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Electropolymerization of ortho-phenylenediamine. Structural characterisation of the resulting polymer film and its interfacial capacitive behaviour

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ABSTRACT

The physico-chemical characteristics of thin poly-(ortho-phenylenediamine) (PPD) films, obtained by electrochemical oxidation of the relevant monomer, are investigated using electrochemical, morphological and spectroscopic techniques. In particular, cyclic voltammetry and electrochemical impedance spectroscopy (EIS) techniques are used to collect information concerning the redox, conductivity and double layer capacitance properties of the PPD film. AFM imaging and Raman spectroscopy results are exploited to characterize the film structure. In this respect, Raman spectra of two possible PPD oligomers are calculated at the B3LYP/6-311G** level of the theory.

1. Introduction

Whenever possible, electrochemical synthesis is the most convenient method to rapidly and simply develop modified electrodes. In the case or redox or electronically conducting polymers, the electrochemically driven polymerization allows the control of some important film parameters, such as (i) the thickness; (ii) the redox state in the case of redox conductive polymers; and (iii) the doping level of intrinsically conducting polymers. Specific functionalities can be either already present in the monomer unit, or incorporated into the polymer in the course of polymerisation, or fixed at the polymer network in an additional step after the synthesis procedure. Thanks to these interesting features, electropolymerization can be used to build up biosensors entrapping enzyme or antibodies immobilized on the electrode surface [1–3] or to synthesize polymer-type artificial receptor directly on the electrode by means of molecularly imprinted polymer (MIP) technology [4–6].

The synergy between the selective properties of MIPs and the transduction offered by electrodes can be advantageously employed in the field of molecular recognition. Different transducing methods have been used in electrochemical sensors based on MIPs [4,7,8]; among them, capacitive detection possesses interesting features in terms of sensitivity, costs and detection limits, and has been already successfully employed in the development of sensors [9–11]. Capacity detection essentially requires that the reception layer is characterised by a low thickness (the relative change in capacity is higher if the increase in thickness due to analyte adsorption is comparable to that of receptor element on the electrode), low leakage and high uniformity. Moreover, the capacitive current under applied ac potential should result higher with respect to the faradic one.

In this context, we have checked whether poly-orto-phenylenediamine (PPD) films, once electropolymerised under suitable experimental conditions, possesses all these characteristics. In a previous work the early stages of the electropolymerization process of oPD and the relevant electrochemical mechanism have been discussed [12]. In the present paper, the characteristics of electropolymerised PPD film are investigated from both an experimental and a theoretical point of view, using electrochemical, morphological and spectroscopic techniques. Among the three isomeric forms of phenylenediamine, the ortho-isomer is the most widely used for the relevant polymer formation and represents one of the first successful examples of electrosynthesised MIPs [6,13]. Recently an amperometric benzophenone sensor based on molecularly imprinted PPD was successfully reported in the literature for the first time [14]. Electrosynthesized PPDs have also been widely reported to possess excellent permselective properties that are particularly meaningful in biosensors, being highly permeable to H_2O_2 and resulting an efficient blocker of interference compounds [15,16]. In the same studies, the influence of the electropolymerisation conditions on the permeability properties of PPD films are investigated [15,16]. Further recent papers dealing with the electropolymerization of oPD concern the PPD film growth on carbonized tissue [17]. In this paper the structural features of

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PPD films are studied and it is shown that the interfacial PPD film capacity is a function of the gallic acid concentration in solution.

2. Experimental

2.1. Reagents

All the reagents were purchased from Sigma Aldrich and used without further purification. The Au disk electrodes with an area of 0.072 cm^2 were purchased from Metrohm. Gold plates were obtained by gold evaporation on a chrome-coated Si(1 1 1) surface, and later submitted to a "gentle-flame" annealing procedure [18]. The alumina used for the cleaning of the surface had a mesh of 1 μm and 0.05 μm, respectively, and was purchased from Buehler. The working electrode Au surface was polished and checked as previously described in Ref. [12]. Millipore MilliQ reagent grade water was used.

2.2. Electroanalytical apparatus and procedures

Cyclic voltammetric (CV) measurements were performed using both Autolab PGSTAT 20 and CHI660A potentiostats and employing a typical three-electrode electrochemical cell arrangement. Impedance measurements were performed using the CHI660A potentiostat, in the 1 Hz–100 kHz frequency range, with a 5 mV sinusoidal peak-to-peak amplitude. Pt wire and $Ag/AgCl/KCl_{sat}$ were used as counter and reference electrodes, respectively. All the potentials reported in this paper are referred to this reference. The MIP PPD film on gold is obtained by electrochemical oxidation (50–250 successive CV cycles, in the +0.1 to +0.8 potential range at a 0.05 V s^{-1} potential scan rate) of a mixed 1 mM oPD and 10 mM of different template molecules. Then, the PPD imprinted film was sonicated for 10 min and washed thoroughly with Millipore water. To assess the behaviour of the electrodes functionalized with the imprinted PPD, the following procedure was followed:

1. An impedance spectrum was acquired immediately after the electropolymerization in a 0.5 M NaF solution free from the template (blank solution).
2. Then, the electrode was washed for one hour in a 50% in volume methanol in water solution, subsequently an impedance spectrum was acquired in the blank solution (free of template).
3. Step 2 was repeated until repeatable impedance spectra were recorded.
4. Once obtained the background curve, the electrode was dipped in a 0.5 M NaF solution containing the template in a millimolar concentration (test solution). A series of EIS spectra were collected at a regular interval time until a steady signal is reached.
5. To assess reproducibility, the procedure from points 2–4 was repeated.
6. To assess selectivity, point 5 was carried out with a similar molecular species instead of the template.

2.3. AFM

AFM measurements were performed with a Park CP instrument operating in contact-mode with a constant applied force of 1.3 nN. All measurements were conducted in ambient air and room temperature. Images were recorded at an optimized linear scan rate of 0.5–1.0 Hz, with image resolution of 256 × 256 pixel and variable scan size. NSG11 probes were purchased from NT-MDT (Head Office in Moscow-Russia) with resonant frequency in the range 190–300 kHz. The force used for scratching was 1 μN. Scratches were made in contact mode, while height measurements were made in non-contact mode configuration. The microscope *Z*-axis was calibrated using a standard grid provided by NT-MDT.

2.4. Raman

The Raman microscope features an He–Ne laser exiting at 632.81 nm, with a max 20 mW power. It is equipped with a 1024 × 256 × 16 CCD detector, Peltier cooled.

2.5. Computational details

Ab initio molecular orbital calculations were performed using the GAMESS and Firefly suite of programs [19,20]. Screening full optimization geometry calculations were performed at the B3LYP/3-21G* level of the theory. Final fully optimized geometries (in the vacuum) and Raman activities are obtained at the B3LYP/6-311G** level of the theory.

3. Results and discussion

3.1. Electrochemical film growth

The PPD film, generated in absence of imprinting templates, is obtained by potentiodynamic growth, by anodic oxidation of a oPD monomer aqueous solution. Fig. 1 shows repetitive CVs recorded at a scan rate (v) of 0.05 V s^{-1}. The first CV cycle shows, in the positive potential region, an anodic current peak with maximum at about +0.60 V, relative to oPD oxidation leading, through subsequent chain propagation reaction, to polymer formation. The oxidation process appears irreversible, as suggested by the absence of any directly associated peak in the backward scan. On subsequent cycles, the peak current decreases, becoming almost undetectable after the tenth cycle. Such behaviour is consistent with slow progressive electrode passivation, indicating the electrically insulating character of the polymer film formed on the electrode surface [12]. Further details concerning the mechanism of the electropolymerization process have been previously reported [12]. The PPD film shows a peculiar redox activity in the negative potential region, as evidenced by a cathodic/anodic peak system, with $E_{p,c}$ (i2c) and $E_{p,a}$ (i2a) equal to −0.16 V and −0.11 V, respectively (see Fig. 1). Notice that the this peak system only appears after the first CV scan in the positive potential region; the current of

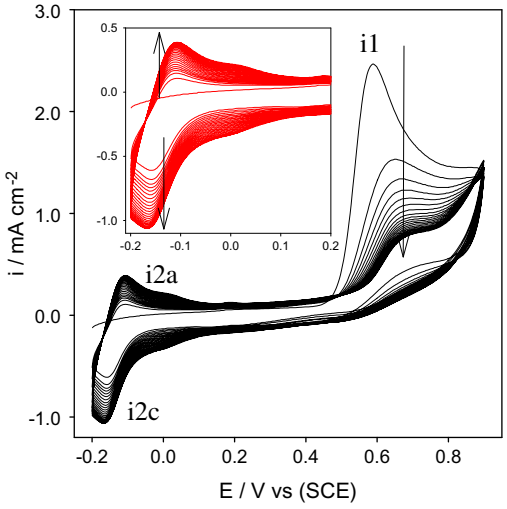

Fig. 1. Repetitive cyclic voltammograms of a 1 mM oPD in aqueous solution, $HClO_4$ 0.1 M base electrolyte. 100 successive cycles are shown. Arrows' vs indicates the trend of the current for increasing number of subsequent scans. 0.05 V s^{-1} scan rate.