

Investigation of Electrochemical Behaviour of Aminophenol Diazonium Salt Covalently Grafted onto the Glassy Carbon Electrode Surface

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In this paper, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) have been used to investigate of the electrochemical behaviour of aminophenol diazonium salt on the modified glassy carbon (GC) electrode. The modification of aminophenol diazonium salt covalently grafted onto the glassy carbon electrode surface was performed between +0.1 and -0.9 V potential ranges for cathodic scan, 0.0 and +1.7 V potential ranges for anodic scan of 0.1 V s⁻¹ and 10 cycles.

Key Words: Aminophenol diazonium salt, Surface modification, Surface characterization.

INTRODUCTION

In the last few decades, research of modification of the carbon based materials for electrochemistry has witnessed major growth¹⁻⁷. Modification of the electrode surface is an important studies in electrochemistry. In electrochemistry, carbon electrodes are widely used because of low background current, low cost, wide potential window, speed, low equipment, chemical inertness and minimum sample pretreatment required prior to analysis^{8,9}. One of the reasons for the considerable current interest in modification of carbon materials is because the carbon material is inert and has good conductivity and resistance to environmental and chemical attack.

The modification of highly ordered mono- or multi-layers on carbon materials surface has been paid great attention because it plays an important role in catalytic, analytical and biotechnological applications¹⁰. In the recent 10 years, free radical grafting method has often been adopted to achieve the formation of covalent bonds between carbon surface and the modifier. The modification process is carried out by electrochemical oxidation of amino-containing compounds, aryl acetates or aliphatic alcohols or by electrochemical reduction of diazonium salts in non-aqueous solution¹¹ or in aqueous solution¹²⁻¹⁵. One irreversible oxidation or reduction peak appears under electrochemical process, the covalent grafting of modifier on glassy carbon electrode surface takes place only once during one potential cycle¹⁶⁻¹⁸.

The most important method for the preparation of diazonium salts is treatment of aromatic amines such as aniline with sodium nitrite in the presence of a mineral acid. In aqueous solution these salts are unstable at temperatures higher than +5 °C; the -N⁺ \equiv N group tends to be lost as N₂. One can isolate diazonium compounds as tetrafluoroborate salts, which are stable at room temperature. Typically diazonium compounds are not isolated and once prepared, used immediately in further reactions.

The modification of surfaces by electrochemical reduction of diazonium salts can be summarized on carbon¹⁹, metal²⁰ or semiconductor²¹ as shown in **Scheme-I**.



Scheme-I

The binding of aryl groups to carbon electrodes is likely a two-step process. The first step involves the electrochemical reduction of the diazonium salt to generate aryl radicals. This is followed by the reaction of the radicals with the carbon surface.

In this paper, aminophenol diazonium salt was covalently modified on the glassy carbon electrode surface by both electrochemical oxidation and electrochemical reduction. Electrochemical behaviours of aminophenol diazonium salt were investigated by cyclic voltammetry. The modification of aminophenol diazonium salt on the glassy carbon electrode was performed between +0.1 and -0.9 V potential ranges for cathodic scan, 0.0 and ± 1.7 V potential ranges for anodic scan of 0.1 mV s⁻¹ and 10 cycles. The presence of aminophenol diazonium salt at the glassy carbon electrode surface was characterized by CV and EIS.

EXPERIMENTAL

Ultra pure quality of water with a resistance of 18.3 M cm (Millipore Milli-Q purification system, Millipore Corp. Bedford, MA, USA) was used in preparations of aquous solutions, cleaning of the glassware and polishing the electrodes. All chemicals were of the highest purity available from Fluka (Buchs SG, Switzerland), Riedel de Haën (Seelze, Germany) or Sigma-Aldrich (Buchs SG, Switzerland), chemical companies and so no further purification was performed. Aminophenol diazonium salt was synthesized from 2,4-diaminophenol dihydrochloride (Aldrich). In all experiments, the solutions and the electrodes were kept in acetonitrile (MeCN) when they were not in use. All the experiment solutions were prepared at 1 mM concentration. Solutions were thoroughly deoxygenated by purging with purified argon gas (99.999 %) for 10 min prior to the electrochemical experiments. Argon blanket was maintained over the solutions to supply an inert atmosphere during voltammetric measurements. All electrochemical experiments were performed at room temperature $(25 \pm 1 \text{ °C})$.

A traditional three-electrode cell system was used in all electrochemical experiments. In present experiments, GAMRY Reference PCI4/750 series Potentiostat/Galvanostat/ZRA from Gamry Instruments (PA, USA) electrochemical analyzer with BAS (Bioanalytical Systems, West Lafayette, IN, USA) Model MF-2012 and Tokai glassy carbon-20 glassy carbon electrodes were used. Ag/Ag⁺ (10 mM AgNO₃ in 0.1 M TBATFB) (BAS Model MF-2042) for non-aqueous media and a Ag/AgCl/₃ M KCl (BAS Model MF-2063) for aqueous media were used as reference electrodes. Pt wire counter electrode (BAS Model MW-1032) was used.

Synthesis of aminophenol diazonium salt: Approximately 0.5 g of 2,4-diaminophenyl dihydrochloride (Aldrich) was weighed into a three-necked 50 mL round-bottom flask; then 10 mL of 50 % fluoroboric acid (Aldrich) was added and the resultant mixture was stirred with a magnetic stirring bar, for an hour at -10 °C. A 5:1 molar ratio of NaNO₂ (relative to amino precursor) was weighed into a separate container, just enough water was added to dissolve the NaNO₂ at room temperature and the solution was cooled to -10 °C. A thermometer was inserted into the three-necked flask and the precursor solution was added dropwise and the temperature was always kept below -10 °C during the reaction. Following the complete addition of NaNO₂, the mixture was filtered in a

Buchner funnel and anhydrous ether (Fluka) was used to remove the remaining sediments from the round-bottom flask. The product was recrystallized by dissolving in cold (+ 4 °C) acetonitrile followed by slow addition of cold anhydrous ether to recover the diazonium tetrafluoroborate salt (Fig. 1). The synthesized aminophenol diazonium salt should be kept in a freezer and should be used within two mounts. Otherwise aminophenol diazonium salt may decompose. It one wants to use the decomposed aminophenol diazonium salt, one should recrystallise it. Aminophenol diazonium salt should be prepared freshly and used immediately within 2 h of preparation²²⁻²⁶.

Electrode modification: The glassy carbon electrodes were prepared for the experiments by polishing to gain a mirror-like appearance, first with fine wet emery papers (grain size 4000) and then with 1.0 and 0.3 μ m alumina slurry on micro cloth pads (Buehler, USA). After the initial polishing, the glassy carbon electrodes were resurfaced with 0.05 μ m alumina slurry. First, the glassy carbon electrodes were sonicated in the water twice then in 1:1 (v/v) isopropyl alcohol and acetonitrile (IPA + MeCN) (Aldrich) mixture for 10 min each²⁵⁻²⁸.

Following polishing, the electrodes were sonicated in ultrapure water and IPA/MeCN mixture. An Ag/AgCl/3 M KCl and a platinum wire were used as reference and counter electrode, respectively. The electrochemical modification of the glassy carbon electrode was performed from an acetonitrile solution containing 1 mM 2-aminophenol diazonium salt and 0.1 M TBATFB and applying a potential of +0.1 to -0.9 V for cathodic scan and 0.0 to +1.7 V for anodic scan *vs* Ag/Ag⁺ at 0.1 V s⁻¹.

RESULTS AND DISCUSSION

The electrochemical behaviours of aminophenol diazonium salt onto glassy carbon electrode surface were investigated using cyclic voltammetric technique. 1 mM aminophenol diazonium salt (in 0.1 M TBATFB in MeCN) was prepared and used in the modification process.

To determine the probability of the surface modification of 2,4-diimino phenyl (DAP) (Fig. 2a) and aminophenol diazonium salt (Fig. 2b) between +0.1 V and -0.9 mV potential ranges for cathodic scan. Similarly, 2,4-diimino phenyl (Fig. 3a) and aminophenol diazonium salt (Fig. 3b) between 0.0 V and +1.7 mV potential ranges for anodic scan, multiple cycles were performed by cycling back from the last peak in the voltammogram.

For the characterization of the modified surface 1 mM ferrocene in 0.1 M TBATFB in non-aqueous media (Fig. 4a) and 1 mM $Fe(CN)_6^{3-}$ in 0.1 M H_2SO_4 in aqueous media (Fig. 4b) for CV and 1 mM $Fe(CN)_6^{3-/4-}$ (1:1) mixture in 0.1 M KCl for EIS (Fig. 4c) were used.

APDAS



2,4-Diaminophenol dihydrochloride Fluoroboric acid





Fig. 2. Cyclic voltammograms of (a) GC-DAP and (b) GC-APDAS on +0.1 and -0.9 V potential range and on GC electrode using 100 mV s⁻¹ with 10 cycles in MeCN containing 0.1 M TBATFB



Fig. 3. Cyclic voltammograms of (a) GC-DAP and (b) GC-APDAS on 0.0 and +1.7 V potential range and on GC electrode using 100 mV s⁻¹ with 10 cycles in MeCN containing 0.1 M TBATFB



Fig. 4. Overlaying cyclic voltammograms for different solution media (a) 1 mM ferrocene redox probe solution vs. Ag/Ag⁺ (10 mM) in MeCN + 0.1 M TBATFB using 0.1 V s⁻¹ scanning rate (b) 1 mM Fe(CN)6³⁻ redox probe solution vs. Ag/AgCl/KCl (sat) reference electrode in BR buffer solution, pH = 2 using 0.1 V s⁻¹ scanning rate and (c) Nyquist plot for electrochemical impedance spectra of 1 mM Fe(CN)6^{3.44} redox couple solution in 0.1 M KCl at the frequency range of 100.000-0.05 Hz at 10 mV wave amplitude

After the modification of glassy carbon electrode, 1 mM ferrocene in 0.1 M TBATFB and 1 mM $Fe(CN)_6^{3-}$ in 0.1 M H_2SO_4 were used for the electrochemical characterization. Fig. 4a and 4b exhibits the voltamograms ferrocene and $Fe(CN)_6^{3-}$, respectively. When the voltammogram obtained in ferrocene and $Fe(CN)_6^{3-}$ is overlayed with the voltammogram obtained for bare glassy carbon electrode, it is clear that the modified surfaces allow electron transfer.

Electrochemical impedance spectroscopy was used to spectroelectrochemical characterization. Fig. 4c shows the Nyquist plots for redox couple $Fe(CN)_6^{3-/4-}$ solution in 0.1 M

KCl at the bare glassy carbon electrode and after modification of glassy carbon electrode with aminophenol diazonium salt. The bare glassy carbon electrode exhibits a low frequency straight line with a very small semi-circle. Aminophenol diazonium salt modified glassy carbon electrode, there is a semi-circle at high frequency region, implying that modified glassy carbon electrode surface depicts a blocking ability for electron transfer reaction.

Conclusion

In this paper, we have demonstrated a simple and convenient method to chemically modify glassy carbons *via* the electrochemical reduction and oxidation of aminophenol diazonium salt in non-aqueous solutions (Fig. 5). Cyclic voltammetry and electrochemical impedance spectroscopy have been used to characterize the glassy carbon-aminophenol diazonium salt. Aminophenol diazonium salt monolayer films on the glassy carbon electrode have good stability and can be used as a charge-rich precursor to assemble oppositely charged species by layer-by-layer electrostatic interaction.



Fig. 5. Reaction mechanism for the APDAS binding to GC electrode surface, (a) +0.1 and -0.9 V potential range using 0.1 mV s⁻¹ with diazonium reduction and (b) 0.0 and +1.7 V potential range using 0.1 mV s⁻¹ with amine oxidation

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