



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

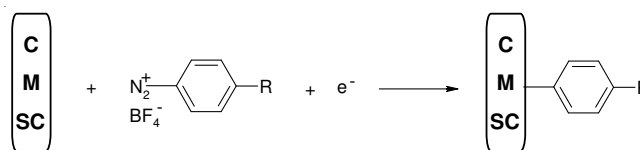
In the last few decades, research of modification of the carbon based materials for electrochemistry has witnessed major growth¹⁻⁷. Modification of the electrode surface is an important studies in electrochemistry. In electrochemistry, carbon electrodes are widely used because of low background current, 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⁺≡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**.



C: Carbon, M: Metal, SC: semiconductor

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

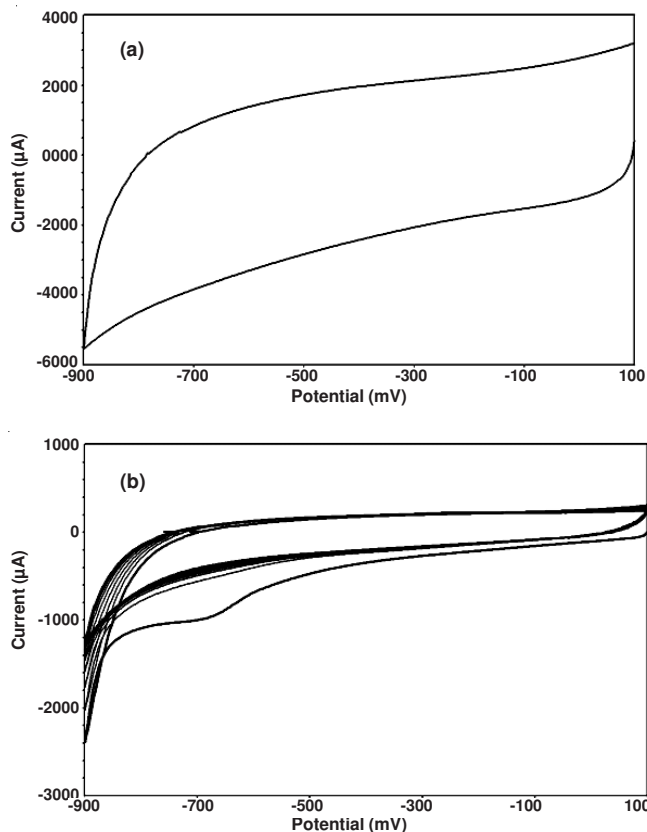


Fig. 2. Cyclic voltammograms of (a) GC-DAP and (b) GC-APDAS on +0.1 and -0.9 V potential range and on GC electrode using 100 mV s^{-1} with 10 cycles in MeCN containing 0.1 M TBATFB

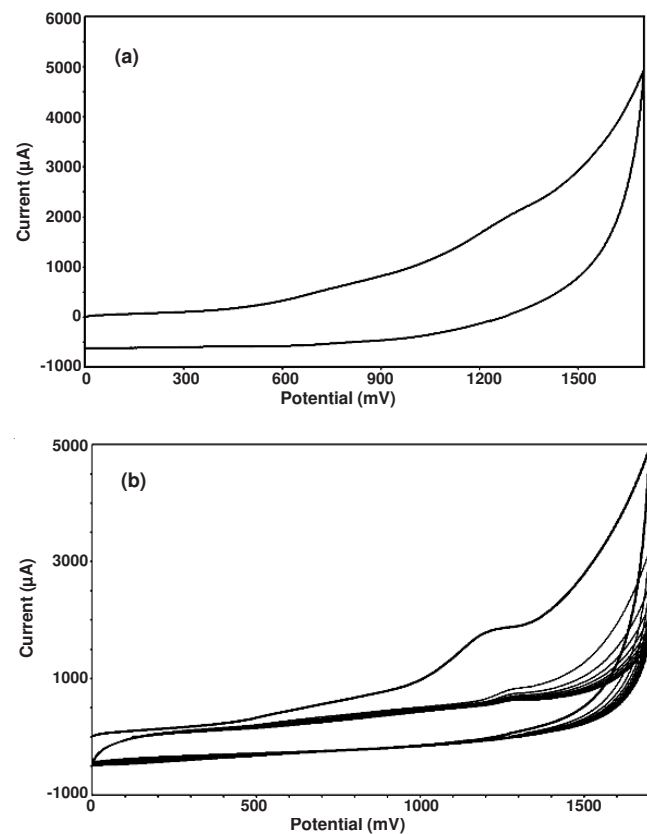


Fig. 3. Cyclic voltammograms of (a) GC-DAP and (b) GC-APDAS on 0.0 and +1.7 V potential range and on GC electrode using 100 mV s^{-1} with 10 cycles in MeCN containing 0.1 M TBATFB

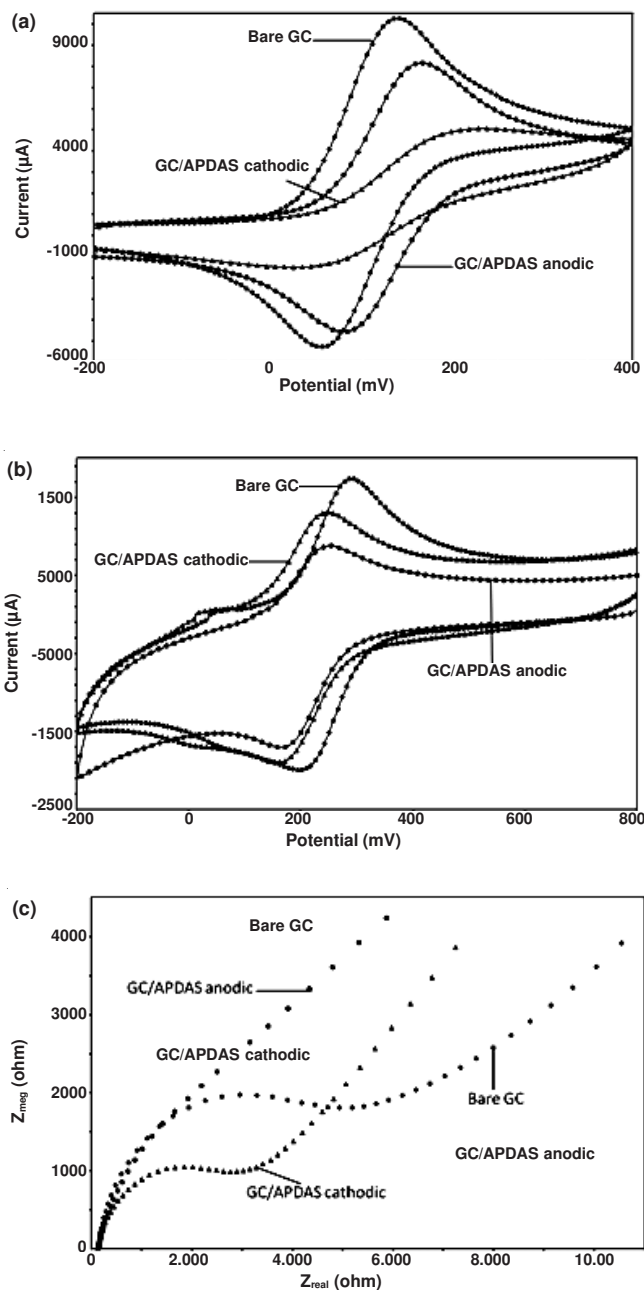


Fig. 4. Overlaying cyclic voltammograms for different solution media (a) 1 mM ferrocene redox probe solution vs. Ag/Ag⁺ (10 mM) in MeCN + 0.1 M TBATFB using 0.1 V s^{-1} scanning rate (b) 1 mM Fe(CN)₆^{3-/4-} redox probe solution vs. Ag/AgCl/KCl (sat) reference electrode in BR buffer solution, pH = 2 using 0.1 V s^{-1} scanning rate and (c) Nyquist plot for electrochemical impedance spectra of 1 mM Fe(CN)₆^{3-/4-} 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)₆³⁻ in 0.1 M H₂SO₄ were used for the electrochemical characterization. Fig. 4a and 4b exhibits the voltammograms ferrocene and Fe(CN)₆³⁻, respectively. When the voltammogram obtained in ferrocene and Fe(CN)₆³⁻ is overlaid 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.

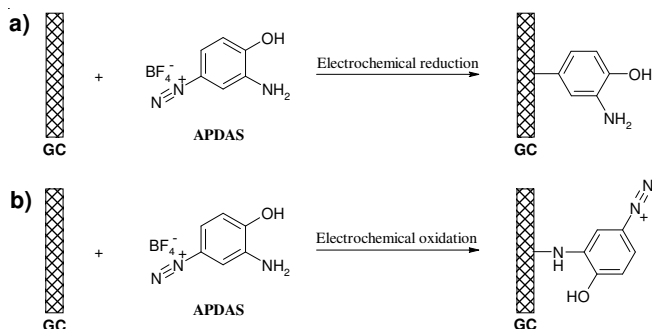


Fig. 5. Reaction mechanism for the APDAS binding to GC electrode surface, (a) +0.1 and -0.9 V potential range using 0.1 mV s^{-1} with diazonium reduction and (b) 0.0 and +1.7 V potential range using 0.1 mV s^{-1} with amine oxidation

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