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Electrosynthesis and physioelectrochemical properties of poly tyramine electroactive film in the presence of the surfactant: Comparable study

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ABSTRACT

We describe in detail the advantages of a novel method of electrochemical preparation of poly tyramine (PT), based on the ability of anionic surfactants to form micelles in aqueous media. We demonstrate that the electropolymerisation process carried out in the presence of sodium dodecyl sulfate (SDS) at an oxidation potential lower than in an aqueous media yields better organized PT films. Theoretical calculations for tyramine (Ty) polymerization were carried out at density functional theory (DFT) level using the 6-31G(d,p) basis set. The improved physicochemical and structural properties of PT obtained in these conditions related to the electrocatalytic effect of SDS and change fractal dimension of the film. With respect to Ni-PT/G, Ni-SDS-PT/G electrode shows a higher catalytic performance for the electrocatalytic oxidation of methanol.

1. Introduction

Conducting polymer such as polypyrrol, polythiophene or poly ortho aminophenol represent a group of conjugated π-electron materials which process a combination of various electrical, optical and other semiconductor properties as a organic semiconductors that with respect to electronic energy levels hardly different from organic semiconductors [1–10]. The electropolymerisation of phenol and phenol derivatives has received considerable attention due to their importance in environmental and industrial applications [7–11]. However, several mechanistic aspects are still unclear due to the complex electrochemistry of the phenol derivatives, which is strongly dependent on the type, position and number of substituents as well as on the chosen experimental conditions [12]. It is known [13,14] that the electrooxidation of phenols produces phenoxy radicals, which, reacting with a phenol molecule yield to a para-linked dimmer; further oxidation leads to oligomers and eventually to the formation of a passivating insulating film. For phenol derivatives with amino groups, the reported voltammetric studies [15] have been interpreted by analogy with the well-established aniline oxidation, i.e. a *E*(CE)*n* mechanism; the oxidation of o-aminophenol was described as producing a ladder-structured film and reactive intermediates of 2-amino-phenoxazin formation in solution. In the case of tyramine (4-(2-aminoethyl)phenol (Ty), because the amino function is separated from the phenolic ring by two methylene groups, it is expected that only the phenol moiety is oxidized to perform the polymerization [16]. Micellar media affect the electrochemical reactions by irreversible adsorption, leading to a change in the solution–electrode interface properties and producing some template effects at the electrode [17]. Moreover, surfactant containing media can also stabilize charged species such as anions or cation radicals [18–20]. Despite these advantages, relatively few works have been devoted to the electrosynthesis of conducting organic polymer films in micellar media [21,22]. The effect of SDS on the electropolymerisation of conducting polymer in aqueous solutions has been investigated [23,24]. Polypyrrol (PPy) films formed in the presence of dodecyl sulfate have better mechanical properties than those obtained with other anions such as NO_3^- or ClO_4^- [23]. PPy films with perpendicularly oriented columnar structures have been synthesized from the electrochemical polymerization of pyrrole in anionic micellar solutions, including SDS or sodium dodecyl benzene sulfonate (SDBS) as surfactants [24]. The improved physicochemical and structural properties of PT obtained in these conditions can be related to the Electrocatalytic effect of SDS and different fractal morphology of film.

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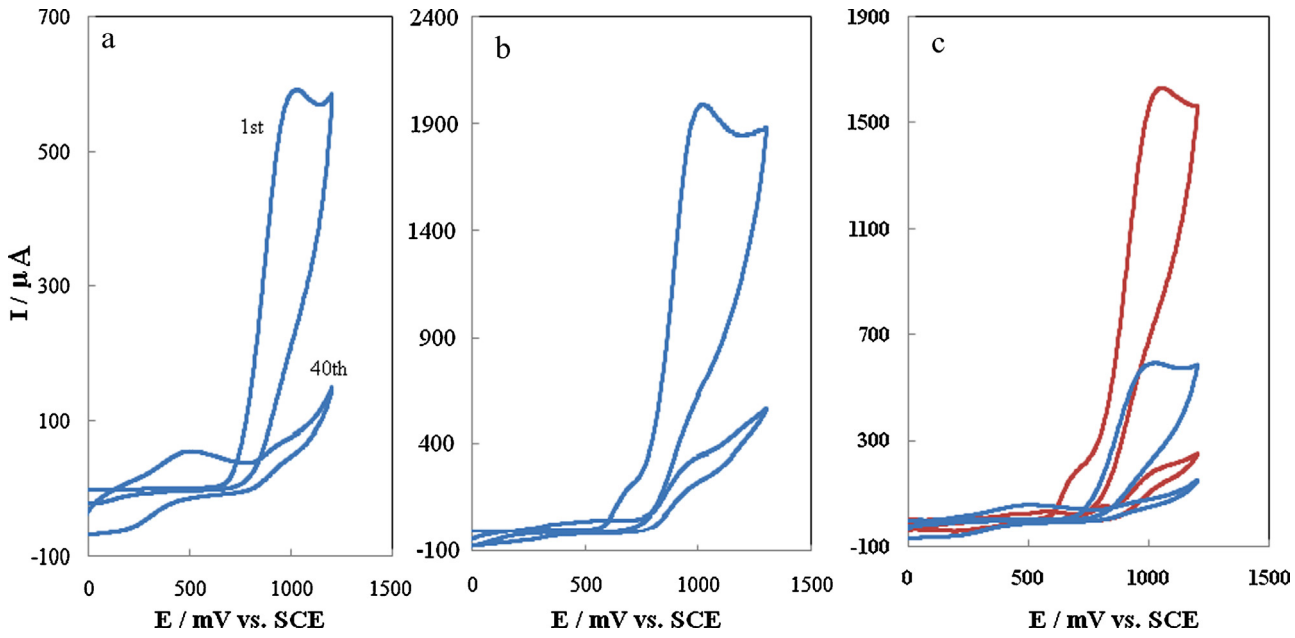

Fig. 1. The typical multi-sweep cyclic voltammograms during electropolymerization of PT with scan rate 50 mV s^{-1} in the absence SDS (a) and presence SDS (b) and comparison of a, b (c).

Fractal dimension (D_f) is a quantitative parameter for analyses of fractal objects, which is widely used for different purposes. In addition, it is one of the most important and useful parameters for analysis of structure of rough surfaces. Fractals have been characterized by several methods that can be classified as physical, chemical and electrochemical [25,26]. Self similarity and self affine are two concepts used in describing rough surfaces. Self similar refers to fractal objects that are equally magnified in all directions. However, many objects in nature, like machined surface, are rather self affine, which means that they have unequal scaling magnification in different directions [27]. The aim of this paper is to present insight into influence of micellar media such as sodium dodecyl sulfate (SDS) on processes that occur during oxidation and reduction of a PT film and the relationship between the fractal dimension of PT film and electrocatalytic activity.

2. Experimental

All chemicals used in this work were of Merck origin and used without further purification. All electrochemical measurements were carried out in a conventional three electrodes cell, powered by a potentiostat/galvanostat (EG&G 273A) and a frequency response analyzer (EG&G, 1025). The system was run by a PC through M270 and M398 software via a GPIB interface. The frequency range of 100 kHz to 15 mHz and modulation amplitude of 5 mV were employed for impedance studies. PT films electrodeposited on a graphite rod (G) of 0.22 cm^2 area were employed as working electrode. A saturated calomel electrode (SCE) and a platinum wire were used as reference and counter electrodes respectively. The PT films were prepared by cycling the potential from -0.2 to 0.85 V SCE in acidic solution containing 0.01 M monomer. The electrochemical experiments were carried out in an acidic solution (pH 2) of $HClO_4$, lithium salt (0.1 M) and SDS (0.005 M) as supporting electrolyte. In order to incorporate Ni (II) ions into the PT film, the freshly electropolymerised PT/G was placed at open circuit in a well stirred aqueous solution of 0.1 M nickel sulfate. All capacitance values used in this paper were normalized by fitting on Z-view program. The microstructure of the obtained films was investigated by a VEGA/TESCAN scanning electron microscope. Theoretical calculations were carried out at density functional theory (DFT) level using the 6–31G(d,p) basis set for all atoms with Gaussian 03 program package for heptamer of PT. The molecular sketche of all compound were drawn using Gauss View 03 [28].

3. Results and discussion

3.1. Effect of SDS on electropolymerization

In previous publications [29,30], we described how poly ortho aminophenol films were deposited in situ electropolymerised on the surface of G electrode by the use of cyclic voltammetry methods. Fig. 1a shows the typical multi-sweep cyclic voltammograms during electropolymerization in the absence and presence of the SDS. As seen in Fig. 1, Tyramine (Ty) is oxidized irreversibly at around 650 mV without corresponding cathodic processes in the reverse scan. During the next cycles, one redox peak appeared at lower potential, and its current did not increase considerably with potential cycling. This occurred because the soluble products produced on the surface of the electrode did not allow the monomer to reach the electrode and produce more monocation radical. Therefore, a longer potential cycling time is needed for transformation of this to PT. By adding 5 mM of SDS anionic surfactant to the monomer solution, the monomer oxidation potential was shifted and its oxidation current increased (Fig. 1b). Moreover, the rate of polymerization increased considerably and the redox peaks due to PT grew. Furthermore, under successive potential cycling, their peak currents increased and their growth continued. These results show that, in the presence of SDS, the monomer can easily reach the electrode surface and produce more monocation radicals. In the case of Ty electropolymerization, the radical cation of Ty monomer is formed on the electrode surface by oxidation of the monomer. This process is considered to be rate determining step. The electronic properties such as highest occupied molecular orbital (HOMO) energy, lowest unoccupied molecular orbital (LUMO) energy and frontier molecular orbital coefficients have been calculated from DFT study. The natural bond orbital (NBO) analysis was applied to determine the atomic charges for Ty polymerization. Results are presented in Fig. 2 and Tables 1 and 2.