



Surface functionalization with redox active molecule-based imidazolium *via* click chemistry



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ABSTRACT

In this study, the redox active molecule *N*-ferrocenylmethyl-*N*-propargylimidazolium bromide was immobilized onto the surface of an electrode. The surface modification was performed by coupling the electrochemical reduction of the 4-azidophenyldiazonium generated *in situ* with a copper(I) catalyzed click chemistry reaction. Surface and electrochemical investigations suggest the attachment of a monolayer of redox active molecules containing an ionic liquid framework onto the electrode surface. Furthermore, scanning electrochemical microscopy studies revealed the conductive behavior of the attached ferrocenyl moieties on the ITO surface.

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1. Introduction

The ability to tailor the physico-chemical properties of surfaces for specific functions by immobilizing a variety of molecules on them has led to successful applications in sensors, smart surfaces and molecular electronics [1,2]. Electrochemical grafting has been demonstrated to be a powerful method for building modified electrodes [3–5]. This method is applicable to a large range of functional groups and can be performed using oxidation or reduction processes, depending on the anchoring groups [6–8]. In the past few years, task-specific ionic liquids have attracted a lot of attention thanks to their unique properties [9,10]. Recently it has been reported that molecules containing an ionic liquid framework have been immobilized on different types of electrodes [11–15]. The attachment of such molecules provides new surface properties, increasing the range of potential applications [16–18]. Such modified surfaces could also be used as a platform for post-functionalization, extending the range of molecules and functionalities that could be immobilized on the surface [3,7,19,20]. One method commonly used for post-functionalization is click chemistry, which involves the covalent attachment of a task specific group to the azido-based layer *via* an alkyne group [7,21,22]. This method has been successfully used to decorate polymer and thin organic layers attached to a surface [23–26]. However, there has not yet been any report on the immobilization of redox molecules containing an ionic liquid framework using click chemistry.

In the present study, we synthesize *N*-ferrocenylmethyl-*N*-propargylimidazolium bromide and investigate its immobilization on an electrode surface through click chemistry. The principle of the grafting strategy is based on coupling the electrochemical reduction of 4-azidophenyldiazonium generated *in situ* with click chemistry as summarized in Scheme 1. The resulting modified electrode is characterized electrochemically and by atomic force microscopy (AFM). Finally, scanning electrochemical microscopy is used to investigate the local electrochemical reactivity of the modified surfaces.

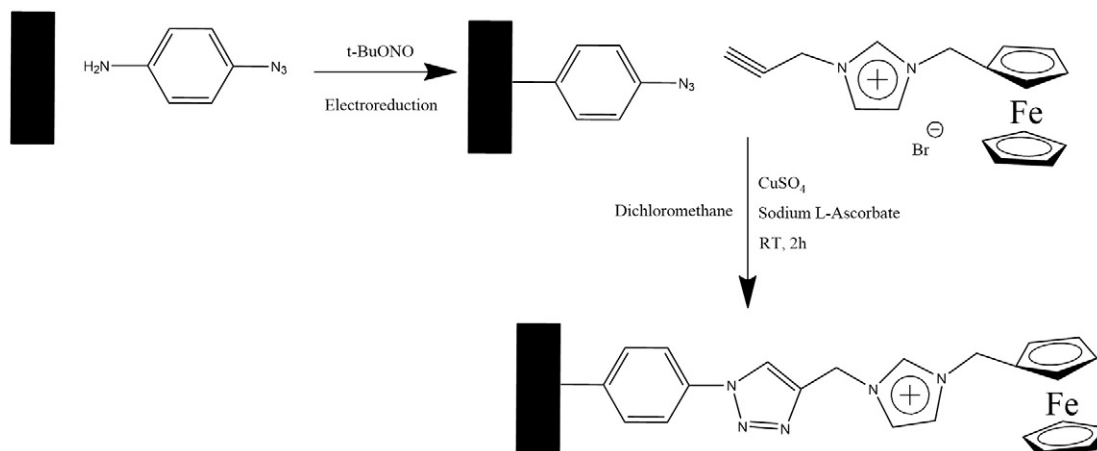
2. Experimental section

Chemicals. All chemicals were supplied from Sigma-Aldrich, except (ferrocenemethyl)trimethylammonium iodide (Alfa-Aesar), and were used as received. The *N*-ferrocenylmethyl-*N*-propargylimidazolium bromide was produced using the following procedure. First, the *N*-ferrocenylmethylimidazole was synthesized according to the previously published procedure [27]. Next, propargyl bromide (1.6 mL, 21 mmol) and *N*-ferrocenylmethylimidazole (1.6 g, 6 mmol) were dissolved in chloroform, and the mixture was then refluxed for 2 h at 70 °C. The solvent and unreacted propargyl bromide were removed by evaporation under reduced pressure to give 2.08 g of a yellow brown oil (yield 90%).

¹H NMR (400 MHz, DMSO-*d*₆) δ(ppm): 3.83 (s, 1H), 4.22 (m, 7H), 4.45 (t, *J* = 1.6 Hz, 2H), 5.15 (s, 2H), 5.18 (s, 2H), 7.76 (s, 1H), 7.81 (s, 1H), 9.25 (s, 1H).

Instruments. A three-electrode cell was used for the electrochemical measurements. A saturated calomel electrode (SCE) and stainless steel mesh were used as reference and counter electrode, respectively.

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Scheme 1. Immobilization of *N*-ferrocenylmethyl-*N*-propargylimidazolium bromide onto the electrode surface via click chemistry.

Indium tin oxide (ITO) plates were used as working electrodes; the electrode area was 1 cm². AFM characterizations were performed using a Molecular Imaging PicoSPM II system. The thickness profile was obtained by scratching the surface with the contact mode. Scanning electrochemical microscopy measurements were performed with a SECM cell in which a silver wire and a platinum wire were used as reference and auxiliary electrode. A platinum microelectrode with a diameter of 10 μm was selected as working electrode and the modified electrodes were used as the substrate. The electrochemical measurements were performed using a CHI920C bipotentiostat (CH Instruments, Austin, Texas).

3. Results and discussion

The electrochemical behavior of the synthesized ferrocenylmethyl-*N*-propargylimidazolium bromide was investigated and the cyclic voltammogram recorded on the ITO electrode is shown in Fig. 1a. The CV exhibits a reversible redox signal corresponding to the oxidation and reduction of the ferrocenyl redox couple. Linear variation of the peak current as a function of the square root of the scan rate is observed, suggesting that mass transport is controlled by the diffusion process. The half-wave potential $E_{1/2}$ of the compound is 150 mV more positive than that of the free Fc^+/Fc couple. This anodic potential shift is ascribed to the withdrawing effect of the positively charged imidazolium ring linked to ferrocene [28]. Next, the 4-azidophenyldiazonium generated

in situ was electrochemically reduced on an ITO surface using different numbers of electrografting cycles (Fig. 1b).

In the presence of a nitrosium source, 4-azidoaniline was transformed *in situ* to the 4-azidophenyldiazonium cation [26]. Sweeping the potential between 0.4 to −0.8 V in the first scan and between 0.2 to −0.8 V in other scans, a reduction peak is observed at −0.35 V, attributed to the reduction of the diazonium group. A decrease in the reduction current observed upon cycling suggests the formation of an azido-phenyl layer on the ITO surface. The azido-modified ITOs were then used for post functionalization with *N*-ferrocenylmethyl-*N*-propargylimidazolium bromide using the click chemistry as presented in Scheme 1. Specifically, the previously modified ITO electrodes were immersed in 5 mM of *N*-ferrocenylmethyl-*N*-propargylimidazolium bromide in dichloromethane solution. A catalytic amount of aqueous solution containing CuSO₄ and sodium L-ascorbate was added under vigorous stirring and the reaction was kept for 2 h. The electrodes were then removed from the reaction medium and washed successively with distilled water, acetone and acetonitrile under sonication. The modified electrode was transferred to an electrolytic solution, and the CV was recorded as shown in Fig. 2a.

The CV shows a reversible redox system at 0.57 V attributed to the oxidation and reduction of the attached ferrocenyl imidazolium moieties. The peak-to-peak separation around 20 mV, and the linear variation of the oxidation peak current as function of the scan rate confirm that the ferrocene-based ionic liquid molecule was successfully attached onto the electrode surface through the click chemistry process.

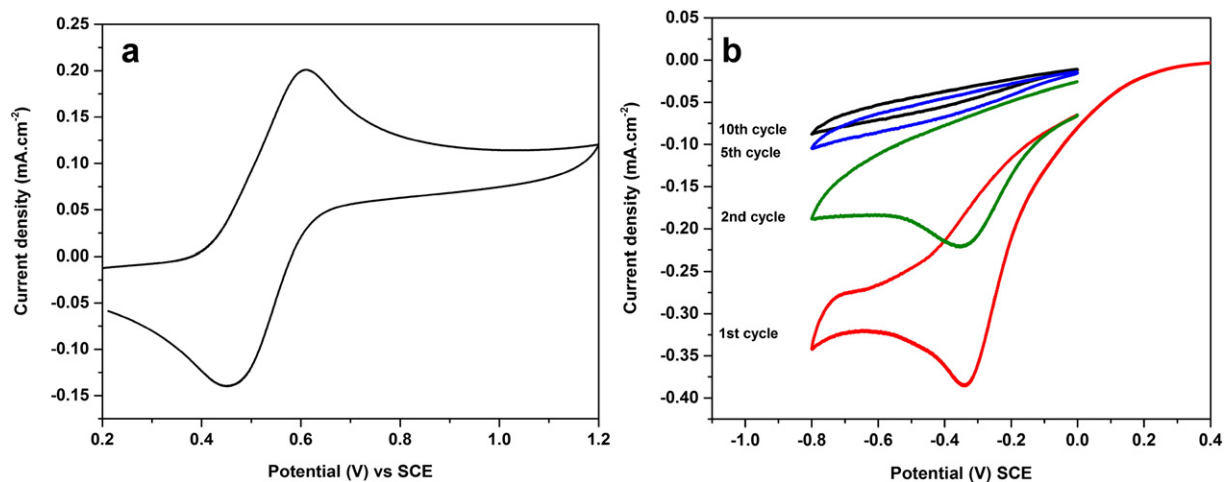


Fig. 1. (a) Cyclic voltammogram on an ITO electrode of 1 mM *N*-ferrocenylmethyl-*N*-propargylimidazolium bromide in acetonitrile containing 0.1 M TBAPF₆. (b) Cyclic voltammograms for the reduction of 1 mM of 4-azidophenyldiazonium in MeCN solution with 0.1 M of TBAPF₆.

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