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Electrochemical modification of carbon electrode with benzylphosphonic groups

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ABSTRACT

Electrochemical modification of carbon electrodes by aryl groups bearing a phosphonate terminal functionality was carried out by both electrochemical reduction of diazonium ions (diazobenzylphosphonic acid) and electrochemical oxidation of an amine (aminobenzylphosphonic acid). The grafting by electrochemical reduction of aryl diazonium ions was found to be more efficient. The surface concentration of phosphonate groups, estimated by electrochemical reduction of electrostatically bound Pb(II) ions, was found to be about 25% higher for the layer formed by electrochemical reduction of diazonium ions than for the layer formed by oxidation of the amine. The acid–base properties of the grafted films were slightly influenced by the grafting procedure and the difference in the apparent pK_a was most likely related to the presence of the substrate –NH-aryl linkage for the film generated by amine oxidation. X-ray photoelectron spectroscopy was used to get some insight on the chemical species present at the carbon electrode surface. For both procedures, the films consist in mixture of at least two different covalently grafted species.

1. Introduction

Electrochemical modification of surfaces has become a widely used method for the functionalization of electrodes [1–5]. These modified electrodes have found applications in diverse areas, but no limited, to the development of biosensors, protection from corrosion and energy storage. Accordingly, modification by electropolymerization of monomers such as pyrrole, aniline and thiophene derivatives has been developed to generate new electrode materials [6]. This method is relatively simple and versatile and initially occurs by electrochemically-induced precipitation of oligomers and polymers when the solubility of these species is reached. Subsequent polymer growth is also possible from the already deposited polymer. A sometime important drawback of such materials is related to the possible desorption of the polymers and loss of electrical contact with the electrode support. This phenomenon can occur upon cycling between different oxidation/reduction states of the polymer as a result of the insertion and deinsertion of dopant ions from the polymer matrix [7].

A potentially simple solution to solve this problem is to use methods that lead to the formation of a covalent bond between the electrode surface and the deposited species. This feature could be achieved by electrochemically-assisted processes based either on the reduction of diazonium ions [8–20] or oxidation of amine [21–26]. Both processes will be described in more details below for aromatic derivatives. Briefly, in both electrochemical processes, reactive radical species generated by electron transfer can react with the surface to form a covalent bond.

Here, we wish to report the functionalization of carbon electrodes by either electrochemical oxidation of amine (I) or electrochemical reduction of in-situ generated diazonium ions (II) obtained from the corresponding amine (Scheme 1).

Electrochemical grafting by oxidation of aminobenzylphosphonic acid has been previously reported [22]. In this report, we extend this previous study by providing complementary X-ray photoelectron spectroscopy data (eg. P 2p core level spectra) and investigating the acid-base properties of the grafted layers. Furthermore, a comparative study of the electrochemical grafting process (e.g. reduction of diazonium ions and oxidation of amine) is carried out as well as a comparison of the resulting modified surfaces by using electrochemical techniques and X-ray photoelectron spectroscopy. The acid-base properties of the two types of grafted layers were also investigated. Finally, the nature of the chemical species present at the modified electrode surface is discussed.

2. Experimental

2.1. Reactants

Aminobenzylphosphonic acid, potassium ferricyanide, potassium ferrocyanide, potassium chloride and sodium nitrite were

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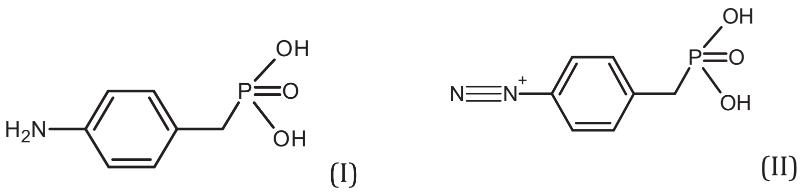

Scheme 1. Structure of the amine precursor (I) and the corresponding in-situ generated diazonium ion (II).

obtained from Sigma Aldrich and were used without further purification. Hydrochloric acid and sodium hydroxide were used as received from Fisherbrand. Glassy carbon electrode and Ag/AgCl reference electrodes were obtained from BASi.

2.2. Modification of glassy carbon electrode

A glassy carbon electrode was polished with alumina powder (1 and 0.05 μm grain size). After each polishing step, the electrode was washed with water (Milli-Q, Millipore, 18.2 MΩ cm) and sonicated for 5 min in water. The electrochemical modification of glassy carbon electrodes was performed in a standard three-electrode cell. The working electrode was a 3 -mm-diameter glassy carbon disk and glassy carbon plate for X-ray photoelectron spectroscopy analysis, the counter electrode a platinum gauze, and a Ag/AgCl electrode was used as reference electrode. A potentiostat electrochemical interface SI480 (Solartron Instruments) controlled with DC Corrware software (Scribner Associates, version 2.8d) was used for electrochemical experiments. For the diazonium method, electrochemical modifications were carried out in aqueous sulfuric acid (0.05 M) electrolyte. The electrolyte also contained 1 mM aminobenzylphosphonic acid and 2 mM sodium nitrite was added to generate the diazonium cations. The electrochemical oxidation of the amine was carried out in the same electrolyte with the same concentration of aminobenzylphosphonic acid but without adding sodium nitrite.

The benzylphosphonic acid molecules were grafted by cyclic voltammetry or at constant potential as indicated below. Following electrografting, the electrodes were thoroughly rinsed with pure water and sonicated 5 min in water. The presence of grafted layers on the electrode surface was confirmed by electrochemical measurements in 0.1 M KCl aqueous solution containing 5 mM each of ferricyanide and ferrocyanide ions.

Electrochemical impedance spectroscopy characterizations were made on modified sample using Solartron 1255B device and results were analyzed using Zplot software (Scribner Associates, 2.8d). Measurements were performed for frequencies ranging from 0.05 Hz to 100 kHz with a 10 mV amplitude sine wave. All measurements were made at open circuit potential in a $Fe(CN)_6^{3-/4-}$ solution. The following solutions of different pHs were used; 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12 and 13. These solutions were obtained by using 1 M HCl and 1 M KOH solutions to adjust the pH to the desired value.

The surface concentration of phosphonate groups was estimated from the amount of Pb(II) electrostatically bound to these ionic sites and that can be electrochemically reduced to metallic lead. Modified electrodes were soaked in a pH 4.1 solution containing 10^{-4} M $Pb(NO_3)_2$ for a period of 2 h. At this solution pH, the ionized groups are mainly present under the $–HPO_3^-$ form. The metal ions loaded electrode was transferred to a 0.1 M acetate buffer solution (pH 5.3) and were characterized by cyclic voltammetry recorded between 0 and–1 V at a scan rate of 10 mV s^{-1}. The amount of electrostatically bound lead was determined from the voltammetric cathodic charge and related to the surface concentration of electrografted phosphonate groups by considering that one Pb(II) ion will bind to two phosphonate groups ($–HPO_3^-$).

2.3. XPS analysis

XPS measurements were performed with an PHI 5600-ci (Physical Electronics, Eden Prairie, MN, USA) set-up using the aluminium monochromatic beam (1486.6 eV, 300 W) for survey spectra and a magnesium anode (1253.6 eV, 300 W) was used for core level spectra. The data were collected with an angle of 45° toward the sample surface at room temperature and the operating pressure in the analysis chamber was set below 10^{-9} Torr. The survey spectra were recorded between 0 and 1400 eV with a resolution of 0.8 eV (10 min for each sample). The core level spectra for C 1s, O 1s, N 1s, and P 2p were recorded with a resolution of 0.05 eV. Collected data were then analyzed using Casa XPS software.

3. Results and discussion

3.1. Electrochemical grafting an indirect evidence for the formation of a layer

3.1.1. Reduction of diazonium ions

Fig. 1A shows cyclic voltammograms in the presence of in-situ generated benzylphosphonic diazonium ions at a glassy carbon electrode. The first sweep is characterized by an irreversible reduction wave at about 0 V that is followed by the onset of another irreversible wave. On the subsequent scans, the intensity of the first wave is decreasing and has completely vanished after five cycles. The first wave is attributed to the reduction of the diazonium cations, which leads to the formation of the corresponding aryl radicals [1]. The decrease of the current is consistent with previous reports involving the electrochemical reduction of diazonium ions and the formation of an organic layer, which significantly impedes further electron transfer [8–20]. The overall process is described in Scheme 2.

The increase of the current after the first cathodic wave is associated to the reduction of residual NO_2^- anions [18]. An indirect way to determine the extent of the coverage of the electrode by an organic film is to investigate its blocking behaviour in the presence of soluble electroactive species [8,20]. In this study, this was performed by using $Fe(CN)_6^{3-/4-}$ as redox system. Various films were obtained by changing deposition parameters such as the applied potential and the deposition time. The current-time transients (not shown) recorded during electrochemical grafting at various constant potentials (between 0.3 and –0.3 V) show a rapid decay which does not follow that predicted by the Cottrell equation and is in agreement with the formation of a passivating layer at the electrode surface [27]. On the other hand, the surface concentration of phosphonate groups was estimated to $8.6 \pm 0.3 \times 10^{-10}$ mol cm^{-2} from the loading of electrostatically bound Pb(II) ions.

Fig. 2A presents a set of cyclic voltammograms for a bare glassy electrode and electrodes modified by electrochemical grafting of benzylphosphonic acid groups at constant potentials of 0.3, 0 and