Functionalization of Polycrystalline Gold Through the Electroreduction of Aryldiazonium Salts in Ionic Liquids

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In this work the electrochemical functionalization of polycrystalline gold with a nitro-phenyl layer has been studied. The surface modification has been performed by cyclic voltammetries through the electroreduction of 4-nitrobenzenediazonium salt (NBD) using as solvent the ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide ([BMP][TFSA]). The presence of phenyl groups on the electrode surface was studied by cyclic voltammetry and electrochemical impedance spectroscopy (EIS). The barrier propriety of nitro-phenyl modified gold surfaces were characterized by EIS using $Fe(CN)_6^{3-}$ / $Fe(CN)_6^{4-}$ as a redox probe. The results indicate that nitro-phenyl groups are present on gold surface. The increase in the scan rate during the reduction of NBD in ionic liquid leads to a less covered surface as indicated by a decrease in the charge transfer resistance for the redox probe.
Moreover, using the ionic liquid as solvent, lower amount of the attached molecules and a less dense layer are obtained.

1. Introduction

The development of hybrid organic/inorganic structures suitable in bioelectronics, clinical diagnostics and biological sensing requires a stable bond between the organic molecules and the surfaces of the conductors (Pinson and Podvorica, 2005). Among different methods to functionalize the surfaces, the electrochemical reduction of aryl diazonium salts is a very versatile alternative to conventional techniques, which was firstly proposed in 1992 (Delamar et al. 1992). This approach has been used to promote covalent bonds between aryl groups with different substituents and several substrates such as glassy carbon, silicon and gold (Pinson, 2012, Vacca et al. 2014). It is well established that the mechanism of the electrografting involves the electrochemical reduction of a phenyl-diazonium cation to form N_2 and the corresponding phenyl radicals, which react with the electrode surface leading to the attachment of phenyl group (Allongue et al. 1997). Different operative modes (cyclic voltammetries, potentiostatic, galvanostatic) and several electrochemical parameters (scan rate, time of reduction) can be selected to control the surface coverage and the density of the resulting film, yielding submonolayer to multilayer films (Ceccato et al. 2011, Combellas et al. 2005). However, the formation of multilayer films was frequently observed due to the difficulties in a fine control of the quantity of material grafted to the surface (Kariuki and McDermott, 2001). Thus, also new solvents for this reaction have been studied: usually the electrochemical reduction of diazonium salts is proposed in acetonitrile solution as aprotic solvent, or in acidic aqueous solution as protic solvent. Recently, also different ionic liquids have been tested for the electrochemical reduction of 4-nitrobenzendiazonium salts on glassy carbon (Actis et al. 2008, Ghilane et al. 2008) and graphene sheets (Jin et al. 2009). Fontaine (2010) showed that the surface concentration of grafted 4-nitrophenyl groups decreases with the viscosity of the ionic liquid used in the deposition experiments. To the best of our knowledge, the functionalization of gold electrodes using ionic liquids as solvents, has not been reported up to now.

In this work the electrochemical functionalization of polycrystalline gold through the electroreduction of 4-nitrobenzenediazonium salts has been studied using the ionic liquid 1-butyl-1-methylpyrrolidinium bis (trifluoromethylsulfonyl) imide as solvent. The 4-nitrophenyldiazonium was chosen because of the presence of nitro group which could be easily detected electrochemically. The electrodeposition has been performed by cyclic voltammetries at different scan rates. The electrodes were characterized before and after the functionalization by electrochemical impedance spectroscopy and cyclic voltammetry using ferro/ferrycyanide as redox probe. The effects of different conditions of deposition on the surface concentration of nitro-phenyl groups and on the fractional coverage of gold surface have been analysed; as a comparison the electrodeposition has been also performed in acetonitrile.

2. Experimental

2.1 Chemicals

1-butyl-1-methylpyrrolidinium bis (trifluoromethylsulfonyl) imide ([BMP][TFSA]), anhydrous acetonitrile (ACN, 99.8 %), 4-nitrobenzenediazonium (NBD) tetrafluoroborate and tetrabutylammonium hexafluorophosfate (TBAPF6) were purchased from Sigma-Aldrich®. Nitric acid, sulfuric acid, potassium ferrocyanide ($K_4Fe(CN)_6$), potassium ferricyanide ($K_3Fe(CN)_6$), potassium dihydrogenophosphate (KH_2PO_4), di-potassium hydrogenophosphate (K_2HPO_4) and potassium nitrate were supplied by Carlo Erba.

2.2 Apparatus

All electrochemical experiments were performed at room temperature using an AUTOLAB PGSTAT302N (Metrohm, Switzerland) potentiostat/galvanostat equipped with a frequency response analyzer controlled with the NOVA software.
A conventional three-electrode cell (V=10 ml) was used in which Saturated Calomel Electrode (SCE) was the reference and Pt wire was used as counter electrode. The working electrodes were prepared from gold foils (Sigma-Aldrich®, 99.99 %) and inserted in a Teflon holder: the exposed geometrical area of the rectangular electrodes (width 0.82 cm, height 0.67 cm) was 0.55 cm^2.

2.3 Modification and characterization of gold electrodes

Prior to modification, gold electrodes were manually polished with water and acetone on a cloth polishing pad and then submitted to 70 voltammetric cycles (-0.45 / 1.4 V, scan rate 100 mV/s) in 0.2 M phosphate buffer at pH 7. The electrodes were then rinsed with double-distilled water. Freshly polished electrodes were modified in [BMP][TFSA] containing 2 mM NBD. Consecutive cyclic voltammetries in the potential range 0.5 / -0.6 V vs. SCE have been performed at different scan rates from 2 to 1000 mV/s. Some electroreductions of NBD were also performed using ACN + 0.1 M (TBAPF6) solutions containing 2 mM NBD in the potential range 0.6 / -0.15 V vs. SCE with scan rate of 100 mV/s.
Electrochemical reduction of nitro group to amino group was performed by cyclic voltammetry in water/ethanol solutions (90/10%v) containing 0.1 M of KCl; the potential was varied from the open circuit potential to -1.2 V vs. SCE and back to 0.2 V vs. SCE. Scan rate was 100 mV/s.
The electrodes were characterized after each step of modification by electrochemical impedance spectroscopy at the open circuit potential (OCP) in solutions containing $Fe(CN)_6^{3-}$ / $Fe(CN)_6^{4-}$ 1 mM in phosphate buffer 0.2 M pH 7: the frequency was varied from 100 kHz down to 0.01 Hz. The impedance spectra have been modelled by equivalent circuits by NOVA software.

3. Results and discussion

Figure 1 displays the cyclic voltammetry of gold electrode in the presence of 4-nitrophenyldiazonium tetrafluoroborate in [BMP][TFSA] (figure 1-a) and in acetonitrile (figure 1-b). As can be seen in ionic liquid the voltammogram presents an irreversible reduction wave at E_p = 0.1 V vs SCE; by analogy with the cyclic voltammogram obtained in acetonitrile, in which the E_p is detected at 0.2 V vs SCE, the reduction wave obtained in [BMP][TFSA] can be attributed to the reduction of the 4-nitrobenzendiazonium leading to the formation of the nitrophenyl radical. Upon the second scan in acetonitrile the cathodic peak is totally suppressed whereas in ionic liquid a decrease of the recorded current can be observed, indicating the progressive blocking of the electroactive surface due to the formation of the nitrophenyl layer onto gold electrode. It is worth to note that, being the same the scan rate adopted for the electroreduction, the value of the current measured in ionic liquid is quite lower than that in acetonitrile.
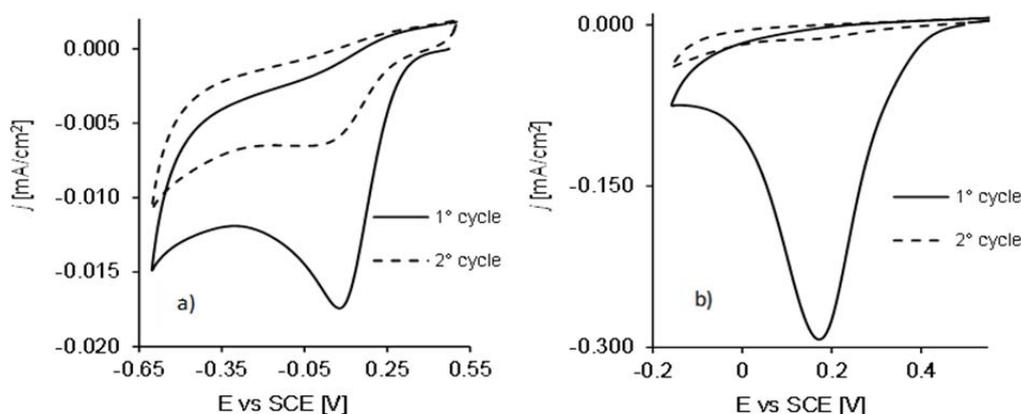
Figure 1: Cyclic voltammograms of gold electrode in 2 mM NBD recorded at 100 mV s^{-1}; a) in [BMP][TFSA]; b) in acetonitrile + 0.1 M (TBAPF6). The first and second potential scans are shown.

The amount of NBD reduced can be roughly estimated from the voltammetric charge related to the relevant peak: values of 7.5×10^{-10} mol cm^{-2} and 8.9×10^{-9} mol cm^{-2} were obtained in ionic liquid and acetonitrile, respectively. Comparing these values with the theoretical value of 1.2×10^{-9} mol cm^{-2} calculated for a close-packing layer of nitrobenezene (Pinson, 2012) it can be observed that in acetonitrile the molar concentration of nitro-phenyl groups is equivalent to about nine layers whereas in ionic liquid a sub-monolayer can be estimated. However, these values are not a measure of the amount of NBD deposited on the surface, because not all the aryl radicals generated graft to the electrode surface, due to the occurrence of reactions with other aryl groups in the solution to give dimers and polymers.

One of the easiest ways to evidence and quantify the presence of nitrophenyl layer attached to the electrode is to reduce the grafted electroactive nitro-groups to amino-groups. To this aim the modified electrodes were removed from the solution and were rinsed with ACN to remove the weakly adsorbed molecules. Then the electrodes were immersed in water/ethanol solutions (90/10%V) containing 0.1 M KCl and cyclic voltammetries were performed at scan rate of 100 mV/s. It is well known that the reduction of nitrophenyl moieties in protic medium occurs through an intermediate reversible step which involves the nitrous/hydroxylamine (NO/NHOH) redox couple, followed by the irreversible amination of the hydroxylamine group (Ortiz et al. 1998, Richard et al. 2012). According to this mechanism, data presented in Figure 2 for the electrode modified in [BMP][TFSA], show the anodic peak related to the intermediate process at about -0.35 V vs SCE: just a knee is observable in the direct scan, assessing the corresponding reduction, due to its partial overlapping with the irreversible reduction wave, which has its maximum at around -0.9 V vs SCE. The presence of this signal indicates that nitro-phenyls are immobilized on the electrode.
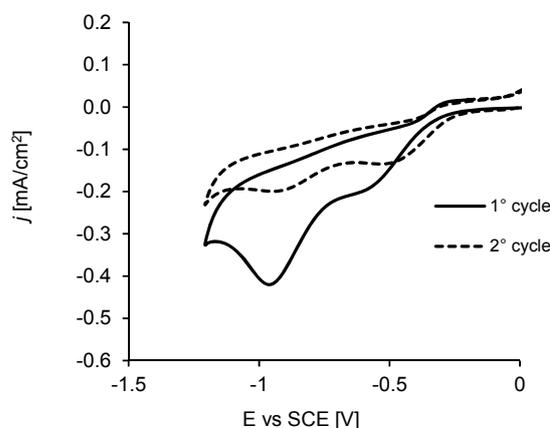

Figure 2: Cyclic voltammetric response of gold electrode modified in [BMP][TFSA] and 2 mM NBD recorded in water/ethanol solutions (90/10%V) containing 0.1 M KCl; scan rate 100 mV s^{-1}.

The nitro-phenyl surface concentration can be evaluated (by the following equation 1), taking into account that the reduction of nitro-groups involves 4 or 6 electrons, corresponding to the formation of NHOH or NH_2, respectively:

$$\Gamma_{NO_2} = \frac{Q(NO_2 \rightarrow NH_2)}{6FA} + \frac{Q(NO_2 \rightarrow NHOH)}{4FA}$$

(1)

Q corresponds to the charge measured by integration of the two electrochemical signals: reduction wave at -0.9, and oxidation wave at -0.35 V vs SCE; F is the faraday constant, and A represents the area of the electrode. Values of 5.42×10^{-10} mol cm^{-2} and 1.3×10^{-9} mol cm^{-2} were obtained in ionic liquid and acetonitrile, respectively. These values are lower than those estimated form the deposition of NBD, since only electro-active nitro groups are reduced and furthermore not all groups are transformed to NH_2.

As reported by Brooksby and Downard (2004), for some nitrophenyl groups far from the surface the electron tunnelling is very inefficient: thus there are electro-inactive groups which are not detected voltammetrically. In acetonitrile, where a multilayer structure has been obtained, the molar concentration calculated with eq. 1 is about one order of magnitude lower than that obtained from deposition of NBD, indicating that many nitro-groups are inaccessible to the electrons, due to the thickness of the layer. In the case of ionic liquid the molar concentration obtained with eq. 1 is quite similar to that evaluated from deposition voltammogram which is in agreement with a higher electrochemical accessibility of nitro-groups due to less dense sub-monolayer.

However, the surface molar concentration does not allow to determine the degree of coverage of the surface, i.e. how the layer is distributed on the gold electrodes. Thus, this evaluation has been performed determining the blocking properties of the film for the electron transfer reactions of the ferri/ferrocyanide redox probe, by faradaic impedance spectroscopy. Figure 3 shows the Nyquist plots of the bare gold (Figure 3-a), the electrodes modified in [BMP][TFSA] (Figure 3-b) and in acetonitrile (Figure 3-c). The Nyquist plot of gold shows the typical shape of a faradaic impedance spectrum for conductive electrodes, with a very small semicircle at high frequencies correlated to a very low electron transfer resistance followed by a 45° straight line which is typical of a diffusion limited electron-transfer process.
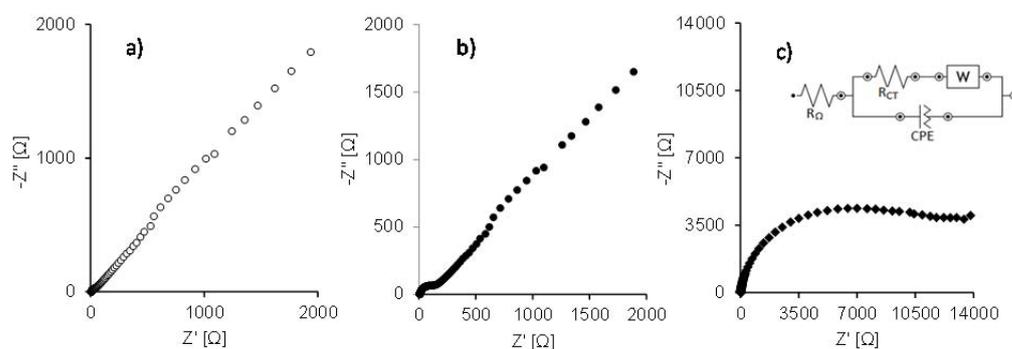

Figure 3: Nyquist plots for the Faradaic impedance measurements in 1 mM [Fe(CN)$_6$]$^{3-/4-}$ + 0.1 M KNO$_3$ (buffered solution pH=7) of a) bare gold; b) electrode modified in [BMP][TFSA] and 2 mM NBD c) electrode modified in acetonitrile + 0.1 M (TBAPF6) and 2 mM NBD. The inset shows the electrical equivalent circuit used to model the impedance spectra.

The impedance plots for the NBD modified electrodes significantly differ from that of bare gold: the diameter of the semicircle is increased indicating that the surface is partially ([BMP][TFSA]) or totally (acetonitrile) blocked to the electron transfer. The electron-transfer kinetics and the diffusional characteristics have been obtained by modelling the EIS spectra with a simple equivalent electrical circuit (see inset in Figure 3), which comprises the solution resistance R_Ω, the charge-transfer resistance R_{ct}, the Warburg impedance W and a constant phase element (CPE) for model the pseudo-capacitance of the surface. The apparent electrode coverage (θ) can be calculated by equation 2, assuming that all the

current is passed via bare spots on the electrode, and R^0_{ct} and R_{ct} represent the charge-transfer resistances measured on bare and modified gold electrodes, respectively (Khoshroo and Rostami, 2010):

$$\theta = 1 - \frac{R^0_{ct}}{R_{ct}} \qquad (2)$$

Table 1 reports the values of charge transfer resistance of the modified electrodes along with the corresponding values for the bare electrodes obtained from the equivalent circuit model. Also the apparent electrode coverage values (θ) calculated by equation 2 are reported for each data set. As can be observed, a fractional coverage close to 100 % was obtained working with acetonitrile solution, indicating that the nitrophenyl film covers the whole surface. When ([BMP][TFSA]) is used as solvent, the fractional coverage is about 80%: this value is in agreement with the voltammetric evaluation, confirming the formation of a less dense organic layer.

Table 1: Values of charge transfer resistances obtained by the impedance analysis and the corresponding apparent fractional coverage (θ).

Scan rate (mV s^{-1})	Solvent	R^0_{ct} (Ω)	R_{ct} (Ω)	θ %
2	[BMP][TFSA]	12	775	98.45
10	[BMP][TFSA]	14	495	97.17
100	Acetonitrile	28	11490	99.75
100	[BMP][TFSA]	21	101	79.25
500	[BMP][TFSA]	15	36	58.33
1000	[BMP][TFSA]	15	32	53.12

The low surface coverages obtained in [BMP][TFSA] agree with data in the literature, in which less dense layers were obtained on carbon electrodes using ionic liquids as solvents (Fontaine et al. 2010): this behaviour has been explained considering the high viscosity of the ionic liquids with respect to acetonitrile and a correlation between viscosity and surface concentration has been also proposed.

To better clarify this point, depositions of NBD in ionic liquid have been performed at different scan rate and each modified electrode has been characterized by EIS. Figure 4-a) shows the current peaks (j_p) related to the deposition process as a function of the square roots of the scan rates. A linear trend can be observed, which may indicate a diffusion controlled process, even if the peak potentials slightly shift towards more positive potentials as the scan rate decreases (data not shown).
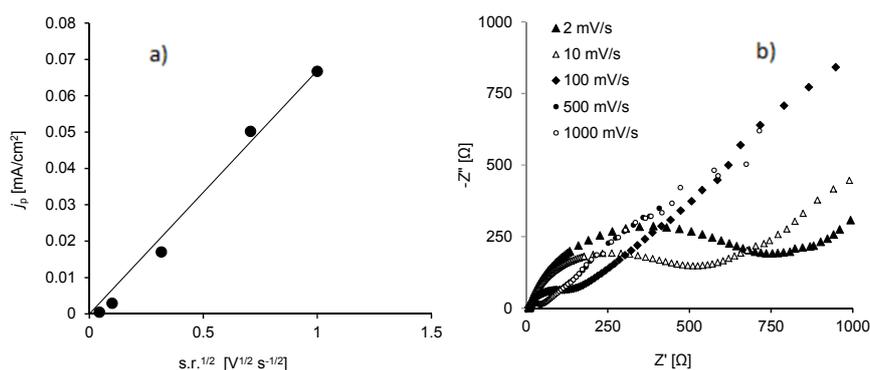
Figure 4: Results obtained for gold electrode modified with NBD at different scan rates: a) Values of current densities measured at the deposition peak as a function of the square roots of the scan rate (s.r.); b) Nyquist plots for the Faradaic impedance measurements in 1 mM [Fe(CN)$_6$]$^{3-/4-}$ + 0.1 M KNO$_3$ (buffered solution pH=7).

Figure 4-b reports the impedance spectra of the electrode modified in ionic liquid and 2 mM NBD at different scan rates; the corresponding values of charge transfer resistance are presented in Table 1. The

decrease of scan rate during the deposition allows to obtaining more covered surface; at 2 mV/s the nitrophenyl film covers the whole surface also when ionic liquid is used as solvent.

4. Conclusions

The results presented in this work indicate that nitro-phenyl groups have been successfully deposited on gold electrodes using [BMP][TFSA] as solvent for the electrochemical reduction. The amount of nitrophenyl grafted on gold and the surface coverage can be controlled by changing the scan rate during the reduction of NBD in ionic liquid. Moreover, the use of a high viscosity ionic liquid instead of acetonitrile as solvent, allows obtaining low amount of the attached molecules and less dense layers.

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