

Short Communication

Covalent Modification of Glassy Carbon Electrode with an Imidazolium based Methoxysilyl Ionic Liquid Nanoparticles: Application in Determination of Redox System

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Abstract

Glassy carbon (GC) is the most commonly used carbon-based electrode in the analytical laboratory. Because of the high background current and low electrode response, modification of this electrode can be done by various materials and techniques. An ionic liquid (IL), 1-methyl-3-(3-trimethoxysilyl propyl) imidazolium bis (trifluoromethylsulfonyl) imide, was covalently cross linked onto the GC surface. GC was activated in sulfuric acid solution by cyclic voltammetry, which generate surface oxygen containing functional groups such as OH group, through which the IL was covalently bonded the surface of GC. The resulting surface was characterized by using cyclic voltammetry, differential pulse voltammetry and atomic force microscopy. Hydroquinone and ascorbic acid were the redox systems used to study the effect of IL-covalent bonding on the electron transfer rate and response decay of the GC. Compared to GC modified with a physically adsorbed layer of IL with an unstable response and decrease in peak current, the chemically IL-modified electrode showed stable and favorable response characteristics.

Keyword: Glassy carbon electrode, Ionic liquid, Electron transfer rate, Electrode response decay.

1. INTRODUCTION

Carbon-based materials are widely used in electroanalytical chemistry [1] and glassy carbon is the most commonly used electrode material [2] because of its good electrical conductivity, low cost, and high chemical inertness [3]. Despite inherently favorable electrochemical characteristics, surface modifications of GCs have been the subject of much research with a view to further enhancing the electrode response for electrochemical sensing applications [4]. The modification can be done through various

techniques. As a promising treatment technique, chemical modification with the layers of modifier molecules, chemically or physically attached to the electrode surface, have been investigated [5, 6]. Various compounds such as polymer films [7], ceramics [8], metal nanoparticles [9], and organic [10] or inorganic redox mediators [11] have been covalently attached or physically adsorbed to GC surface and their effects on the electron transfer kinetics have been investigated. Recently, great deals of attention have focused on room temperature ILs as attractive compounds for electrode modification in view of their physicochemical properties [12]. In some research

papers, a layer of IL/carbon-based powder composite is applied physically onto the GC surface. For example, Zhao et al [13] and Tu *et al.* [14] developed a composite material based on carbon nanotube and IL to modify GC in order to study the voltammetric response of p-nitroaniline and porphyrins respectively. Tang et al developed a layer of sol-gel composite film on GC containing IL and chitosan and AuNPs to form a disposable immunosensor for the detection of hepatitis B surface antigen in human serum [15]. The presence of particular functional groups in ionic liquids plays very important role in their application. There are few reports on application of IL with thiol functionalities for gold electrode modification [16]. Wang et al showed that a carboxylic acid functional group of imidazolium based IL, has been used to covalently modify boron doped diamond electrode [17].

In this paper, imidazolium based IL, was covalently cross linked onto the GC surface and compared to GC modified with a physically adsorbed layer of IL with an unstable response and decrease in peak current, the chemically IL-modified electrode showed stable, repeatable and favorable response characteristics. A scheme of the IL chemically cross linked GC is shown in Figure 1.

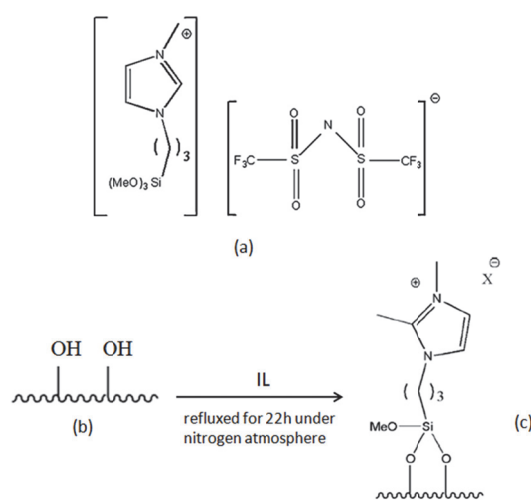


Figure 1. a) Structural formula of 1-methyl-3-(3-trimethoxysilyl propyl) imidazolium bis (trifluoromethylsulfonyl) imide, b) Surface of an anodized GC electrode, c) Most probable pattern of the IL chemically cross linked to the surface of the GC electrode. X^- : bis (trifluoromethylsulfonyl) imide

2. MATERIAL AND METHODS

2.1 Reagent and equipment

An IL, 1-methyl-3-(3-trimethoxysilyl propyl) imidazolium bis (trifluoromethylsulfonyl) were synthesized similar to those reported in previous work [18]. All chemicals purchased from Merck (Darmstadt, Germany) as analytical reagent grade and used without further purification. Dichloromethane was used for dilution of the IL prior to the physical modification of GC. The stock solutions of hydroquinone (1mM HQ) and ascorbic acid (1mM AA) were prepared daily. Buffer solution (PBS, pH 4.5) was prepared from KH_2PO_4 - H_3PO_4 (0.1 M, Merck).

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed with an AUTOLAB Potentiostat/ Galvanostat electrochemical workstation (made by Echo chemie, Netherland). The reference electrode was saturated Ag/ AgCl-KCl. The auxiliary electrode was graphite rod and working electrode was GC. The surface morphology of electrodes was examined by Atomic force microscopy (AFM) with DME DS95-50 scanner and C26 controller with the tip curvature radius less than 10 nm.

2.2 Electrode preparation

2.2.1 GC activation

GC was polished with 0.3 μm and 0.05 μm alumina slurry and then cleaned ultrasonically in distilled water. Freshly polished electrode was anodized by cyclic voltammetry (versus a KCl-saturated Ag/ AgCl electrode) in the solution of 0.1M H_2SO_4 in the potential range of -1.1 to 2.2V after optimization.

2.2.2 Physically modified GC

A 5% solution of IL in dichloromethane was prepared; a drop of solution was poured on the surface of an activated GC. It was put in 70°C ovens for 2min. GC was remained at room temperature for 15min until solvent evaporated. Then, it was put in PBS with pH= 4.5 and 20 cycles were taken in the range of (0.0 to 1.0V) until the current of electrode was stable [19].

2.2.3. Chemically modified GC

After anodization step, an active electrode was put into a solution comprising of 0.1% IL in chloroform. The system was refluxed for 22h under nitrogen atmosphere. Then the electrode was washed several times with chloroform in order to remove the excess IL which was not reacting chemically to the surface of the electrode.

3. RESULTS AND DISCUSSION

3.1.

Figure 2 shows the CVs of GC activation in 0.1M sulfuric acid solution. Potential was continuously cycled between -1.1 to 2.2V at 50mVs^{-1} . GC surfaces were oxidized at potentials higher than 1.8V [20]. A cathodic peak built up at around -0.25V on the reverse cycles which corresponded to the continuous increase of surface functionalities resulted from the anodization of glassy carbon. This characteristic was similar to those reported by Shiu [21]. The surface oxides typically exist in submonolayer coverage and are located on edge plane site. As cycle number increased, the oxygen content at glassy carbon surfaces increased gradually as a result of electrochemical activation, especially OH group increased progressively, which we need them to react with IL and form chemically modified surface [22-24].

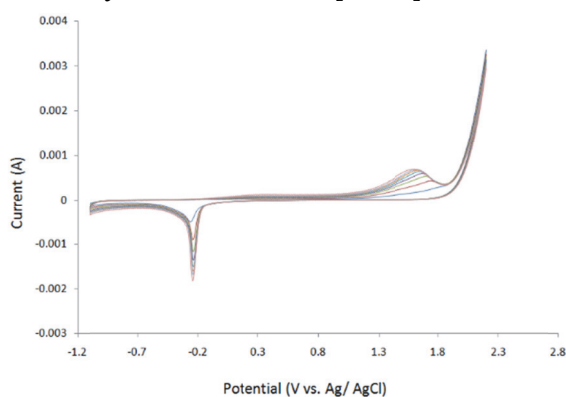


Figure 2. Cyclic voltammogram of an anodic activation of glassy carbon electrode in the solution of 0.1M H_2SO_4

3.2. Cyclic voltammetric studies of redox system

The electrochemical behavior of HQ and AA in 0.1M H_2SO_4 are shown in Figure 3A and B respectively. At bare GC, peak separation is

225mV for HQ, which shows the irreversibility mechanism of redox system (Fig. 3.A.a). After anodization, the oxygen functional groups at GC surface can assist the electron transfer rate by acting as the catalytic site for adsorption or participating in a proton exchange mechanism for redox reaction involving both electron and proton transfer [18] so ΔE_p for HQ decreased to 48mV (177mV decrease in comparison to bare GC) (Fig. 3. B.b). After physical modification of GC, Figure (3. A.c), peak separation increased to 57mV and peak current decreased because of slow electrochemical probe transport in viscous IL film which hindered ion transfer, so blocked the surface of the electrode and mask the active sites of GC surface. On chemically attaching of IL into the surface of GC, the peak current increased, and peak separation decreased to 30mV, this shows high electron and ion transfer rate through IL (Fig. 3. A.d). The same behavior was observed for AA, which peak current increased 1.5 times higher than anodized GC (Fig. 3. B). The most important data are shown in Figure 3. C.

3.3. Scan rate effect

With the scan rates in the range of $20\text{-}100\text{ mVs}^{-1}$, a linear relationship was established between the peak current and scan rate, revealing the surface controlled mechanism was significant at low scan rate. While in the range of $100\text{-}500\text{ mVs}^{-1}$, the linear relationship was found between the peak current and the square root of scan rate, suggesting that the diffusion controlled behavior was predominated, in fact there were two types of HQ, some molecules were attached on the surface of chemically modified GC and other molecules were in the solution. Adsorption molecules reacted in low scan rate and other molecules should have diffused on the surface of an electrode in high scan rate.

Figure 4.B shows chemically modified GC durability for over 120 CVs. This suggests that the synthesized IL was bonded successfully to the surface groups of an anodized GC. After 120 separate CVs by chemically modified GC, 10.41% decrease in peak current was occurred.

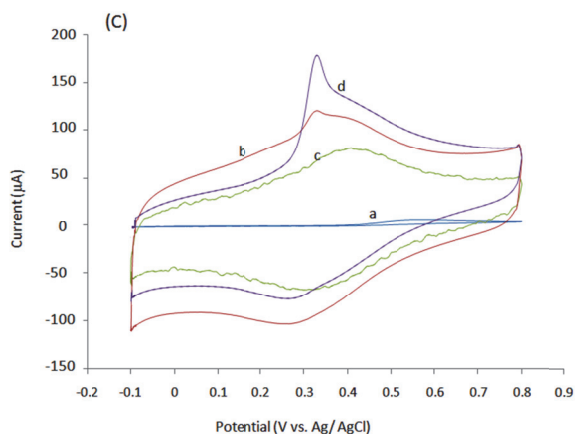
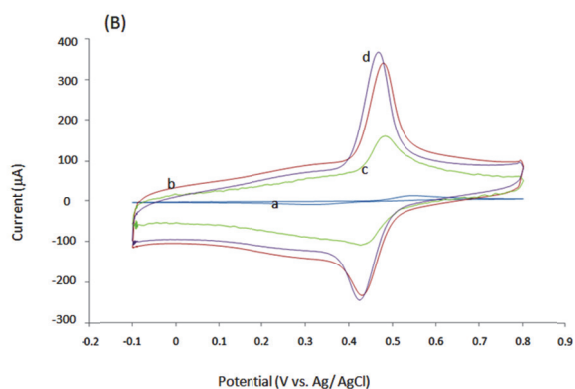


Figure 3. A) CVs from HQ, B) AA. For each voltammogram, a) bare GCE, b) anodized GCE, c) physically modified and d) chemically modified GCE. C) Cyclic voltammetry data for HQ and AA

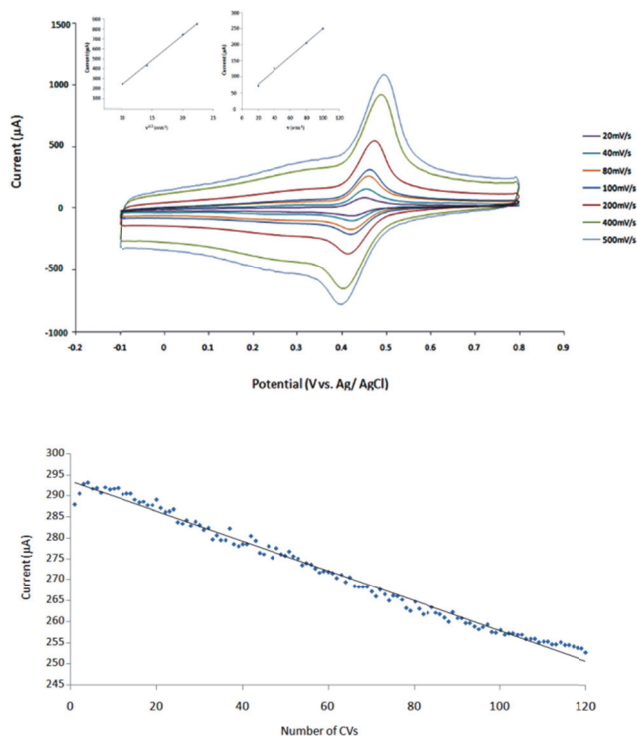


Figure 4. A, CVs of HQ at different scan rates, B) Anodic peak current related to the HQ redox system in 120 Cvs.

3.4. Differential pulse voltammetric studies of redox systems

Determination of HQ was performed with DPV by the use of chemically modified GC in Figure 5. The oxidation peak current increased linearly with the addition of HQ in the concentration range of 10 μM to 1 mM. The detection limit was evaluated as 2.1 μM and by repeating the measurement of 0.1mM HQ, good reproducibility with a relative standard deviation (RSD) 3.6 % was performed.

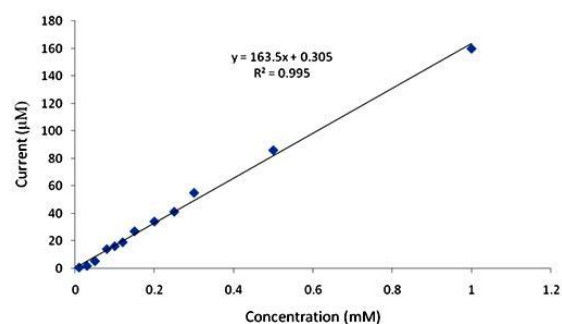


Figure 5. Calibration curve for determination of HQ in different concentration (0.01, 0.03, 0.05, 0.08, 0.1, 0.12, 0.15, 0.2, 0.25, 0.3, 0.5 and 1mM)

3.5. Surface morphology

Surface morphology changes of GC were monitored by AFM. Figure 6. A shows the topography image of an anodized GC (phase image is inset), the GC surface becomes rough after continued cycling between -1.1 to 2.2V. After chemically modification of GC, an IL was attached to the surface of an anodized GC. Figure 4. B shows the topography image of IL nanodomains on the GC surface. The size of nanodomains is variable from 7 ± 3 nm, which indicate that a molecule of IL attached chemically on the surface, and several of them accumulated to the molecule. This electrocatalytic behavior is attributed to a combination of different suitable properties of IL. Also, high stability of chemically modified GC attracts great consideration to use it in many determinations.

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