

# SMART POLYMER MODIFIED ELECTRODE SWITCHED BY IONIC STRENGTH AND pH

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**ABSTRACT** – Poly(N,N-dimethylaminoethyl methacrylate) modified ITO (indium tin oxide) covered with gold nanoparticles electrode was synthesized by grafting to method and stimuli responses to pH and ionic strength (IS) was evaluated in PBS solution. At pH<5 PDMAEMA chains were found to be stretched generating a great electrochemical signal and at pH<5 collapsed with a signal decreasing. In  $IS \leq 0.001 \text{ mol L}^{-1}$  NaCl polymer chains were stretched and  $IS \geq 0.001 \text{ mol L}^{-1}$  collapsed. An interesting fact was observed when adding  $0.001 \text{ mol L}^{-1}$  NaCl in a pH 7.40 solution, the signal response was increased comparing to pH 7.40 and  $0 \text{ mol L}^{-1}$  NaCl, but when adding  $0.001 \text{ mol L}^{-1}$  NaCl to a pH 3.00 solution, the signal response was decreased. This behavior can be explained in terms of protonation/deprotonation process and polymer brush regime. PDMAEMA brushes response was investigated by localized surface plasmonic resonance measurements (L-SPR), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS).

## 1. INTRODUCTION

Stimuli-responsive interfaces, which switch their physical and chemical properties in response to external stimuli, have attract interest of many field of technology such as drug delivery, diagnostics, tissue engineering and ‘smart’ optical systems, as well as biosensors, micro-electromechanical systems, coatings and textiles (Cohen *et al.*, 2010). Polymer brushes interfaces are typical example of such materials, they are polymer chains with one end attached to a surface, and have the property to switch the configuration, they can be stretched away from the surface (swollen), when in a good solvent for example, or they can be collapsed (shanked), in a bad solvent.

Poly(acrylic acid) has been extensively used as sensor pattern, in a previously work (Sempionatto *et al.*, 2014) it was demonstrated the behavior of PAA when pH solution was changed, in a range pH of 3.00 to 5.00 the polymer chains were stretched and at  $pH \geq 6$  the chains were collapsed. Poly(2,2 DMAEMA) are also largely study, in a recent work (Crulhas *et al.*, 2014) it was also demonstrated the PDMAEMA brush application as a glucose sensor – with glucose oxidase as an enzyme probe, which demonstrated a detection limit of  $5.6 \times 10^{-6} \text{ mol L}^{-1}$ .

The use of gold nanoparticles enhances the electrical signal and provide plasmon signal, plasmon is the phenomena that occurs when confined electrons on the boundaries of their materials oscillate within the electron-magnetic waves, generating quantified plasmon (Link and El-Sayed, 1999). In this work PDMAEMA brushes and gold nanoparticles were used to study their behavior when submitted to a pH range from 3.00 to 7.40 with different IS. Adding  $0.001 \text{ mol L}^{-1}$  NaCl in a pH 7.40 solution, the signal response increased comparing to pH 7.40 and  $0 \text{ mol L}^{-1}$  NaCl and when adding  $0.001 \text{ mol L}^{-1}$  NaCl to a pH 3.00 solution, the signal response decreased.

## 2. EXPERIMENTAL PROCEDURE

### 2.1 Chemicals and Reagents

PDMAEMA (P-9739-DMAEMA,  $M_w = 3100 \text{ g mol}^{-1}$ , Polymer Source), 3-glycidyloxypropyl-trimethoxysilane (GPS, Sigma-Aldrich), trisodium citrate dehydrate, toluene, Potassium hexacyanoferrate(III)  $[\text{Fe}(\text{CN})_6]^{-4}$  (Sigma-Aldrich), hydrogen tetrachloroaurate(III) ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ). ITO-coated glass ( $60 \text{ } \Omega/\text{sq}$  surface resistivity, Sigma-Aldrich) served as the working electrode, Pt/Ti Titanium Wire Anode ETO78 was employed as a counter electrode, and the reference electrode was a Ag/AgCl ( $3.0 \text{ mol L}^{-1}$ ) 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 PDMAEMA brushes using the "grafting-to" method (Witte mann *et al*, 2005) according to the following procedure. ITO-coated glass slides were cut into  $30 \text{ mm} \times 8 \text{ mm}$  strips. They were cleaned with ethanol in an ultrasonic bath for 15 min and dried in the atmosphere. The cleaning step was repeated using 2-butanone as a solvent. The initial cleaning steps were followed by immersing the strips into a cleaning solution composed of  $\text{NH}_4\text{OH}$ ,  $\text{H}_2\text{O}_2$ , and  $\text{H}_2\text{O}$  in a ratio of 1:1:1 (v/v/v) for 30 min. Subsequently, the glass strips were rinsed with water and then dried under atmosphere. The freshly cleaned ITO strips were reacted with 0.1% v/v GPS in dry toluene overnight. The silanized ITO was rinsed with several aliquots of toluene. Then  $60 \text{ } \mu\text{L}$  of a 1% wt PDMAEMA solution in toluene was spin coated to the surface of each ITO glass strip at 3000 rpm and left to react in a vacuum oven at  $140 \text{ } ^\circ\text{C}$  overnight. The final cleaning step to remove the unbound polymer consisted of soaking the samples in toluene for 10 min.

### 2.3 Preparation of Gold Nanoparticles

The synthesis of gold nanoparticles is described elsewhere (Roiter *et al*, 2012). Gold nanoparticles were attached on the PDMAEMA polymer brushes from a  $1 \text{ mmol L}^{-1}$  solution in water by incubating the samples overnight. The electrode was rinsed by several times with water to removed unbound gold nanoparticles.

### 2.4 Equipment and Measurement

Electrochemical measurements were performed with an ECO Chemie Autolab Microautolab

III/FRA2 with an electrochemical analyzer and a NOVA 10.0 software package. CV measurements and EIS analysis were performed with a three-electrode system in a standard eDAQ (Australia) ET-073 cell, using the polymer brush-modified ITO as working electrode, a Ag/AgCl/KCl 3 molL<sup>-1</sup> as a reference electrode, and a Pt/Ti Titanium Wire anode ETO78 as a counter electrode. CVs were performed from -0.2 to 0.7 V and the EIS analysis were recorded while applying a bias potential of 0.3 V and using a 10 mV alternative voltage in the frequency range of 100 kHz – 100 mHz. All solutions were buffered (0.01 molL<sup>-1</sup> phosphate buffer titrated to the pH values specified in the text with the use of NaOH or HCl) and 1.2 mmolL<sup>-1</sup> [Fe(CN)<sub>6</sub>]<sup>-4</sup> was used as redox probe. The measurements were carried out at ambient temperature. The pH measurements were performed with a Metrohm 827 pH Lab. TEM images were recording using a CM100, Philips. The AFM experiments were carried out with an Explorer model from Digital Instruments model Multimade. To minimize the surface deformation and material removal, the experiments were performed in intermittent non-contact mode, using a silicon cantilever with a spring constant of 70 Nm<sup>-1</sup> at scan rate of 1Hz. All measurements were taken under air at room temperature. As the roughness value depends on the observation scale, all experiments were carried out on a scale of 4 µm. UV-vis spectra were obtained using a Biochrom Libra S11 spectrophotometer from 400-600 nm with 1.0 nm step and speed of 500 nm min<sup>-1</sup>. A reference of PBS at specified pH was taken before each scan.

### 3. RESULTS AND DISCUATION

#### 3.1 Gold Nanoparticles characterization

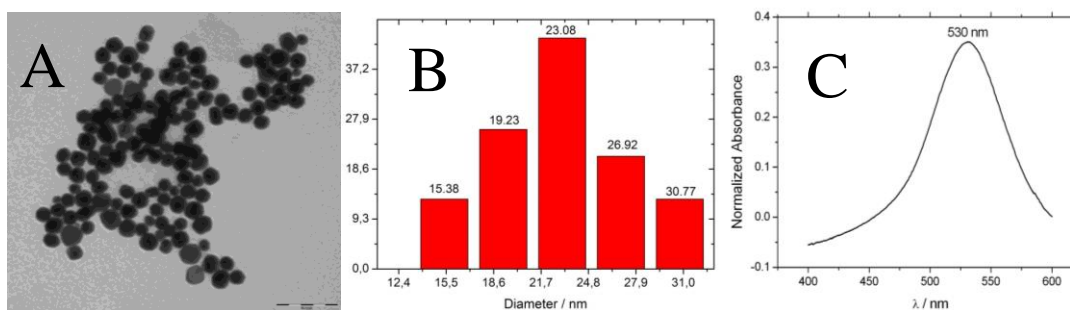


Figure 1 – A) MEV gold nanoparticle, bar scale: 0.1 µm. B) Size distribution histogram, N=400 (ImageJ). C) Absorbance measurement of gold nanoparticles.

Gold colloids are composed of an internal core of pure gold that is surrounded by a surface layer of adsorbed AuCl<sup>-2</sup> ions. These negatively charged ions confer a negative charge to the colloidal gold and thus, through electrostatic repulsion, prevent particle aggregation. All gold colloids display a single absorption peak in the visible range between 510 and 550 nm (Chaudhuri and Raychaudhuri, 2001), in this work the absorption peak was 530 nm (Figure 1C) which agrees with the average diameter 23.06 nm (Figure 1B). The gold nanoparticles showed a good size distribution and a relatively good dispersion.

#### 3.2 Electrode Characterization

MEV micrographs were taken before ITO modification with PDMAEMA brush (Figure 2A), after polymer modification and after gold nanoparticles covering (Figure 2B and 2C). As one can notice, the surface roughness was increased after polymer and gold nanoparticle modification. The film formed was homogeneous. On Figure 2C the gold nanoparticles is shown to be well distributed along the surface.

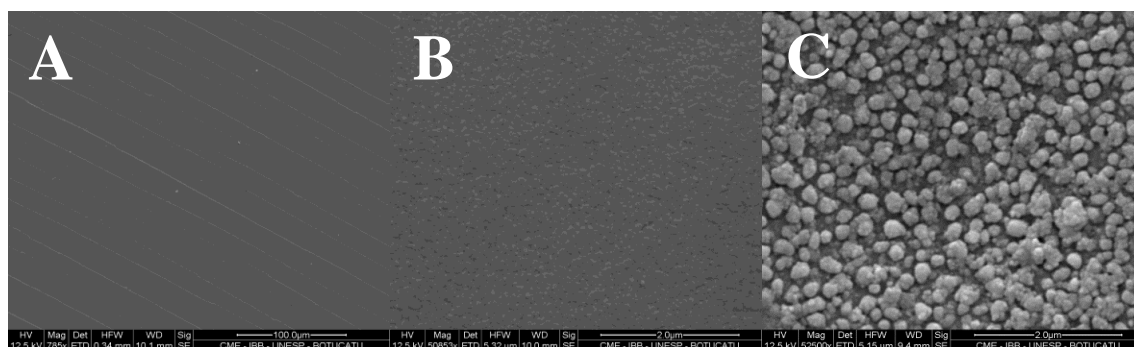


Figure 2 - MEV micrographs A) ITO, bar scale: 100 µm. B) ITO covered with PDMAEMA film, bar scale: 2 µm. C) ITO covered with PDMAEMA film and gold nanoparticles, bar scale: 2 µm.

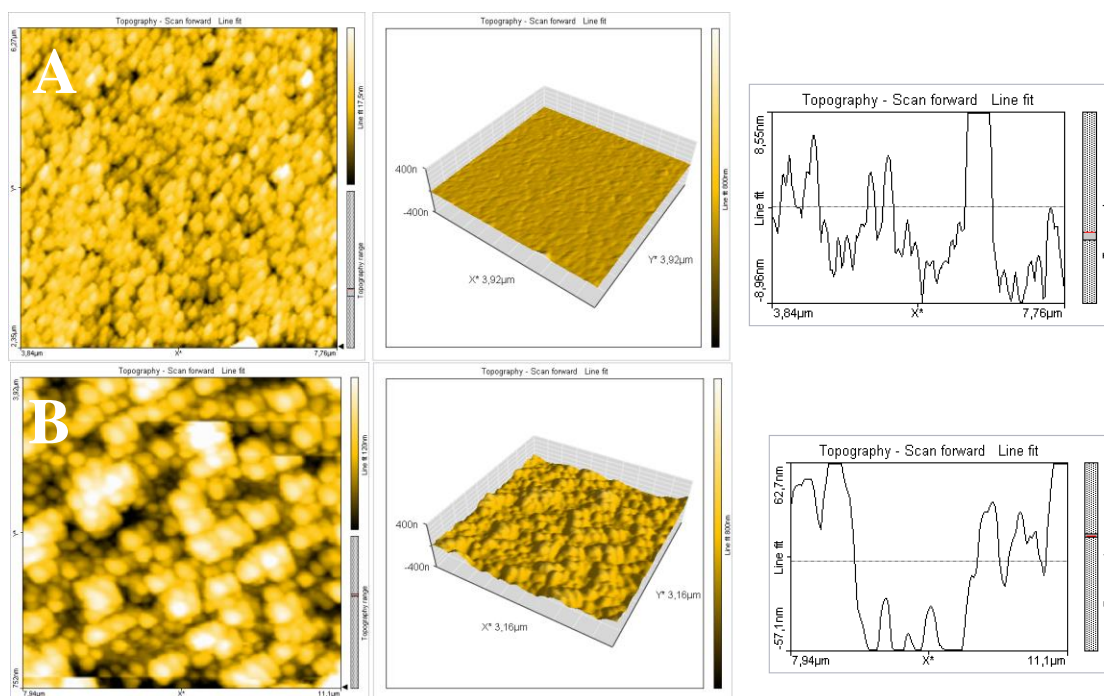


Figure 3 - AFM images and cross-sections of homopolymer brushes from PDMAEMA in air. A) PDMAEMA brush ITO modified electrode, rms roughness 2.6 nm. B) PDMAEMA brush ITO modified electrode covered with gold nanoparticles, rms roughness 28.0 nm.

The microscopic morphology of the PDMAEMA homopolymer brush grafted to the ITO was visualized with AFM (Figure 3A and 3B). The film appears as a macroscopically homogeneous flat

thin film with segregated domains (clusters with a  $0.13 \pm 0.02$   $\mu\text{m}$  diameter, rms roughness of 2.6 nm without gold nanoparticles and 28.0 nm with gold nanoparticles) that indicates the dimple (pinned micelles) regime of the brush.

### 3.3 pH selective switching

The PDMAEMA brush ITO modified electrode is a sensor of weak polyelectrolyte brush capable of change polymer chains configuration upon pH changes. The pH controllable shrinking-swelling of the thin film was studied by electrochemical and plasmonic analysis. The experiment started at pH 4.00 when the PDMAEMA was protonated, positively charged, swollen and permeable to anionic species  $[\text{Fe}(\text{CN})_6]^{4-}$  allowing their electrochemical process. Figure 3A shows CVs of  $[\text{Fe}(\text{CN})_6]^{4-}$  which redox reaction occurs with anodic peak potential at 0.3 V and cathodic peak potential at -0.1 V. The well-defined electrochemical response of the soluble redox species confirms the electrode “ON state”. At pH 7.40 the CV obtained showed a very small magnitude of current for both anodic and cathodic process, confirming that the sensor was in an “OFF state”. These results originates from the different states of the polymer brush, in pH 4.00 the polymer is stretched and allows the diffusional translocation of the polymer chains providing the electrochemical process and at pH 7.40 the polymer is collapsed decreasing the electrochemical process. The proposed behavior is in accordance with the previously reported systems based on polymer brushes (Cohen *et al.*, 2010). The peak-to-peak separation of CV for the redox couple increased gradually with increasing of pH, which is probably due to the increase of the electron-transfer resistance. Figure 4B shows that the resistance increased from 587.5 (ON state pH 4.00) to 3663.5 k $\Omega$  (OFF state pH 7.40) with increasing of pH, which is consistent with the evidence obtained by CV. The  $R_{ct}$  values were estimated by extrapolation of the semi-circle observed in Nyquist plot. On the insert of Figure 4B  $R_{ct}$  and  $R_s$  (surface and electrolyte solution resistance) values are shown for each pH.

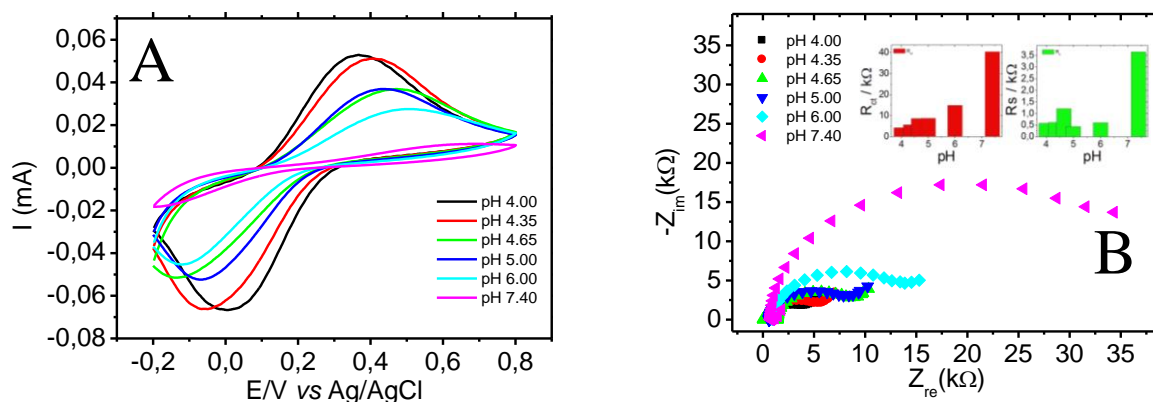


Figure 4 – A) Polymer brush sensor CV,  $1.2 \text{ mmolL}^{-1}$   $[\text{Fe}(\text{CN})_6]^{4-}$  in  $0.01 \text{ molL}^{-1}$  PBS buffer and  $50 \text{ mVs}^{-1}$ . B) EIS for the polymer brush sensor,  $0.01 \text{ molL}^{-1}$  PBS buffer,  $1.2 \text{ mmolL}^{-1}$   $[\text{Fe}(\text{CN})_6]^{4-}$ , bias potential 0.3 V vs Ag/AgCl.

Such specific behavior regarding active state of brush polymers with pH changes has been observed by UV-vis light, L-SPR measurements. L-SPR measurements were also performed to confirm the attachment of the gold nanoparticles on the polymer brush endings. In Figure 5, one can see the shift caused by different solution pHs. The measurements confirmed that the film was sensitive to pH changes.

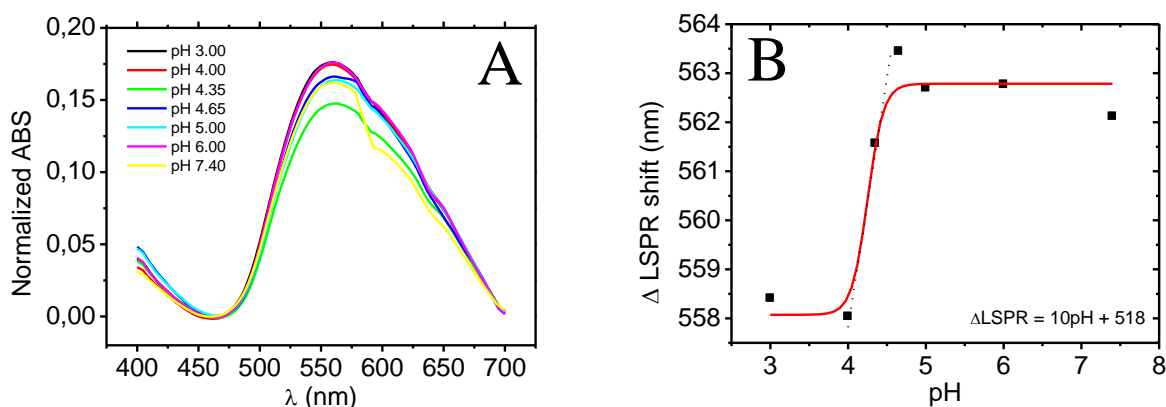


Figure 5 – A) L-SPR in a pH range from 4.00 to 7.40 for ITO/PDMAEMA/Au electrode; B) Titration curve pH 4.00 to 7.40.

Changes in absorption spectra were reproducible, indicating that the PDMAEMA brushes take a reversible stretching motion depending on the pH change. These data are consistent with the results obtained from CV experiments and demonstrate that the gold nanoparticles are successfully immobilized on the brush-modified electrode. In Figure 5B one is able to see the titration curve of the ITO/PDMAEMA/Au electrode, with the pH range varying from 4.00 to 7.40. In a pH range from 4.00 to 4.50 there is a linear behavior, the linear fit indicates a 10 nm shift for each pH unit change. This pH-sensing range suggests potential application for pH determination.

### 3.4 Ionic strength selective switching

In addition to being pH responsive, weakly polybase polyelectrolyte brushes such as PDMAEMA are also responsible to changes in solution IS. Figure 6 and 7 show CV and EIS response of PDMAEMA brushes at two concentrations of background NaCl electrolyte: 0.001 and 1.000 molL<sup>-1</sup>, at pH 7.40 and 4.00. By studying low and high IS values, one is able to see a reduction in the CV magnitude using either high or low IS at pH 4.00 (Figure 6A) and an increasing of magnitude at pH 7.40 when using low IS and decreasing when using high IS at the same pH (Figure 6C). At pH 4.00 the brush is fully stretched, however the thickness of brushes decreases as the solution IS is increased, this because the polymer brushes start to collapse. This is in line with the theoretical understanding of an equilibrium weak polyelectrolyte brush response (Zhulina *et al*, 1996). As solution IS is increased, a higher pH is required to avoid the brushes to collapse, for that, at pH 7.40 and IS 0.001 molL<sup>-1</sup> the signal magnitude is bigger than the same IS at pH 4.00.

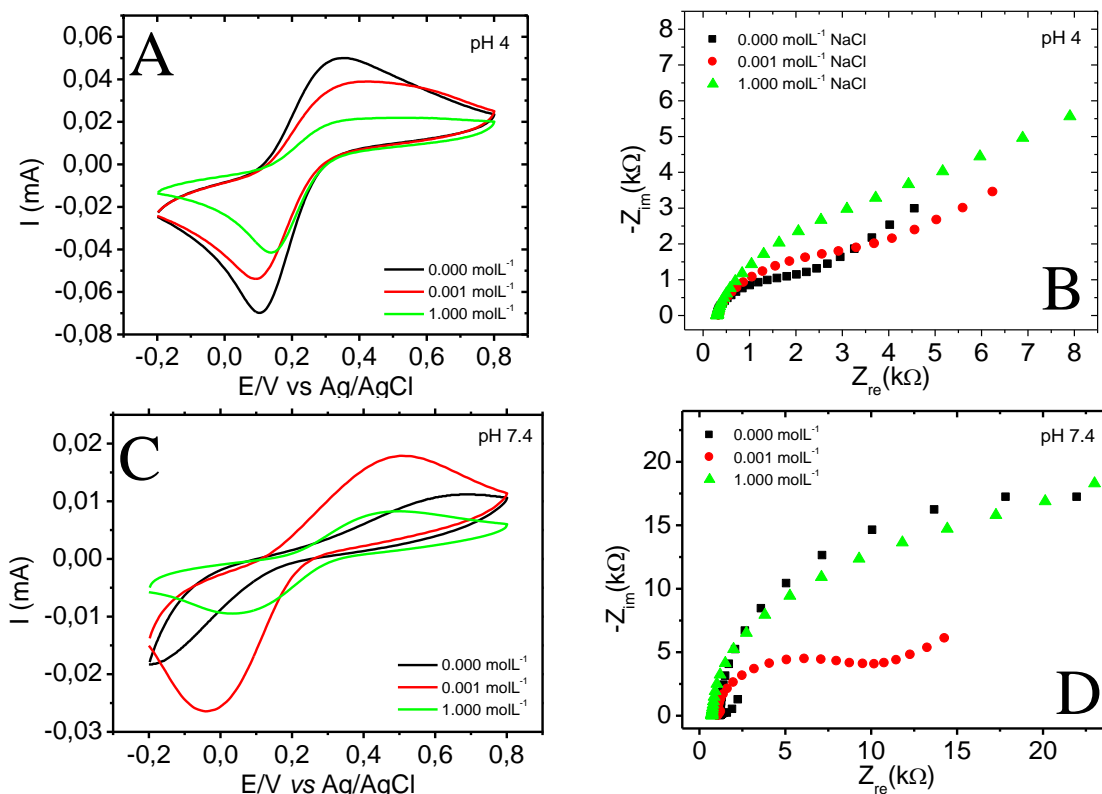


Figure - A) pH 4.00 C) pH 7.4. - CV 50 mVs<sup>-1</sup>, 0.01 molL<sup>-1</sup> PBS. B) pH 4.00 D) pH 7.4 - EIS bias potential 0.3 V, 0.01 molL<sup>-1</sup> PBS vs Ag/AgCl.

With these results it is possible to distinguish two kinds of osmotic regimes for weak polyelectrolyte brush. The conventional osmotic regime is achieved within a low concentration of salt; in the osmotic regime the concentration of salt in bulk solution is small and the concentration of counter ions inside the brush is almost equal to that of the immobilized charge. This kind of regime is found at pH 4.00 and 0.001 molL<sup>-1</sup> IS, in this case, the brushes become almost neutral and the signal intensity is decreased. The non-conventional osmotic regime is achieved when the IS is increased, one can notice this behavior at pH 7.40 and 0.001 molL<sup>-1</sup> IS. In this case, the positively charged counter ion of the salt acts just like the hydronium ion (H<sub>3</sub>O<sup>+</sup>), changing the degree of brush ionization, causing the swollen of the brushes by electrostatic repulsion increasing the redox reaction of [Fe(CN)<sub>6</sub>]<sup>4-</sup> (Zhulina *et al*, 1996). When a very high IS value is used, the regime changes from osmotic to salted regime. In the salted brush regime the salt ion charges dominate compared to the immobilized charges inside the brushes due to the high concentration of salt in the bulk. This regime is found in both pH when 1.000 molL<sup>-1</sup> IS is used. The brushes are completely neutralized by the counter ions and the redox reaction of [Fe(CN)<sub>6</sub>]<sup>4-</sup> is diminished.

## 4. CONCLUSION

The synthesized electrode showed to be switchable by changing solution pH. At pH 4.00 the

sensor was in an “ON state” and at pH 7.40 in an “OFF state”; CV and EIS confirmed this behavior. L-SPR measurements showed a 10 nm shift for each pH unit increased, what is a great sensibility for a pH sensor. In addition to being pH responsive, the sensor was also responsible to changes in solution IS. At pH 4.00 when the brushes were in an ON state,  $\geq 0.001 \text{ molL}^{-1}$  IS was able to drive it to the OFF state, and at pH 7.40 when the brushes were in an OFF state  $\geq 0.001 \text{ molL}^{-1}$  IS was able to drive it to the ON state. It was also reported a change in the brush regime when using high and low IS, for  $\text{IS} \leq 0.001 \text{ molL}^{-1}$  the brushes were at the osmotic regime and at  $\text{IS} \geq 0.001 \text{ molL}^{-1}$  in the salted brush regime. These results presented in this work are of great value to contribute to PDMAEMA brush knowledge and also suggest an excellent candidate for pH and salt platforms sensor, which can be used in lots of science fields.

## 5. REFERENCES

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