Available online at www.sciencedirect.com

SCIENCE DIRECT®

ELSEVIER

Electrochimica Acta 51 (2006) 1304–1312

ELECTROCHIMICA Acta

www.elsevier.com/locate/electacta

Investigations of ultrathin polypyrrole films: Formation and effects of doping/dedoping processes on its optical properties by electrochemical surface plasmon resonance (ESPR)

Flavio S. Damos, Rita C.S. Luz, Lauro T. Kubota*,[1]

Institute of Chemistry, UNICAMP, P.O. Box 6154, 13084-971 Campinas, SP, Brazil

Received 17 March 2005; received in revised form 29 April 2005; accepted 25 June 2005

Available online 1 August 2005

Abstract

In the present work an investigation of the effects of the electropolymerization mode on the optical properties associated to the doping/dedoping processes of nanometric films of polypyrrole (PPy) is reported, monitoring in situ and in real time using simultaneously surface plasmon resonance and electrochemical techniques (ESPR). The electropolymerization of pyrrole was performed by potentiostatic, potentiodynamic and galvanostatic methods and the use of the ESPR technique showed that the electropolymerization mode is essential to the stability of polymer and the reversibility of its optical properties during the doping and dedoping processes. Thus, the optical properties of oxidized and reduced film were obtained by nonlinear least square fitting using Fresnel equations for a four-layer system. Then, the values of the real and imaginary parts of the complex dielectric constant for PPy fims were correlated with the polymer doping level. Finally, quartz crystal microbalance measurements were also applied to obtain correlation between doping/dedoping processes and the changes in the real and imaginary parts of the dielectric constant of the polypyrrole film, showing that the doping and dedoping processes in the polypyrrole film can act directly on its optical properties while the ESPR technique can give the same information indirectly.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Pyrrole; Electrochemical surface plasmon resonance; Electrochemical quartz crystal microbalance; Doping; Dedoping

1. Introduction

In recent years, conducting polymers (CPs) have attracted much attention due to their promising applications, including battery electrodes [1], sensors and biosensors [2], electrochromic displays [3], light-emitting devices [4], controlled release drug systems [5], etc. The applicability of these conducting polymers is based on their unique optical, electrical and structural properties [6]. Among these conducting polymers, polypyrrole (PPy) is especially promising for commercial applications due to its good stability, facile synthesis, and higher conductivity than many other conducting polymers [7].

Several techniques coupled to electrochemistry have been used for in situ investigation of optical and electrical properties of polypyrrole conducting films, for example, quartz crystal microbalance (QCM) [8], Fourier transform infrared spectroscopy (FTIR) [9], electron spin resonance (ESR) [10], scanning probe microscopy (SPM) [11] and, more recently, electrochemical surface plasmon resonance (ESPR) [12–16]. The interest in ultrathin films of these polymers has proportioned a growing interest on the ESPR technique due to its high sensitivity, in situ and real time measurements in characterizing films [14]. In the ESPR technique, the modulation in the electrode potential (ΔV) induces changes in the real ($\Delta\varepsilon_{\text{real}}$) and imaginary ($\Delta\varepsilon_{\text{imaginary}}$) parts of the dielectric constant, and the average thickness of the adsorbed layer

---

* Corresponding author. Tel.: +55 19 3788 3127; fax: +55 19 3788 3023.
E-mail address: kubota@iqm.unicamp.br (L.T. Kubota).

[1] ISE member.

0013-4686/$ – see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2005.06.019

(Δd) as well as changes in the surface charge density ($\Delta\delta$) as follows [17,18]:

$$\frac{\Delta\theta_{\mathrm{SPR}}}{\Delta V} \approx c_1\left(\frac{\Delta\varepsilon_{\mathrm{real}}}{\Delta V}\right) + c_2\left(\frac{\Delta\varepsilon_{\mathrm{imaginary}}}{\Delta V}\right) + c_3\left(\frac{\Delta d}{\Delta V}\right) + c_4\left(\frac{\Delta\delta}{\Delta V}\right) \quad (1)$$

where c_1, c_2, c_3 and c_4 are constants.

The first and second terms in the above equation describe changes in the electronic states of the adsorbed molecules upon electrode potential shift. The third term describes the change of the average thickness of the adsorbed layer and the fourth term is associated with the effects of the electron density on the surface plasmon resonance angle.

Based on the above considerations, it can be seen that the combination of surface plasmon resonance with electrochemical measurements is a powerful technique for the simultaneous optical characterization and electrochemical manipulation of the electrode–electrolyte interface and, consequently, has been applied in the investigation of ultrathin polymer films [19], protein monolayers [20], charge transfer reactions [21], sequential multilayer electropolymerization [22], electrochemically induced orientation of molecules [23], etc. Consequently, the application of electrochemical surface plasmon resonance in the investigation of conducting polymer processes has generated considerable information about electropolymerization [24], layer-by-layer assembly [25], doping and dedoping processes [26], etc. Although the growing interest in the investigation of conducting properties is due to their broad fields of applications, there are few studies of the effects of the polymerization mode and film thickness on its properties in the initial stages of polymerization as well as the effects of doping/dedoping processes on its optical processes. In this paper, the effects of the polymerization mode on the optical and electrical properties of polypyrrole thin films by the combined electrochemical-surface plasmon resonance (ESPR) technique are presented. The ESPR technique was used to monitor the doping and dedoping processes of these conducting ultrathin polymer films in initial stages of polymerization and the effects of the dopant on its optical properties were investigated.

2. Experimental

2.1. Reagents and materials

All chemicals used were analytical grade. Pyrrole (98%) from Aldrich (Milwalkee, USA) was destilled prior to use. The pyrrole aqueous solution was stored in a dark flask at a low temperature. Potassium chloride (KCl) and sulfuric acid (H_2SO_4) were from Synth (São Paulo, Brazil) and were used as received. Hydrogen peroxide (H_2O_2) was acquired from Merck (Darmstadt, Germany). All solutions were prepared with water purified in a Milli-Q system and the actual pH of the solutions were determined with a Corning pH/ion analyser model 350.

A gold sensor disk composed of a gold sensing surface (thickness of 50 nm) deposited onto a glass microscope slide using a titanium adhesion layer (thickness of 1.5 nm) was acquired from Xantec Bioanalytics (Muenster, Germany). The titanium adhesion layer was used in order to avoid the peeling of gold during the ESPR experiments. The sensor disk was optically attached to the prism using an index-matching fluid n_d (25 °C) = 1.518, Cargille Laboratories (Cedar Grove, NJ, USA). The quartz crystals, AT-cut with a fundamental frequency of 5 MHz sandwiched between gold electrodes, were acquired from Maxtek Inc., CA, USA.

2.2. Electrochemical surface plasmon resonance measurements

An ESPRIT instrument (Echo Chemie B.V., Ultrech, The Netherlands) was used to perform the optical measurements of the SPR angle and cyclic voltammetry was carried out with a potentiostat μAUTOLAB model from Echo Chemie (Ultrecht, The Netherlands). The ESPRIT instrument is based upon the Kretschmann configuration [27] with a scannning-angle setup. The intensity of the reflected light (p-polarized, λ = 670 nm) is measured over a range of 4° by using a photodiode detector. The incidence angle was varied by using a vibrating mirror (rotating over a angle of 5° at 77 Hz in approximately 13 ms), which directs p-polarized laser light (wavelength = 670 nm) onto a 1 mm × 2 mm spot of the sensor disk via a hemicylindrical prism of BK7 glass. In each cycle the reflectivity curves were scanned on both forward and backward moviments of the mirror. In this vibrating mirror setup, the resolution is 1 millidegree (m°).

In the experiments, a gold sensor disk containing a glass hemicylinder was mounted into a precleaned SPR cuvette. In order to obtain high inertless it was made of Teflon®. The solutions were injected into the cuvette using a syringe with a stainless steel needle (Fig. 1). In order to avoid contamination on gold surface between the polymerization experiments the following procedure was adopted. Initially, before polymerizing, the bare gold disk was exposed to a freshly prepared H_2SO_4/H_2O_2 solution (piranha solution) for about 5 min and intensely rinsed with water purified in a Millipore Milli-Q system until the SPR spectra for a cleaned gold disk presented good repeatability. The repeatability for six successives measurements was evaluated using a relative standard deviation (R.S.D. < 4%). In order to promote better accuracy of the measurements the temperature was kept constant (25 °C) using a RTE/7 model cooled water recirculating bath from Neslab (Thermo Electron Corporation). The refractive index of the bulk solution was measured with an Abbe-refratometer (ATTO Instruments Co., Hong Kong).

Download English Version:

https://daneshyari.com/en/article/196915

Download Persian Version:

https://daneshyari.com/article/196915

Daneshyari.com