



Short communication

## Electrochemical immobilization of redox active molecule based ionic liquid



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## ARTICLE INFO

## Article history:

Received 3 June 2015

Received in revised form 17 June 2015

Accepted 18 June 2015

Available online 26 June 2015

## Keywords:

Electrochemical grafting

Diazonium

Redox ionic liquid

Surface wettability

Functional material

## ABSTRACT

The electrochemical immobilization of redox active molecule based ionic liquid onto glassy carbon electrode has been performed. 1-Nitrophenylethyl-3-methylferrocenylimidazolium bis(trifluoromethylsulfonyl)imide was synthesized and characterized by electrochemistry showing the presence of two redox couples. Following that, the electrochemical reduction of this molecule in acidic media containing sodium nitrite leads to the in situ formation of the corresponding diazonium, in the vicinity of the electrode, and subsequently the grafting of redox based ionic liquid molecule onto the electrode surface. The surface analysis of the attached layer confirms the formation of organic thin film strongly attached to the electrode surface, and evidences the presence of the components of the imidazolium ring, ferrocenyl unit, and TFSI anion. In addition, the modified electrode was electrochemically characterized by following the electrochemical signal of the attached ferrocenyl unit. Finally, the electrochemical reversible wettability of the modified electrode upon oxidation and reduction process was demonstrated.

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### 1. Introduction

Introducing molecules by their attachment onto surface material reveals to be a powerful way to provide new interfaces. The generated interfaces have been used in various applications including molecular electronics, energy storage, sensing, and surface wettability [1–3]. Thus, several strategies have been proposed for the immobilization of thin organic film onto various electrodes materials [4,5]. In this field, electrochemical grafting, through oxidative or reductive processes, has been proposed as an efficient and simplest method for such purpose. Several reviews describing the electrochemical grafting have been reported [6,7].

Besides that, the designs of new molecules with specific functionalities make it possible to tune in desirable way the physicochemical properties of the electrodes interface [8,9]. More recently, research focus on the immobilization of molecule based ionic liquid. Ionic liquids have been proved to be a promising medium in electrochemistry and found suitable for several applications including energy storage, photovoltaic, supercapacitor, electrocatalysis, and smart surface [10, 11]. However, ionic liquid suffer from some limitations including their high cost and high viscosity which limits their use at industrial scale. To overcome these limitations, the immobilization of molecule based ionic liquid appears to be a good compromise to fulfill the industry requirement. Indeed, the attachment of molecule based ionic liquid requires synthesis of small amount of material and acquires to the surface the properties of the ionic liquid. In the literature, this strategy

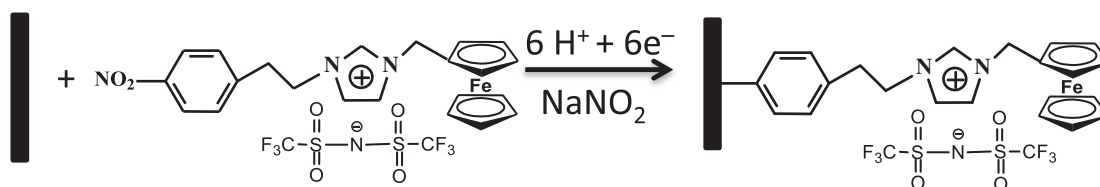
was developed through the formation of self-assembled monolayer using molecule based ionic liquid bearing various anchoring groups [12, 13]. Most of the studied molecules are based on thiol or trialkoxysilyl functionalized imidazolium followed by surface immobilization onto gold or silicon oxide surfaces. However, only few works report on the electrochemical grafting, using the diazonium reduction, of molecule based ionic liquid and more specifically redox molecule based ionic liquid [14,15].

In this work, the electrochemical reduction process is used for the attachment of redox active molecule based ionic liquid on the electrode surface. To this end 1-nitrophenylethyl-3-methylferrocenylimidazolium bis(trifluoromethylsulfonyl)imide, [NO<sub>2</sub>PhElmMFc] [TFSI], was synthesized. The proposed molecule is based on imidazolium ring, ionic liquid cation, bearing two redox units nitrophenyl and ferrocenyl and bis(trifluoromethylsulfonyl)imide, ionic liquid anion. The nitrophenyl end group will be used as anchoring group for the immobilization of the molecule on electrode surface. Scheme 1 summarizes the used strategy for the electrochemical grafting onto the carbon electrode.

The grafting procedure is based on the electrochemical reduction of nitrophenyl group in acidic media leading to the formation of aminophenyl derivative; the later generated in the vicinity of the electrode and in the presence of sodium nitrite undergoes chemical diazotization. The generated diazonium within the diffusion layer of the electrode is reduced leading to the formation of the corresponding radical followed by its covalent attachment onto the electrode surface. One has to note that the reduction potential of nitrophenyl group is sufficiently negative to reduce, in a second step, the generated diazonium. Next, the modified electrodes were characterized by X-ray photoelectron spectroscopy and by electrochemistry. Finally, the wettability

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**Scheme 1.** Proposed pathway for the electrochemical grafting of ferrocene based ionic liquid molecule.

of the generated surface was measured and the electrochemical reversible wettability upon oxidation and reduction process was investigated.

## 2. Material and methods

### 2.1. Chemicals and synthesis

Sodium nitrite ( $\text{NaNO}_2$ ), perchloric acid ( $\text{HClO}_4$ ) and lithium bis(trifluoromethylsulfonyl)imide were purchased from Sigma-Aldrich. Acetonitrile was supplied by VWR Chemicals and stored over molecular sieves. The synthesis of 1-nitrophenylethyl-3-methylferrocenyliimidazolium bis(trifluoromethylsulfonyl)imide was performed by combining the previously published procedure [14, 16].

### 2.2. Electrochemical investigations

Electrochemical measurements were performed using CHI 660C workstation (CH Instruments). Glassy carbon electrode was used as working electrode, platinum wire used as counter electrode and saturated calomel electrode (SCE) as reference electrode. Before electrochemical investigations the solution was deoxygenated by bubbling argon gas and the working electrode was polished using decreasing size of diamond pastes.

### 2.3. X-ray photoelectron spectroscopy

XPS analysis were performed using Thermo VG Scientific ESCALAB 250 system with monochromatic Al  $K\alpha$  ( $h\nu = 1486.6$  eV) 200 W X-ray source.

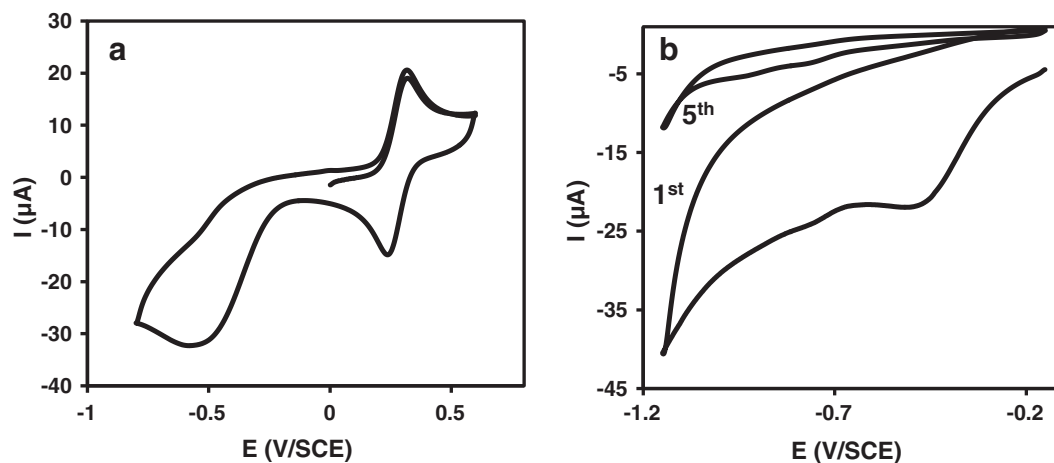
## 3. Results and discussion

The electrochemical behavior onto glassy carbon electrode of 1-nitrophenylethyl-3-methylferrocenyliimidazolium

bis(trifluoromethylsulfonyl)imide at  $10^{-3}$  M in acetonitrile solution containing 0.1 M LiTFSI and  $\text{HClO}_4$  was recorded as shown in Fig. 1a.

The cyclic voltammogram (CV) exhibits a reversible redox system at 0.3 V corresponding to the ferrocenium/ferrocene redox couple and reduction wave at  $-0.5$  V attributed to the irreversible reduction of nitrophenyl group in acidic media. The reduction wave involves  $6e^-$  and  $6H^+$  [17], with a peak current around  $-30 \mu\text{A}$  while the oxidation of Fc involves  $1e^-$  with a peak current of about  $18 \mu\text{A}$ . One could expect that the reduction peak current will be 6 times bigger than that of Fc oxidation peak current. However, for a clear comparison the charge involved during the two processes should be considered, especially, as the reduction wave is large when compared to the oxidation wave. The measured charge during the reduction of nitrophenyl is around  $-1.6 \times 10^{-4}$  C while the charge corresponding to Fc oxidation is around  $3.5 \times 10^{-5}$  C which is roughly 6 times lower when compared to the cathodic charge. This result confirms the possibility to perform electrochemical measurement on molecule based ionic liquid bearing two different redox units. Next, sodium nitrite ( $\text{NaNO}_2$ ) was introduced in the electrochemical cell and the CV was recorded on GC electrode as shown in Fig. 1b. During the first scan, the curve shows an irreversible reduction wave at  $-0.5$  V corresponding to the reduction of nitrophenyl group onto aminophenyl. This reduction wave disappears after few cycles indicating the passivation of the electrode surface. Indeed, during the reduction process the nitrophenyl group is reduced in the vicinity of the electrode to its corresponding amino group. The latter and in the presence of  $H^+$  and  $\text{NaNO}_2$  is rapidly transformed to diazonium which is subsequently reduced at the electrode conducting to the formation of the corresponding radical followed by its subsequent attachment on the electrode surface. Overall, the observed electrochemical behavior is similar to the well-established electrochemical reduction of diazonium derivatives and confirms the formation of thin organic layer onto GC electrode [15,18].

In order to confirm the occurrence of the electrochemical grafting, the modified electrode was rinsed and sonicated in acetonitrile to remove the weakly adsorbed species and the chemical composition of



**Fig. 1.** (a) Cyclic voltammogram recorded on GC electrode in solution containing  $10^{-3}$  M  $[\text{NO}_2\text{PhElmMFC}]$  [TFSI] and  $\text{HClO}_4$  in acetonitrile. (b) Cyclic voltammogram performed in the same conditions as (a) after addition of  $5 \times 10^{-3}$  M of  $\text{NaNO}_2$ . Scan rate  $0.1 \text{ V s}^{-1}$ .

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