

Spectroelectrochemical study of the electrosynthesis of Pt nanoparticles/poly(3,4-(ethylenedioxythiophene) composite



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ABSTRACT

UV-Visible, NIR and Raman spectroelectrochemistry techniques have been used for the *in-situ* study of Pt nanoparticles (PtNPs) electrosynthesis on an electrochemically generated poly(3,4-ethylenedioxythiophene) film. Two electrochemical steps have been used to obtain in a reproducible way PtNPs with catalytic properties towards methanol oxidation: 1) deposition of Pt nuclei on the polymer modified electrode, 2) growth of these nuclei to form nanoparticles yielding drastic changes in the spectroscopic signal and a significant increase of the amount of Pt. A two steps procedure facilitates an interfacial growth mechanism of the nuclei over a diffusion controlled growth. Evolution of UV-Visible and NIR spectra during these two PtNPs synthesis steps helps to understand and explain the mechanism of generation of these nanoparticles. Besides, Energy Dispersive X-Ray analysis and Scanning Electron Microscopy images registered of the composite after each step of synthesis confirm the conclusions extracted from spectroelectrochemistry data.

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1. Introduction

Spectroelectrochemistry, a multiresponse technique that allows obtaining individual and complementary information about a complex system, has been successfully used to study multiple types of systems and reactions. Very different reaction mechanisms have been evaluated, providing insight into the reaction intermediates, the electrosynthesis of diverse materials or the behavior of a material towards a specific analyte [1–4]. In particular, UV-Visible-NIR and Raman spectroelectrochemistry have been proven to be very useful for studying the synthesis and for characterizing conducting polymers [5–8]. These types of polymers have been applied in different material science areas such as light emitting diodes, sensors and biosensors, solar cells or fuel cells [9–13]. In the case of fuel cells, modification of these polymers with suitable catalysts to improve the efficiency has been extensively studied [14–16]. Conducting polymers act as supporting material where the catalysts are anchored, allowing good dispersion and high stability. Most of these studies are mainly focused on characterizing the final product, not in understanding, and hence, optimizing the process towards a good final material. The most common techniques in these studies are electrochemistry, scanning electron microscopy

(SEM) and some spectroscopic techniques [13–15,17–20], while the use of spectroelectrochemistry is comparatively more scarce.

Poly(3,4-ethylenedioxythiophene), PEDOT, is one of the most popular and widely used intrinsically conducting polymers (ICPs) due to its high conductivity, electrochemical stability, high transparency, catalytic ability and low band-gap [21–23]. Some ICPs, such as PEDOT, are ionic and electronic conductors, making them excellent and very efficient catalyst supports in hydrogen and methanol fuel cells [18,19,24,25]. Platinum is the most widespread catalyst used in direct methanol fuel cells (DMFC) despite some drawbacks, such as poisoning during oxidation of methanol or the high cost of this metal. The use of Pt nanoparticles (PtNPs) is a typical strategy to decrease the amount of Pt in fuel cells and increase its efficiency.

To know how the polymer has been modified, it is usual to perform *ex-situ* analysis with, for example, electron microscopy techniques, X-Ray diffraction or some spectroscopies such as X-Ray Photoelectron Spectroscopy. Nevertheless, it is not widespread to carry out *in-situ* analysis to study the process of polymer modification and to characterize the modified polymer.

In this regard, the main objective of this work is to electrosynthesize in a reproducible way a composite material consisting of PEDOT and PtNPs. UV-Vis-NIR and Raman spectroelectrochemistry has been selected to study the mechanism and the different steps of synthesis. The results and conclusions obtained with this multiresponse technique will be compared with scanning

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electron microscopy (SEM) images and energy-dispersive X-ray (EDX) analysis. The electrocatalytic properties of this nanocomposite for methanol oxidation will be also studied.

2. Experimental

2.1. Materials

3,4-Ethylenedioxythiophene, EDOT (Aldrich), potassium hexachloroplatinate (IV), K_2PtCl_6 (Aldrich, >98%), lithium perchlorate trihydrate, $LiClO_4 \cdot 3 H_2O$ (Panreac, >98%), perchloric acid, $HClO_4$ (Merk, 60%), and methanol (BDH Prolabo) were used as received. Aqueous solutions were prepared using high-quality water (resistivity of $18.2 M\Omega \cdot cm$, Milli-Q A10 system, Millipore).

2.2. Microscopy measurements

Scanning Electron Microscopy (SEM) images were taken under high vacuum conditions with a JEOL JSM-6335F. Energy Dispersive X-Ray (EDX) spectra were recorded with the X-Ray spectrometer of a Scanning Electron Microscope JEOL JSM-6460LV.

2.3. Spectroelectrochemistry measurements

UV-Visible spectroelectrochemical set-up (Fig. 1) consisted of a potentiostat PGSTAT 10 (Eco Chemie B.V.) coupled with a QE65000 Spectrometer (Ocean Optics) made up of a 1044×64 element diode array. The light beam, supplied by an Avalight DH-S deuterium-halogen light source (Avantes), was both conducted to and collected from the spectroelectrochemical cell by a $200 \mu m$ reflection probe (RP200-7-UV/Vis, Ocean Optics). The reflection probe was placed in the solution $1.25 mm$ in front of the working electrode surface to collect the reflected light.

Near-infrared (NIR) spectroelectrochemical experiments were performed in the same cell arrangement described in Fig. 1, coupling in this case the potentiostat PGSTAT 10 (Eco Chemie B.V.) with a NIRQuest spectrometer (Ocean Optics) made up of a 512 pixels, covering the spectral range between 900 and 1700 nm. The light beam was supplied by the same light source indicated in the UV-Visible device and it was conducted to and collected from the spectroelectrochemical cell by a $200 \mu m$ reflection probe (FCR-7IR200, Avantes).

All the measurements were carried out using a home-made spectroelectrochemical cell that operates in near normal incidence reflection mode [26] (Fig. 1). A conventional three-electrode system was used consisting of a 3 mm diameter glassy carbon (GC) disk working electrode (CHI Inc), a home-made Ag/AgCl/KCl (3 M) microreference electrode and a Pt wire auxiliary electrode. Prior to electrosynthesis, the bare GC electrode was polished with alumina powder and then rinsed with ultrapure water in an ultrasonic bath for 30 min, changing the bath every 10 min.

Using a near-normal incidence reflectance set-up [26], the major component of the optical signal is due to specular reflectance, but diffusive reflectance cannot be discarded. Optical reflectance spectroelectrochemical set-ups are very suitable for the study of compounds in solution, of surface films on electrodes, and of adsorption or electrodeposition processes [26–30]. All the spectroscopic data are reported in this work as normalized differential reflectance: $\Delta R/R = (I_{E_i} - I_{E_0})/I_{E_0}$, where I_{E_i} and I_{E_0} represents the light intensities measured by the UV/Vis or NIR detector at an arbitrary potential (E_i) and at the reference potential (E_0), respectively [31,32]. In all experiments reported here the reference potential (E_0) is the initial potential (no equilibration potential is applied in any experiment).

Raman spectroelectrochemical experiments were carried out coupling the potentiostat PGSTAT 20 (Eco Chemie B.V.) to a Voyager

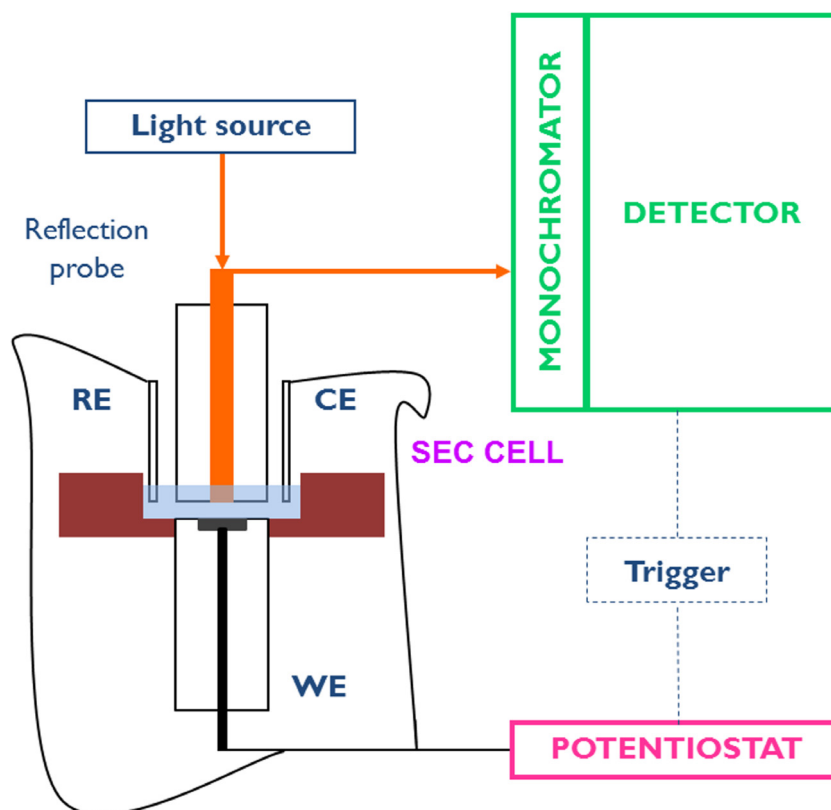


Fig. 1. Schematic diagram of the experimental set-up used for UV/Vis and NIR spectroelectrochemistry measurements. WE: working electrode, RE: reference electrode, CE: auxiliary electrode.

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