



Electrochemical functionalization of glassy carbon electrode by reduction of diazonium cations in protic ionic liquid



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ABSTRACT

Protic ionic liquid based on 2-methoxypyridine and trifluoroacetic acid was used as electrolyte for the functionalization of a glassy carbon electrode surface by electrochemical reduction of in situ generated 4-chlorobenzene diazonium and 4-nitrobenzene diazonium cations. The diazonium cations were synthesized in an electrochemical cell by reaction of the corresponding amines with NaNO₂ dissolved in protic ionic liquid. The resulting electrografted organic layers exhibit similar properties to those layers obtained by the derivatization from isolated diazonium salts dissolved in protic ionic liquid. Functionalized glassy carbon electrode surfaces were characterized by cyclic voltammetry, Fourier transform infrared and X-ray photoelectron spectroscopies. Atomic force microscopy thickness measurements revealed that, in our experimental conditions, the use of protic ionic liquid led to the formation of film with a thickness of about 1.5 nm. It is also demonstrated that the nitrobenzene chemisorbed on glassy carbon electrode or dissolved in protic ionic liquid undergoes electrochemical conversion to hydroxyaminobenzene.

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1. Introduction

The electrochemical attachment of an organic layer onto carbon-based materials that can change their chemical and physical properties is a very active area of research due to their potential application in catalysis, sensing and energy storage [1,2]. A convenient method for the electrochemical functionalization of the electrode surface is based on the reduction of substituted diazonium salt which involves the formation of a phenyl radical that reacts with a carbon atom of the electrode to form a covalent C–C bond [2–7]. This versatile method allows the modification of an electrode surface with a variety of substituted aryl groups on different carbon-based materials like glassy carbon [6], diamond electrode [8], carbon powder [9–11], nanotubes and graphene [12–14]. The electrochemical modification of carbon via diazonium salts reduction became even more attractive when in situ generation of aryl diazonium cations from corresponding arylamine was proposed and later widely exploited [15–17]. The synthesis of aryl diazonium cations can be carried out either in aqueous solution with presence of NaNO₂ [15–17] or in acetonitrile solution with

tert-butyl nitrite [18]. In aqueous media, the modification with diazonium cations has been carried out in acidic [15,16], neutral [19] and alkaline media [20]. Nonetheless, the diazonium ions are more stable in acidic media and more specifically for pH lower than 3 [21]. The increasing interest in room-temperature ionic liquids as alternative reaction media to volatile organic solvents led several research groups to perform the functionalization in ionic liquid [22–24] or with in situ generated diazonium salt by itself acting as an ionic liquid [25,26].

Ionic liquids have attracted a great interest in the last decade generally due to their versatility and multifunctionalities [27–31]. They differ from other conventional solvents by their unique ionic character and the chemical structure of their ions can be tuned depending on specific tasks. Particularly in electrochemistry, ionic liquids have been widely used as recyclable solvents and catalysts, as electrode modifier, as electrolytes in batteries, electrosynthesis and photoelectrochemistry [27–31]. In one class of ionic liquids, protic ionic liquids are formed by the proton transfer from a Brønsted (or inorganic) acid to a Brønsted base [27,31]. Very recently, several protic ionic liquids were assessed for use as electrolytes in electrochemical applications [32]. The usefulness of protic ionic liquids as electrolyte in various electrochemical systems such as polymer electrolyte fuel cells [33], or Li-ion batteries [34] composite electrocatalyst for the oxygen reduction reaction [35], electrochemical capacitors [36,37] and metal deposition [32]

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has been also demonstrated. Despite the recent significant increase of the interest to protic ionic liquids, their use in electrochemical applications and as electrolyte for surface modification is rather limited as well as their behaviour in the presence of electroactive species.

Herein, protic ionic liquid synthesized from 2-methoxy pyridine and trifluoroacetic acid (at a 1:2 ratio) was used as the medium to investigate the electrochemical reduction of both diazonium salt and in situ generated substituted benzenediazonium cations from corresponding amine and the functionalization of a glassy carbon electrode surface. To the best of our knowledge, this is the first report concerning electrochemical grafting in protic ionic liquid with aryldiazonium cations generated in situ. Furthermore, this study reports the electrochemical behaviour for nitrobenzene chemisorbed on glassy carbon and dissolved in protic ionic liquid.

2. Experimental

2.1. Reagents and ionic liquid preparation

The following compounds: 4-chlorobenzenediazonium hexafluorophosphate, 4-chloroaniline, 4-nitrobenzenediazonium tetrafluoroborate, 4-nitroaniline, potassium ferricyanide, potassium ferrocyanide, potassium chloride, and sodium nitrite were used as received from Aldrich–Sigma. The protic ionic liquid used in this study was composed of a mixture of 2-methoxy pyridine and trifluoroacetic acid in a 1:2 ratio. This protic ionic liquid was obtained by the slow addition of 77.1 mL of trifluoroacetic acid (Alfa Aesar, 99.5+%, $d = 1.480 \text{ g/mL}$) in 53.6 mL of 2-methoxy pyridine (Sigma–Aldrich, 98%, $d = 1.038 \text{ g/mL}$) under constant stirring. Following the addition, the mixture was heated at 85°C under vacuum for 48 h to remove water. The water content of the protic ionic liquid was measured immediately after this heating step with a coulometric Karl–Fisher titrator (Mettler–Toledo model C20) and was found between 0.1 and 0.3 wt%. The sealed vials were kept in a desiccator between experiments.

2.2. Electrode preparation and modification

Glassy carbon electrodes were obtained from Bioanalytical System Inc. (Model MF 2012; diameter 3 mm or plate $10 \text{ mm} \times 10 \text{ mm}$ for XPS analysis). Pyrolyzed photoresist film electrode was prepared as reported previously [38]. Pt mesh and Ag wire were used as counter and reference electrode, respectively. The Ag wire was conditioned in protic ionic liquid for 1 h before measurements. For experiments carried out in aqueous solution, an Ag/AgCl (3 M NaCl), reference electrode was used. The glassy carbon surface was polished with Buehler $1 \mu\text{m}$ alumina powder and washed with Nanopure water ($18.2 \text{ M}\Omega \text{ cm}$) by sonication during 10 min. The electrode was dried by an air flow before each experiment.

Electrochemical modification of the glassy carbon or pyrolyzed photoresist film electrodes was carried out in protic ionic liquid solution containing: (i) 5 mM 4-chlorobenzenediazonium salt or 4-nitrobenzenediazonium salt; (ii) 5 mM 4-chloroaniline or 4-nitroaniline and 10 mM NaNO_2 by potential scanning between 0.5 and -0.5 V for 5 cycles at a scan rate of 50 mV/s . After modification the glassy carbon electrode was washed with acetonitrile by sonication for 10 min to remove all physically adsorbed species. Protic ionic liquid was kept in a desiccator and all its solutions were freshly prepared before the electrochemical experiments. The solutions used for electrochemical characterization of the modified electrode were either; aqueous 0.1 M H_2SO_4 , or 5 mM $\text{Fe}(\text{CN})_6^{3-/4-}/0.1 \text{ M}$ KCl adjusted to pH 5 using HCl or KOH. All solutions were deaerated with nitrogen for 20 min.

2.3. Instrumentation

Electrochemical measurements were performed in a one-compartment cell using a three-electrode configuration. Cyclic voltammetry was carried on using a Solartron Instruments (SI1287) interfaced with a PC, and the electrochemical setups were controlled with DC CorrWare (Scribner Associates, version 2.8d) software. X-ray photoelectron spectra (XPS) measurements were obtained on glassy carbon plates (SPI Supplies/Structure Probes, Inc.) with XPS PHI 5600-ci (Physical Electronics, Eden Prairie, MN, USA) equipped with a monochromatic Al anode (1486.6 eV) at 300 W for survey spectra (resolution 0.8 eV) and a Mg $K\alpha$ (1253.6 eV) anode at 300 W for high-resolution spectra (resolution 0.05 eV). The survey spectra do not require the compensation of charge (neutralizer). The data were obtained at room temperature and typically the operating pressure in the analysis chamber was below 10^{-9} Torr. Analysis was carried out in specular reflection mode at an angle of 45° between the sample and the analyzer. The infrared absorption spectrum for 4-nitrobenzene modified pyrolyzed photoresist film plate was recorded with a Brüker Vertex 80v Fourier transform spectrometer equipped with a liquid nitrogen cooled MCT detector. 1024 Scans were co-added with a spectral resolution of 4 cm^{-1} . The background recorded before the spectrum was that of a clean substrate.

AFM images were obtained using Bruker Multimode8 Atomic Force Microscope operated in a ScanAsyst-air mode with a silicon tip on nitride lever operating at frequencies 50–90 kHz with 0.4 N/m spring constant. The images were scanned in topography with the resolution 512×512 pixels. The AFM was mounted on a floating table to achieve vibration isolation during investigations.

3. Results and discussion

3.1. Electrochemical measurements

The electrochemical functionalization of glassy carbon electrode by reduction of in situ generated aryldiazonium cations from corresponding amines was examined and compared with results obtained for dissolved aryldiazonium salts in a protic ionic liquid composed of 2-methoxy pyridinium and trifluoroacetate at a 1:2 ratio. This pyridinium-based protic ionic liquid is more stable at a 1:2 base:acid ratio due to the proposed formation of dimeric anionic species $[(\text{CF}_3\text{CO}_2)_2\text{H}]^-$ [39]. 4-Chloroaniline and 4-nitroaniline were dissolved in protic ionic liquid together with NaNO_2 in order to generate 4-chlorobenzene diazonium and 4-nitrobenzene diazonium ions, respectively (Scheme 1, step i).

Following their electrochemical reduction in the same solution, the aryl groups were covalently attached to a glassy carbon electrode according to the mechanism presented in Scheme 1. The first five cyclic voltammograms for glassy carbon electrode in a 5 mM 4-chloroaniline solution in protic ionic liquid and in the presence of NaNO_2 are shown in Fig. 1. The first cycle is characterized by an irreversible reduction wave, attributed to the formation of 4-chlorobenzene radicals (Scheme 1, step ii), which disappeared during the following cycles. Such electrochemical behaviour was already observed in previous studies of in situ generated aryldiazonium salt reduction in aqueous acidic solutions [15,16], acetonitrile solution [15,16] and aprotic ionic liquids [40]. The electrochemically generated 4-chlorobenzene radicals bind to the glassy carbon electrode to form an organic layer on the electrode surface (Scheme 1, step iii). The grafted layer significantly inhibits further reduction of diazonium salt as inferred from the disappearance of the reduction peak in the second and subsequent cycles. A similar behaviour was observed for the electrochemical reduction of the 4-chlorobenzenediazonium tetrafluoroborate salt

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