11th International Conference on Advanced Materials
Rio de Janeiro Brazil
September 20 - 25
ICAM2009

Kinetics and Stability Studies of PPID/NiTsPC LbL Films as pH Sensitive Membrane

N. C. S. Vieira[(1)*], E. G. R. Fernandes[(1)], A. A. A. de Queiroz[(2)], V. Zucolotto[(1)] and F. E. G. Guimarães[(1)]

(1) Instituto de Física de São Carlos/Universidade de São Paulo, São Carlos – SP – Brasil e-mail: nirton@ursa.ifsc.usp.br
(2) Instituto de Ciências Exatas/Universidade Federal de Itajubá, Itajubá – MG – Brasil
* Corresponding author.

Abstract – We presented the fabrication and stability of layer by layer (LbL) films based on poly(propylene imine) dendrimers (PPID) and nickel tetrasulfonated phthalocyanines (NiTsPc) as pH sensitive membranes. Relevant parameters of the films preparation were examined and optimized. The pH sensitivity was determined by an Extended Gate Field Effect Transistor (EGFET). As chemically sensitive membrane, PPID/NiTsPc films deposited on ITO substrate presented pH sensitivity close to the ITO itself, indicating that the LbL film porosity allows ion transport from the solution to the substrate.

Several redox enzymes produce H^+ ions as catalysis product, changing the pH of the chemical environment. In this way, pH sensitive films for biosensing applications are of great interest. Oppositely charged layers of different materials can be adsorbed on different substrates in the form of thin films using the layer by layer technique (LbL) [1]. Here, we describe the fabrication and stability of LbL films based on poly(propylene imine) dendrimers (PPID) and nickel tetrasulfonated phthalocyanines (NiTsPc) which are suitable as template for enzyme immobilization and as pH sensitive membranes.

Fig. 1 shows the NiTsPc absorption evaluated at 610 nm after each bilayer deposition of PPID/NiTsPc during the growth procedure. The PPID/NiTsPc system exhibits a linear growth regime after 10 bilayers. A significant exponential growth of the system is observed only for the first 10 bilayers as reported elsewhere for other dendrimer/NiTsPc system [2]. The insert of Fig. 1 demonstrates that the NiTsPc Q-band in the LbL film shows a blue shift 13 nm from the solution spectrum as result of the formation of H-aggregates [2].

The PPID/NiTsPc pH sensitivity was determined by EGFET [3]. Here we measured the threshold voltage (V_T) of a MOSFET for different pH buffer solutions. The 5 bilayes of PPID/NiTsPc deposited on ITO and Au substrates presented pH sensitivity of 52.4 mV/pH and 30.3 mV/pH, respectively, and a linear behaviour in a pH range between 4 and 10 (Fig. 2). For ITO alone, the sensitivity was around 58 mV/pH, indicating that the PPID/NiTsPc film porosity allows that ion transport from solution to the ITO surface. The insert of Fig. 2 indicates that the PPID/NiTsPc films are unstable in pH higher than 10 and that the EGFET signal is probably due to ITO substrate. Aiming for further applications in biosensors, PPID/NiTsPc layers would support the immobilization of redox enzymes which produces H^+ ions, since the pH in the environment of the LbL film can be changed after a catalysis reaction.

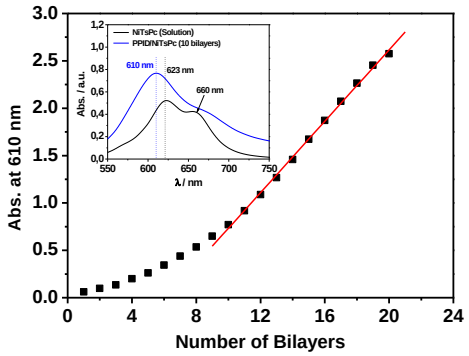

Figure 1: Growth regime for PPID/NiTsPc system. Insert: Absorption spectra for NiTsPc in solution and for a LbL film.

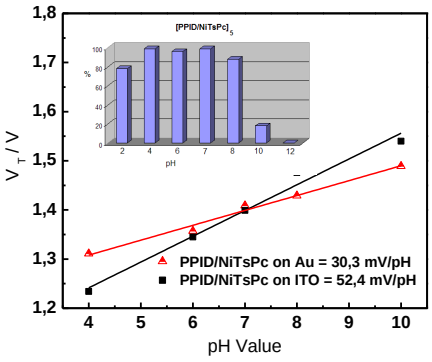

Figure 2: Characteristics of PPID/NiTsPc as pH sensing membrane in EGFET configuration. Insert: PPID/NiTsPc film stability in different phosphate buffer solution.

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