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SPR SENSITIVITY IMPLICATIONS ON PYRROLE POLYMERIZATION

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The Surface Plasmon Resonance (SPR) is a technique well established as a highly sensitive biosensing tool. This work expanded the use of the SPR by the real-time monitoring of the pyrrole electropolymerization, thus obtaining an intrinsically conductive polymer. The high sensitivity of SPR indicates a specific range in which accurate measurements can be achieved. This paper also defined the optimal range from which reliable data can be acquired with the SPR during the polymerization.

Keywords: Surface Plasmon Resonance, Polypyrrole, Electrochemical Polymerization, Conducting polymers, Cyclic voltammetry

1. Introduction

The intrinsically conductive polymers (ICP) are a class of polymers that received special attention since the work of Bolto et al in 1963 [1,2]. Diaz et al looked at the electrochemical polymerization and characterization of the polypyrrole (PPy) films, highlighting the possibility of PPy states that can be either conductive or non-conductive [3,4]. Since then the research interest has been sparked, culminating with a Nobel prize award in 2000 for the conductive polymers [5]. The PPy films touches a wide range of applications such as corrosion protection [6,7], highly sensitive DNA sensor [8,9] and, due to its biocompatibility [10], it can find its use in tissue engineering applications [11–13] such as the use of PPy as substrate-mediated promotion of osteogenesis [14,15] or to study *in-vitro* the dental plaque formation [16]. Into the recent trend of lowered sizes, the PPy was synthesized as microwires [17], micro- and nano shells [18], one-dimensional self-assembled nano-structures [19] and ultrathin nanosheets [20]. In this work the focus will be on the pyrrole (Py) polymerization through a technique known to have a sensitivity in the range of 1 ng/mm^2 [21]. The technique is known as Surface Plasmon Resonance (SPR) and due to its high sensitivity [22] it is an already well established analysis technique for biosensors

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applications [23] and lab-on-a-chip sensors [24]. To our knowledge, until now the literature has dealt only with *i)* the lower part of the SPR sensitivity spectrum [21,23] and *ii)* the PPy film characterization (either during or after Py polymerization) [1,2,10,11,18]. This paper will follow a new approach of probing the SPR sensitivity spectrum by the study of double layer charge and of the Py polymerization on the surface.

2. Materials and methods

The $LiClO_4$ and Py reagents were purchased from Sigma Aldrich. Ultrapure Millipore water of 18 MΩ·cm was used for the experiments.

The SPR measurements were carried out on a gold surface, using an Autolab SPR Springle instrument which has the advantage of analysis of biomolecular interactions in real time without labelling. The SPR couvette served also as an electrochemical cell. The electrochemical cell is composed of the SPR's gold surface as working electrode, an Ag/AgCl reference electrode and a Pt counter electrode. The three electrode system was connected to a Metrohm Autolab PGStat 100N potentiostat. The electrochemical data were acquired and processed with Nova 1.10 software while the SPR data were acquired with Data Acquisition 4.3.1 software with the processing made by Kinetic Evaluation 5.1 software.

The SPR data were recorded during electrochemical cyclic voltammetry measurements in the potential range from 0 V to 0.9 V. The cyclic voltammetry was performed with a scan rate of 0.1 V/s at room temperature.

3. Results and discussion

3.1. SPR signal during cyclic voltammetry

The cyclic voltammetry involved five positive potential sweeps from 0 V to 0.9 V vs Ag/AgCl electrode. The SPR angle response is shown in Fig. 1.

In the lithium perchlorate electrolyte (0.1 M $LiClO_4$) a phenomenon of surface charging is occurring. Considering the positive potential range, we suppose that the ClO_4^- anions are contributing to the surface charge.

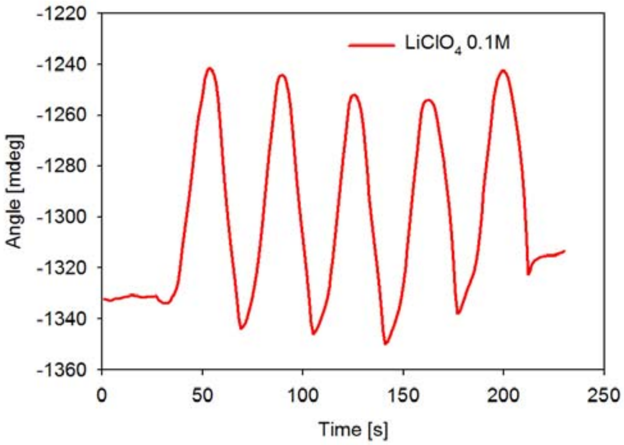


Fig. 1. The SPR response in LiClO$_4$ electrolyte during the cyclic voltammetry sweep (5 cycles) between 0 and 0.9 V

Since Au (or gold) serves as the common interface for the working electrode and for the SPR detection, the change in surface charge is sensed by a change in SPR angle (measured in millidegrees, mdeg) as a function of time during the potential sweep (of 0.1 V/s rate). It can be observed that a positive change around 100 mdeg is recorded during the surface charge (positive sweep) which returns approximately to initial state during the surface discharge (reverse sweep). This aspect shows the SPR’s high sensitivity in the lower range, which allows the sensing of double layer charging at the interface between the Au electrode and the electrolyte.

Subsequently, we will look into the other system, pyrrole polymerization, which also involves electrochemical reactions at the interface.

3.2. The Py concentration and the SPR signal during polymerization

To study the kinetics of Py electropolymerization, the SPR signal needs to be in the appropriate range. The Autolab SPR Springle used in these experiments has a 4 degrees range for the reflection minima shift.

The reflection minima shift in sensing is usually related to a proportional measure of mass change [25]. A Py concentration of 0.02 M was initially added into 0.1 M LiClO$_4$ electrolyte to study the polymerization kinetics and the same cyclic voltammetry conditions were applied in order to polymerize Py to PPy. We noticed that when the 0.8 V potential value is reaching, the polymerization is initiated [7]. In Fig. 2, the 5 succesive cycles of cyclic voltammetry cannot be observed, as they are covered (hidden) by SPR artefacts.

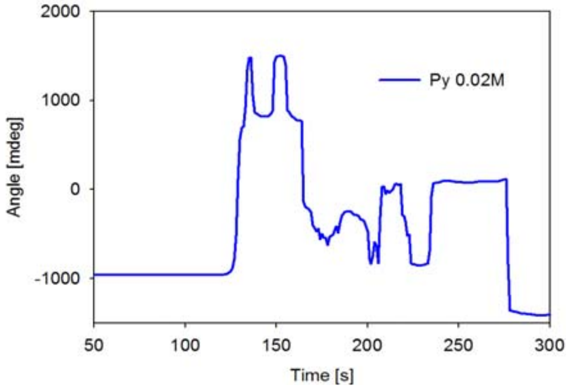


Fig. 2. The SPR response for the cyclic voltammetry polymerization during 5 cycles sweep between 0 and 0.9 V from a solution containing 0.02 M Py and 0.1 M $LiClO_4$

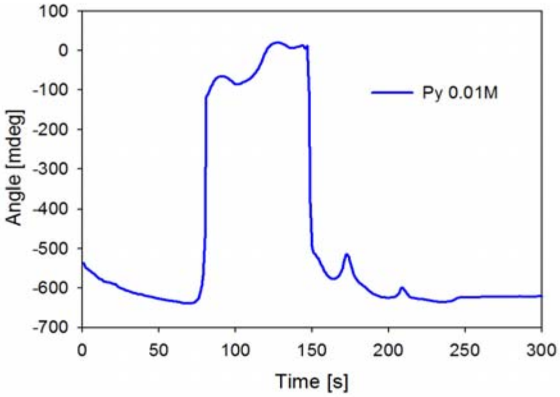


Fig. 3. SPR response for the cyclic voltammetry polymerization during 5 cycles sweep between 0 and 0.9 V from a solution containing 10 mM Py and 0.1 M $LiClO_4$

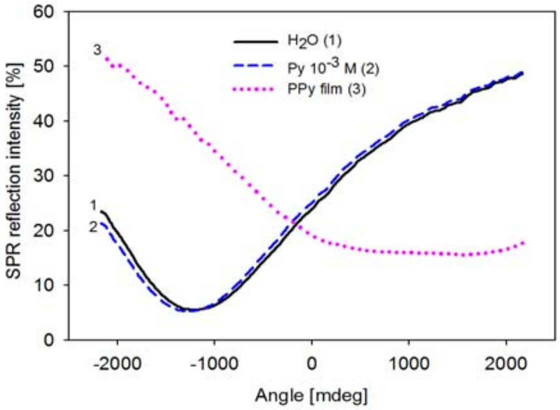
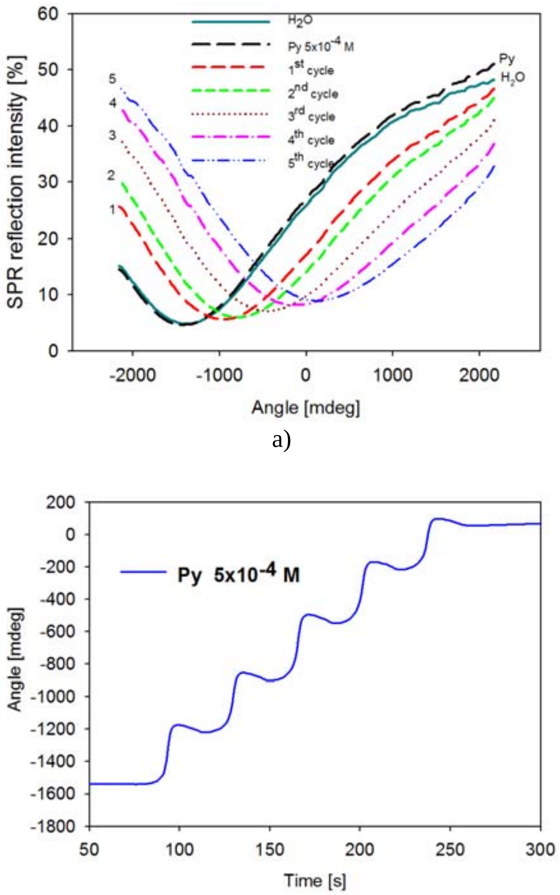


Fig. 4. A comparison between the SPR angle minima for the ultrapure water (H_2O), the $1 \cdot 10^{-3}$ M Py polymerization solution and the final obtained PPy film.

When decreasing the Py concentration to 0.01 M the polymerization maxima can be observed with better clarity in Fig. 3. However, the same type of artefact prevents a proper reading. Notably, in the experiments with 0.02 M and 0.01 M of Py concentration, the current profile is similar with the one obtained in a previous published work [26], indicating a normal polymerization.



a)

b)

Fig. 5. (a) The SPR angle minima vs. the angle value for water, $5 \cdot 10^{-4}$ M Py solution and during the 5 voltammetric cycles; (b) The corresponding angle evolution of the angle in time for the polymerization of a $5 \cdot 10^{-4}$ M Py electrolyte during the 5 cyclic voltammetry sweeps

Examples of relevance for this case are shown in Fig. 4 for *i)* ultrapure water (H_2O), *ii)* the polymerization electrolyte with Py at a concentration of $1 \cdot 10^{-3}$ M and *iii)* the resulting PPy film after the polymerization. It can be observed that although the SPR signal kept the same shape for the liquid solutions, the PPy film changed the profile of the minima. This fact represents a difficulty in reading the kinetics of the angle change as a function of time. Consequently, the concentration needs to be further decreased for an adequate measurement.

Using a $5 \cdot 10^{-4}$ M Py concentration in the electrolyte during polymerization SPR signal yields an appropriate reflectivity curve. During each voltammetric cycle the reflectivity preserves its minima, as observed in Fig. 5 a. In the same figure a noticeable difference is observed in the SPR reflectivity for the water comparing to the Py/electrolyte solution, confirming the high sensitivity of the SPR technique [21].

We noticed that this low concentration of $5 \cdot 10^{-4}$ M Py in solution is sufficient for an accurate measuring of the polymerization kinetics. As observed in Fig. 5 b, the polymerization kinetics (namely the mass buildup due to Py oxidation and polymerization into PPy) can be easily monitored for each of the 5 voltammetric cycles. Therefore this concentration value can be considered as the upper limit from which reliable kinetic data can be recorded with the SPR instrument.

4. Conclusions

This study investigated the optimal concentration of Py monomer in the aqueous electrolyte that would allow reliable measurement of PPy polymerization kinetics. The Py concentration range was experimented between 0.02 M down to $5 \cdot 10^{-4}$ M. However, the $5 \cdot 10^{-4}$ M was found as the maximal concentration which allowed SPR monitoring.

The results indicated that the limitation was not given by the measuring range of the instrument, but rather by the Py concentration in the supporting electrolyte.

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