Surface Plasmon Resonance in the Study of Phenol Electropolymerization at Ultralow Concentration

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Electrochemical and Surface Plasmon Resonance (SPR) experiments are made in ultrapure water at ultralow concentrations of phenol. SPR technique has been proved to be complementary to the electrochemical technique in the study of surface adsorption/desorption and phenol polymerization process.

Keywords: Surface Plasmon Resonance, Cyclic Voltammetry, phenol, polymerization, adsorption

Phenol is a chemical compound that received scientific attention especially due to the necessity of its control and removal from the wastewaters [1,2]. This requirement resides mainly in its inherent toxicity when certain threshold levels of concentration and exposure times are reached [3]. The phenols presence have a distinct contribution to the sensory characteristic of drinking water [4], wines [5,6], olive oils [7], and other aqueous solutions [8]. The phenols are also readily present in plants at low concentrations, or as part of compounds such as hormones, vitamins, and antioxidants [8], with the phenol as a prominent candidate in metabolite signaling of the plants [9]. The phenols are excreted with urine and they can be an indication of both increased exposure to phenol [10] but also of chronic kidney disease [11]. Recent studies promote the phenols detection through High Performance Liquid Chromatography (HPLC) [11], Gas Chromatography–Mass Spectrometry (GC-MS) [12] and Selected Ion Flow Tube-Mass Spectrometry (SIFT-MS) [13] techniques. Other techniques that can detect phenol are the electrochemical techniques via modified electrodes [14-17] and the Surface Plasmon Resonance (SPR) technique with inorganically or organically functionalized substrates [18-20]. The objective of this paper is to use the highly sensitive electrochemical and SPR techniques into an approach that focuses on the phenol electro-polymerization reaction at the gold interface by keeping the phenol concentration as low as 50 μM in the aqueous solution.

The electrochemical investigation on the phenol oxidation is performed at the interface of a gold working electrode. The same interface also allows for Surface Plasmon Resonance measurements, which provides a sensitive investigation on the surface kinetics down to the picogram range [21]. The hybrid use of these two techniques (the electrochemical technique and the SPR technique) reflects aspects of the reactions that occur at interface form both a coulomb perspective but also from an indirect masic perspective [22].

Experimental part

Materials and methods

The electrochemical cell was composed of a gold (Au) working electrode, an Ag/AgCl reference electrode and a platinum counter electrode connected to an Autolab PGStat 302N. Millipore 18MΩ · cm ultrapure water (UW) was used for the experiments, in which 50 μM of phenol (Phe) was added as needed. In order to prevent the ohmic drop, the distance between the Au and the Ag/AgCl electrodes was at >1 mm. The Au electrode interface is also the sensing surface for the SPR measurements, recorded on Autolab SPR Springle equipment. Details on the experimental setup can be found in a previous work [23].

Results and discussions

The electrochemically coupled SPR technique is a good candidate to study both the non-Faraday current due to surface charge, but also the Faraday currents produced by the redox reactions at the interface [24]. Gold is a noble metal that does not oxidize only until around 1.23 V vs Ag/AgCl [25], while in the range used in this study only charging due to water molecule arrangement on gold as Au(OH) and Au(O), but only as adsorbed molecules [26]. Since the ultrapure water (UW) is not a completely pure water [27], other ions that are present in negligible quantity and are adsorbed on the surface, leading to a surface charging. This is experimentally observed by an overall surface charging during one voltammetric cycle of 1.3 C/cm^2, but also to an SPR response of 3.33 m°/s·cm^2, as observed form the experimental data shown in figure 1.

In a previous work it had been highlighted that the SPR angle change is proportionally to an applied potential change as a function of three main variables [26]: *i*) changes in the electronic states for the adsorbed molecules (in both real and imaginary parts of the interface dielectric permittivity, namely ε_r and ε_i), *ii*) changes in the average thickness of the adsorbed layer (d_a) and *iii*) changes of dielectric constant for the metal film (ε_m). In figure 1 until around 0.4 V the change of the metal ε_m leads to a SPR angle decrease, while after subsequent increase of the

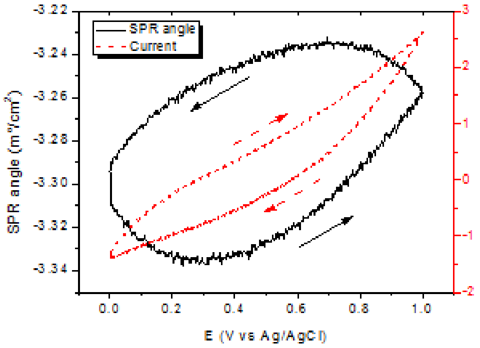

Fig. 1. Current and SPR angle response during first potential scan in ultrapure water

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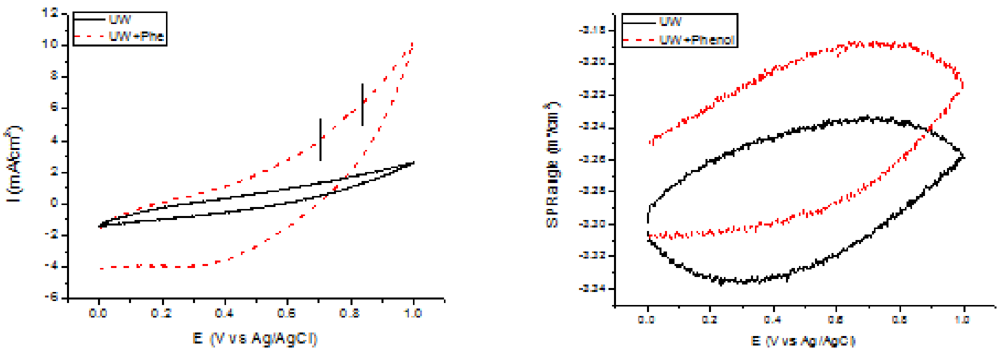

Fig. 2. The electrochemical (a) and SPR responses (b) in the presence and absence of Phenol in ultrapure water

potential, the adsorbed molecules thickness, d_a, have an measurable contribution to the SPR. Notably, the electrochemical data in figure 1 shows that the adsorption is reversible.

In the same anodic region the phenol is electrochemically oxidized at +0.7 V vs Ag/AgCl [28], where by an reaction mechanism via phenate anions, the polyphenol film is obtained [29,30]. In figure 2a the surface charge build-up during the potential ramping can be observed. This is associated mainly to the phenol mass transfer to the Au surface via an electropolymerization reaction. However the resulted electron obtained in the phenol reaction does not migrate through the ultrapure water as it would in an electrolyte with high ionic strength. This leads to an almost undistinguishable oxidation peak at around +0.7 V, as observed in figure 2a. Since the SPR response is related to the dielectric permittivity (namely ε_r, ε_i and ε_m) and to the film thickness (d_a) [26], thus is not constrained by the ionic strength. This allows a reliable study of the oxidation and implicitly the polymerization of the phenol in ultralow ionic strength. In figure 2b an evidence of the phenol polymerization around the +0.7 V region is shown by a significant SPR angle increase for carbolic acid. Comparing the SPR profile for the phenol polymerization to the SPR profile for the ultrapure water, a clear cumulative process is occurring. This process is generally associated to the changes in the real part of the dielectric permittivity, ε_r, but mainly to the increase in film thickness, d_a [26].

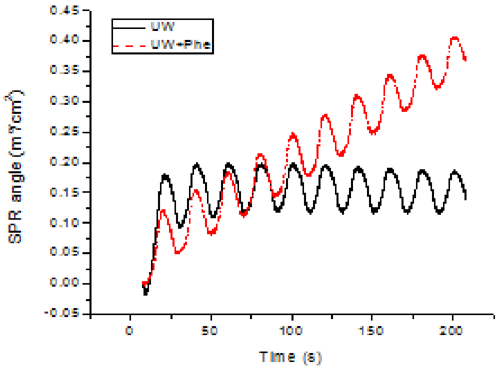

Fig. 3. SPR response evolution in time during ten potential scans in ultrapure water with and without 50 μM Phenol

The SPR response was monitored for a longer period of time, during 10 voltammetry cycles, as shown in figure 3. For ultrapure water the averaged slope of the SPR is slightly below 0.19 μ°/s (or $2\cdot10^{-4}$ m°). This is mainly associated to the reversible adsorption of the deionzed water species on the surface, which in turn produces changes in ε_r at the interface. When considering the phenol oxidation and polymerization during the voltammetric cycling, the slope increases with an order of magnitude to 1.7 μ°/s. Such an increase is associated to the irreversible overall increase of the polyphenol film thickness d_{a-} obtained by the electropolymerization.

Because of the different phenomena involved in the cyclic voltammetry, namely adsorption and desorption of species on Au and the electropolymerization in the case of phenol addition, the SPR profile is particular for each polarization cycle. For a better quantification, each cyclic polarization was dividend in two mathematical values that describe the SPR behaviour: i) the amplitude (*A*) value and ii) the increment (Δ) value. The two parameters are highlighted in figure 4 for ultrapure water with and without carbolic acid.

In figure 4 the amplitude (*A*) behaviour describes essentially all number of the species that are adsorbed onto the Au surface. The higher the amplitude value, the more species are adsorbed onto the surface. This *A* value can be defined as the angle gain from the start of the polarization (at 0 V vs Ag/AgCl) to the reverse point of the polarization (1 V vs Ag/AgCl) for each individual voltammetry cycle. The increment value can be defined as the difference between the value of the initial and the final angle for one voltammetry cycle. The increment value, *Ä*, describes the species that are adsorbed irreversible to the surface (such as the case of surface bonding due to the phenol polymerization) and gives an essential overview on the average thickness of the polymerized polyphenol layer, d_a, as it has been shown previously [26]. The difference form *A* and Δ implicitly give contribution of the species that are desorbed form the surface.

In figure 5 the numerical values for amplitude and Δ are represented in bar graphics. The most important difference is observed for the first cycles of electrochemical

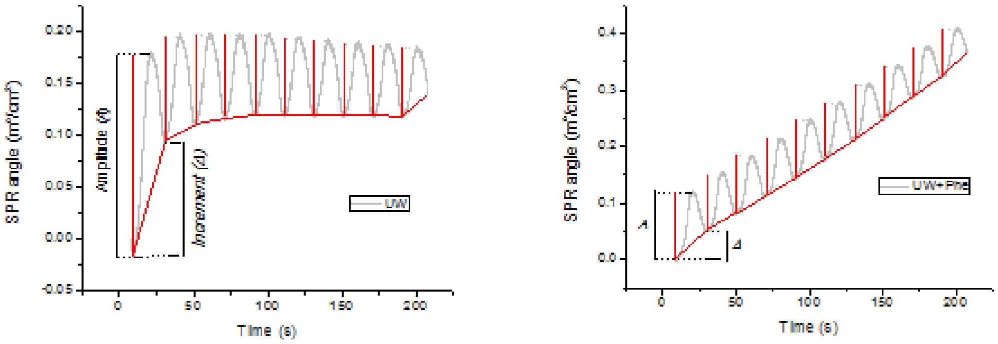

Fig. 4. The representation of the amplitude and the angle increment for the SPR resonse after each voltammetry cycling with a) ultrapure water and b) ultrapure water containing 50 μM Phenol

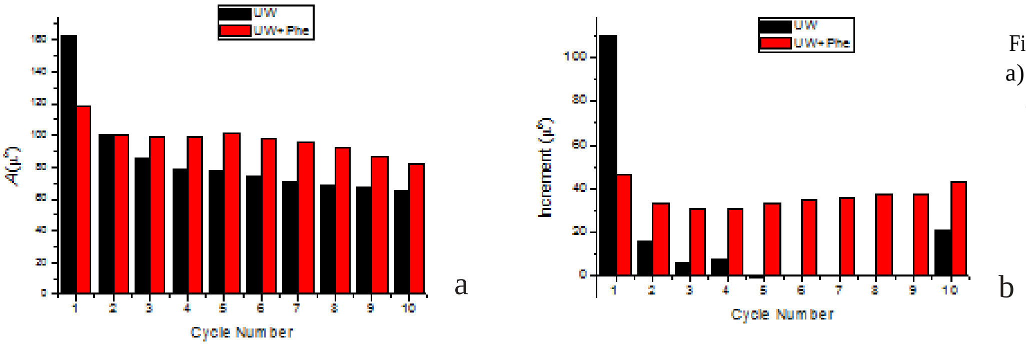

Fig. 5. The representation of the a) amplitude (A) value and the b) angle increment (Δ) for each cyclic voltammetry with and without 50 μM Phenol in ultrapure water

polarization, for both the amplitude value and the Δ value. This is mainly because it is an initial adsorption step that proceeds from a metastability state, a state that is not recurring during the repetitive voltammetric cycling. This means that an increased number of molecules are adsorbed onto the Au surface for the starting cycle.

The amplitude valued in figure 5a for ultrapure water shows a slight decrease for each polarization cycle. This indicates a slight decrease of the adsorbed/desorbed species on to the interface as cycling proceeds. During the phenol polymerization, the amplitude values show an overall increase in the adsorbed/desorbed species. This can be associated mainly to the changes in ε_r but also to the increase of the film thickness, d_a, via what can be called as permanently adsorbed species of polymerized phenol.

The angle increment, Δ, in figure 5b shows a decreasing trend until the 4th cycle of voltammetry. This means that a hydration layer is cyclically adsorbed and desorbed until an overall equilibrium is obtained from the 5th cycle, when $\Delta \approx 0$. The value for the last polarization cycle is different from the previous cycles most likely due to the change in ε_m of the thin Au film induced by the interface change of ε_r from the one for ultrapure water to the one for the polyphenol film. The different values of Δ for the phenol polymerization are most likely due to a diffusion process [31] which is not occurring homogenously for each of the voltammetry cycles.

Conclusions

Aspects of the hybrid electrochemical and SPR measurements were highlighted. The limitations of the electrochemical technique in ultrapure water were complementarily overcome by SPR measurements. The SPR results were highlighted based on three key parameters: *i*) the complex dielectric permittivity, *ii*) the change in dielectric permittivity of Au and *iii*) the adsorbed layer thickness.

Original processing of the SPR data obtained after the cyclic voltammetry allowed us to define two new experimental parameters: a) amplitude and the b) increment value. The amplitude measurements highlighted aspects of the adsorption and desorption processes on the surface, while the increment of the SPR angle for each voltammetry cycle provided experimental insight on the increasing thickness of the polyphenol film.

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