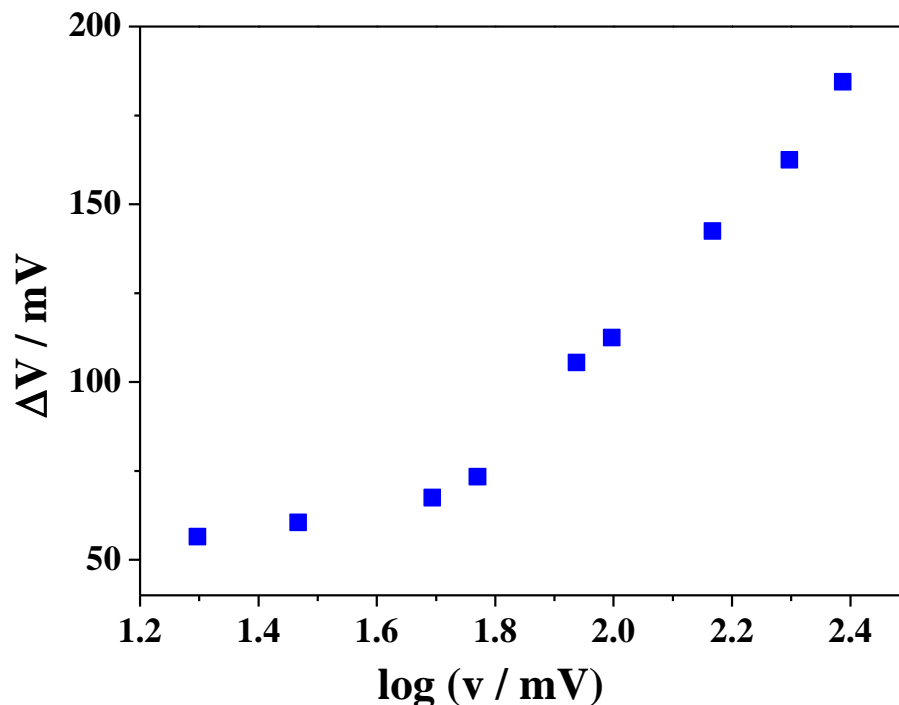

Figure 2. Peak-to-peak separation as a function of the potential scan rate. The measurements were performed in 10 mM PBS buffer (pH 4.0) + 0.5 mM FcMA.

3.2. Effect of pH

Fig. 3 shows the effect of pH on Ep and Ip was examined for 0.5 mM FcMA using the PSCOOH-Au electrode in a 10 mM PBS buffer medium varying the pH in the interval 4.0-8.0. The peak potential was strongly pH-dependent as showed in a linear section (insert). In this way, the Ip *vs.* pH plot revealed that the peak current has a maximum value for pH 4.0 decreasing sharply with increase of pH values. It may be explained by the stimuli-responsive behaviour of PSCOOH-Au, which in pH 4.0 the polymer is swollen, positively charged and allows the diffusional translocation of the polymer chains providing the electrochemical accessibility for the pendant redox groups, while in pH 8.0 the polymer is shrunken, negatively charged and the chains movements are "frozen" restricting the electrochemical process. This behavior was already observed using Poly(*N',N'-diethylaminoethyl methacrylate*) modified with gold nanoparticles (PDMAEMA-Au) [24].

The experiment resulted in the titration curves where one of the redox probes (FcMA) is decreasing the electrochemical response, by deactivated upon re-charging the polymer film from its

positive to the negative state, figure 6. The slope of -0.065 mV/pH unit was obtained which was close to the theoretical value of -0.059 mV/pH unit for the one electron one proton process.
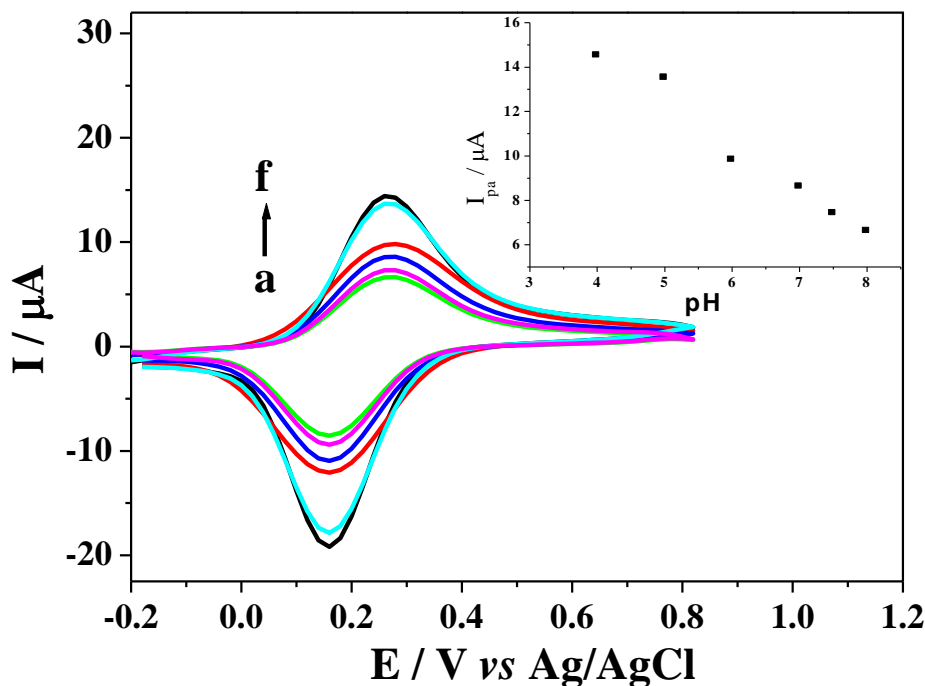

Figure 3. (a) Cyclic voltammograms obtained at the PSCOOH-Au modified electrode in 0.5 mM FcMA 10 mM PBS buffer solutions in pH values, (a) 4.0 (b) 5.0 (c) 6.0 (d) 7.0, (e) 7.5, and (f) 8.0, at scan rate of 90 mV/s. Insert: the plot of standard redox peak current of FcMA on cyclic voltammograms versus pH values.

3.3. Electrochemical investigation of stability of the PSCOOH-Au electrode

In addition, cyclic voltammograms measurements were performed in order to demonstrate the stablility and reproducible behavior on the PSCOOH-Au modified film. The switchable interfacial properties of the modified electrode were observed by cyclic voltammetry measurements performed in the presence of 0.5 mM FcMA. Figure 4 shows the switching behavior between the inactive and the active states of the modified electrode. The interfacial changes allowed and inhibited the redox reactions of differently charged redox species were reversible. Indeed, similar cyclic voltammograms were obtained repeatedly upon pH changes between 4 ((a) and (c)) and 8 ((b) and (d)). The insert shows the peak current vs. steps plot built considering when the polymer is on its active state and on its inactive state. This switch originates from the different states of the polymer brush shows in pH 4.0 the polymer is swollen, while in pH 8.0 the polymer is shrunken as explained above. The proposed mechanism is in accordance with the previously reported system based on polymer brushes [22]. In short, changing the pH value and recording cyclic voltammograms can predicted the intermediate states of the polymer transition from the positively charged state to the negatively charged state at the modified interface.
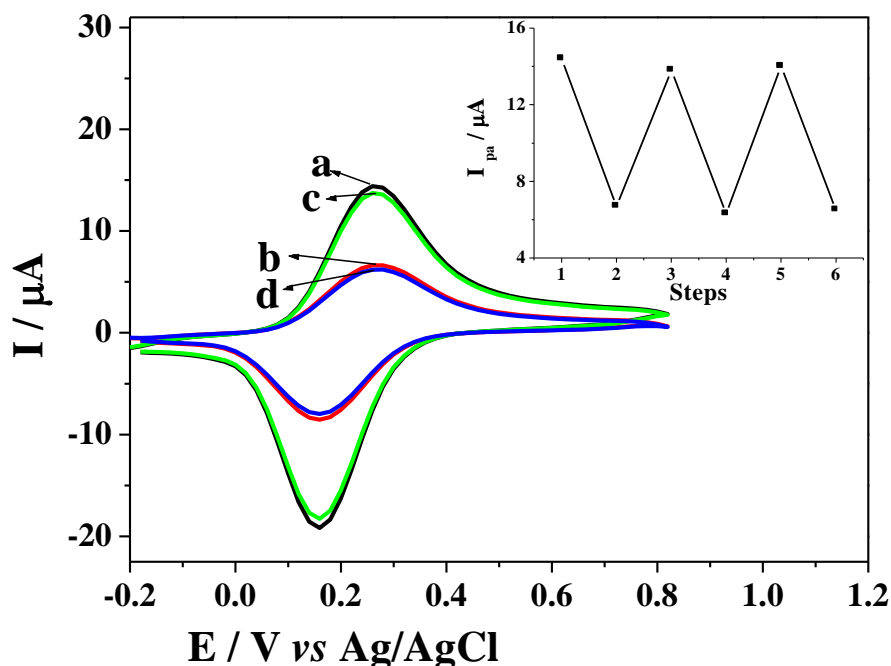
Figure 4. Cyclic voltammograms of the PSCOOH-modified electrode obtained upon stepwise measurements performed in neutral and acidic solutions in 10 mM PBS buffer + 0.5 mM FcMA: at (a) pH 4.0, (b) 8.0, (c) again pH 4.0, and (d) again pH 8.0. Inset: Reversible switching of modified electrode activity.

3.4 Localized Surface Plasmon Resonance Studies

The spectroscopic measurements were carried out in PBS buffer and confirmed that the film was sensitive to local pH changes in terms of different interaction of charges with Au nanoparticles. Figure 5 shows a red shift (from 534 to 567 nm) is observed after increase pH from 3.0 (4.0) (protonated) to 7.0 (8.0) (deprotonated), and there was a blue shift when the pH decreased from pH 7.0 (8.0) to 3.0 (4.0). Changes in absorption spectra were reproducible, indicating that the PSCOOH brushes take a reversible stretching motion depending on the pH change, whereas Au NPs are tethered firmly on the solid substrates. This behavior was previously reported as the swelling hysteresis, and it was reported from other polyelectrolyte materials and is originated from the hydrophobic interactions of aliphatic backbones [18]. The spectral shifts have shown a reversible behavior as confirmed by repeating the pH change for couple of times, which implies that our system is stable and reversible. These data are consistent with the results obtained from CV experiments and demonstrate that gold nanoparticles are successfully immobilized on the brush-modified electrode. Also this result is in accordance with previously paper reported based on stimuli-responsive polymer/noble metal nanoparticle composite thin film [19].
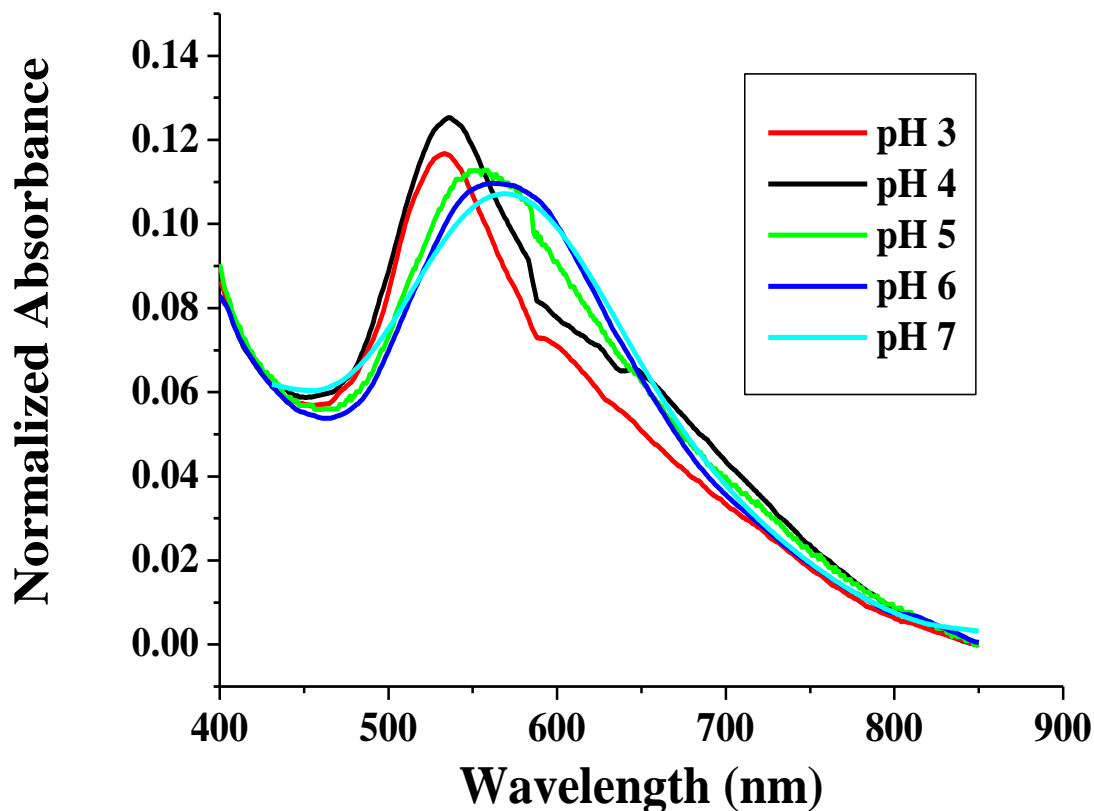
Figure 5. Representative LSPR spectra of the plasmonic sensing device acquired in an buffered that was titrated with a base to the following pH (insert figure).

4. CONCLUSION

The use of switchable properties of polystyrene brushes modified with gold nanoparticles was successfully applied to evaluate the behavior of the polymer under different pH conditions. In the range of pH values studied, activate and inactivate states were observed, and on the activate state further electrochemical studies were carried out. These results extend our previous findings for PDMAEMA [24], a system that is mechanistically comparable to the PSCOOH-Au one, but posses a sophisticated behavior when combined with HPR. From activated state of the PSCOOH-Au was possible to see an unlike electrochemical behavior in terms of charge transfer inside the polymer chain, since the determining step is controlled by mass transport while would be expected by electron transfer. By LSPR the changes in the solution pH were detected with the plasmonic device, and the device has showed good stability and can be used multiple times without significant deterioration in the optical response. This outcome opens good possibilities for the development of nanoscale sensor.

References

1. S. J. Ahn, M. Kaholek, W. K. Lee, B. LaMattina, T. H. LaBean, S. Zauscher *Adv. Mater*. 16 (2004) 2141.
2. M. Kaholek, W. K. Lee, S. J. Ahn, H. W. Ma, K. C. Caster, B. LaMattina, S. Zauscher, *Chem. Mater.* 16 (2004) 3688.
3. T. L. Sun, G. J. Wang, L. Feng, B. Q. Liu, Y. M. Ma, L. Jiang, D. Zhu, *Angew. Chem. Int. Ed.*, 43 (2004) 357.
4. Q. He, A. Kueller, S. Schilp, F. Leisten, H. A. Kolb, M. Grunze, J. Li, *Small* 3 (2007) 1860.
5. M. Motornov, R. Sheparovych, E. Katz, S. Minko, *ACS Nano*, 2 (2008) 41.
6. T. Kin Tam , M. Pita , O. Trotsenko, M. Motornov , I. Tokarev , J. Halámek , S. Minko, E. Katz, *Langmuir* 26 (2010) 4506.
7. A. Wittemann, M. Drechsler, Y. Talmon, M. Ballauff, *J. Am. Chem. Soc*. 127 (2005) 9688.
8. K. Fries, S. Samanta, S. Orski, J. Locklin, *Chem. Commun* (2008) 6288.
9. L. Ionov, N. Houbenov, A. Sidorenko, M. Stamm, S. Minko, *Adv. Funct. Mater*. 16 (2006) 1153.
10. M. Welch , A. Rastogi, C. Ober, *Soft Matter.* 7 (2011) 297.
11. L. Amir , T.K. Tam, M. Pita, M. M. Meijler, L. Alfonta, E. Katz, *J. Am. Chem. Soc.* 131(2009) 826.
12. S. J. Lue, J. J. Hsu, T. C. Wei, *J. Membr. Sci*. 321 (2008) 146.
13. T. K. Tam, M. Pita, M. Motornov, I. Tokarev, S. Minko, E. Katz, Adv. Mater. 22 (2010) 1863.
14. T. K. Tam , M. Ornatska , M. Pita , S. Minko, E. Katz, *J. Phys. Chem. C* 112 (2008) 8438.
15. J. J. Harris and M. L. Bruening, *Langmuir* 16 (2000) 2006.
16. M. K. Park, S. X. Deng, R. C. Advincula, *J. Am. Chem. Soc.* 126 (2004) 13723.
17. B. Yameen, M. Ali, R. Neumann, W. Ensinger, W. Knoll, O. Azzaroni, *Nano Lett.* 9 (2009) 2788.
18. I. Tokarev, I. Tokareva, S. Minko, *ACS Appl. Mater. Inter.* 3 (2011) 143.
19. Y. Roiter, I. Minko, D. Nykypanchuk, I. Tokarev, S. Minko *Nanoscale*, 4 (2012) 284.
20. D. D. Carlo, K. Jeong, L. P. Lee, *Lab Chip* 3 (2003) 287.
21. E. Laviron, L. Roullier, C. Degrand, *J. Electroanal. Chem. Inter. Electrochem.* 112 (1980) 11-23
22. Southampton Electrochemistry Group, *Instrumental Methods in Electrochemistry,* Ellis Horwood Ltd, England (1990), Chapter 6.
23. M. Santhiago, P. R. Lima, W. J. R. Santos, L. T. Kubota, *Sensors and Actuators B* 146 (2010) 213–220
24. T. R. T. A. Antonio, M. F. Cabral, I. Cesarino, S. A. S. Machado, V. A. Pedrosa, accepted to publication*, Electrochemistry Communications* (2013), doi: 10.1016/j.elecom.2012.12.026.