

Covalent Modification of a Glassy Carbon Surface by Electrochemical Oxidation of 3,3'-Diaminobenzidine

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3,3'-Diaminobenzidine was covalently modified on the glassy carbon electrode surface by electrochemical oxidation. Electrochemical and spectroelectrochemical behaviours of 3,3'-diaminobenzidine were investigated by cyclic voltammetry and electrochemical impedance spectroscopy (EIS). The modification of 3,3'-diaminobenzidine on the glassy carbon electrode was performed in the -500 and +1500 mV potential range with a scan rate of 100 mV s⁻¹ and 10 cycles. The presence of 3,3'-diaminobenzidine at the glassy carbon electrode surface was characterized by cyclic voltammetry and electrochemical impedance spectroscopy. Cyclic voltammetric studies indicate that the process was irreversible and diffusion controlled.

Key Words: Surface modification, Surface characterization, 3,3'-Diaminobenzidine.

INTRODUCTION

Modification of the electrode surface is an important aim 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^{1,2}. Several forms of solid state electrodes carbon suitable for electroanalytical applications are available. Among these glassy carbon electrode (GCE) and carbon paste electrode (CPE) are popular. For modifying the carbon surface, there are mainly two methods through free radical grafting; one is the electrochemical reduction of diazonium salts to result in covalent attachment of aryl radicals onto the carbon surface³⁻⁵. The other is the electrochemical oxidation amine containing compounds to lead to amino cation radical and subsequently form a carbon-nitrogen linkage on the carbon surface^{6,7}.

Cai and Khoo⁸ reported the polymerization of 3,3'-diaminobenzidine in aqueous acidic solutions at the solid substrate electrodes (platinum, gold and glassy carbon). Optimum conditions of polymerization were investigated by anodic stripping voltammetry⁸. Nateghi *et al.*⁹ reported the polymerization of 3,3'-diaminobenzidine in aqueous as well as in some organic solvents. Moreover, polymer modified electrode prepared in ethanol was used to collect and determined Se(IV). In present study,

3,3'-diaminobenzidine was covalently modified on the glassy carbon electrode surface by electrochemical oxidation. Electrochemical behaviours of 3,3'-diaminobenzidine were investigated by cyclic voltammetry. The modification of 3,3'-diaminobenzidine on the glassy carbon electrode was performed in the -500 and +1500 mV potential range with a scan rate of 100 mV s⁻¹ and 10 cycles. The presence of 3,3'-diaminobenzidine at the glassy carbon electrode surface was characterized by cyclic voltammetry and electrochemical impedance spectroscopy.

EXPERIMENTAL

All the chemicals were of analytical-reagent grade from Fluka and Sigma-Aldrich and were used directly without further purification. All solutions and supporting electrolyte were used to prepare with 0.1 M TBATFB in acetonitrile. All electrochemical experiments were performed at room temperature (25 ± 1 °C). A traditional three-electrode cell system was used in all electrochemical experiments. Glassy carbon electrode was used as a working electrode. 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. Platinum wire counter electrode (BAS Model MW-1032) was used. Reference electrodes calibrated to the E_{1/2} of 1 mM ferrocene in 0.1 M TBATFB and 1 mM hexacyanoferrate in 0.1 M H₂SO₄. Cyclic voltammetry and electrochemical impedance spectroscopy techniques were performed using a GAMRY Reference PCI4/750 Potentiostat/Galvanostat/ZRA from Gamry Instruments (PA, USA) equipped with a BAS model C3 cell stand. Electrochemical impedance spectroscopy experiments were carried out with a Gamry Reference PCI4/750 potentiostat in conjunction with electrochemical impedance spectroscopy 300 software. Electrochemical impedance spectroscopy surface data were obtained in the 1 mM Fe(CN)₆^{3-/4-} redox couple at the frequency range of 100.000-0.050 Hz at 10 mV wave amplitude.

Prior to each experiment, the glassy carbon electrodes were polished to a mirror-like surface with 0.30 and 0.05 μm of alumina slurry on a polishing cloth with ultrapure water and then sonicated in an ultrasonic bath for about 5 min to eliminate any trace of polishing paste from the surface in water and then in 1:1 (v/v) isopropyl alcohol and acetonitrile (IPA + MeCN) (Aldrich) mixture for 5 min. Electrochemical surface modification experiments were performed in the -500 and +1500 mV potential range at a scan rate of 100 mV s⁻¹ with 10 cycles.

RESULTS AND DISCUSSION

The electrochemical behaviours of 3,3'-diaminobenzidine onto glassy carbon electrode surface were investigated using cyclic voltammetric technique. 1 mM 3,3'-diaminobenzidine (in 0.1 M TBATFB in MeCN) was prepared and used in the modification process. The modification of the 3,3'-diaminobenzidine to the glassy carbon electrode surface was performed in the -500 and +1500 mV potential range at a scan rate of 100 mV s⁻¹ with 10 cycles (Fig. 1). Three different irreversible oxidation peaks were observed at 104.0, 247.7 and 1105.0 mV.

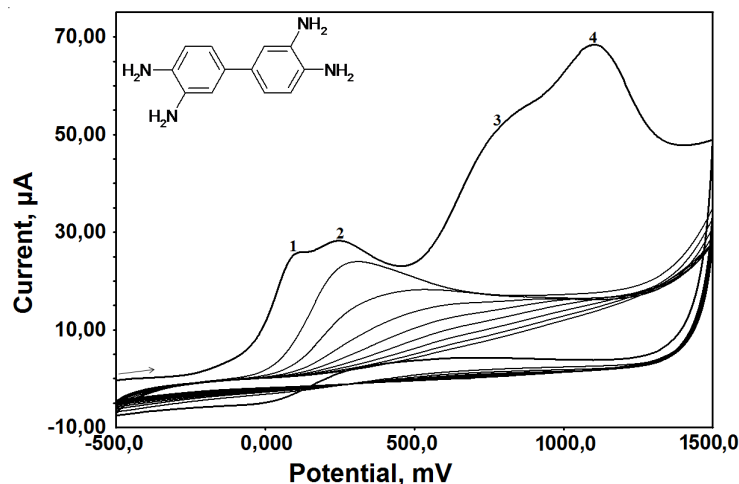


Fig. 1. Cyclic voltammogram of glassy carbon electrode-3,3'-diaminobenzidine in MeCN containing 0.1 M TBATFB, -500 and +1500 mV potential range on glassy carbon electrode using 100 mV s^{-1} with 10 cycle

After the modification of glassy carbon electrode, 1 mM ferrocene in 0.1 M TBATFB and 1 mM $\text{Fe}(\text{CN})_6^{3-}$ in 0.1 M H_2SO_4 were used for the electrochemical characterization. Fig. 2(a-b) exhibits the voltammograms ferrocene and $\text{Fe}(\text{CN})_6^{3-}$, respectively. For both of the redox probes, the redox reaction is completely blocked on the modified electrode, whereas it has a well defined quasi-reversible redox couple on the unmodified glassy carbon electrode surface. When the voltammogram obtained in ferrocene and hexacyanoferrate is overlayed with the voltammogram obtained for bare glassy carbon electrode, it is clear that the modified surfaces don't allow electron transfer.

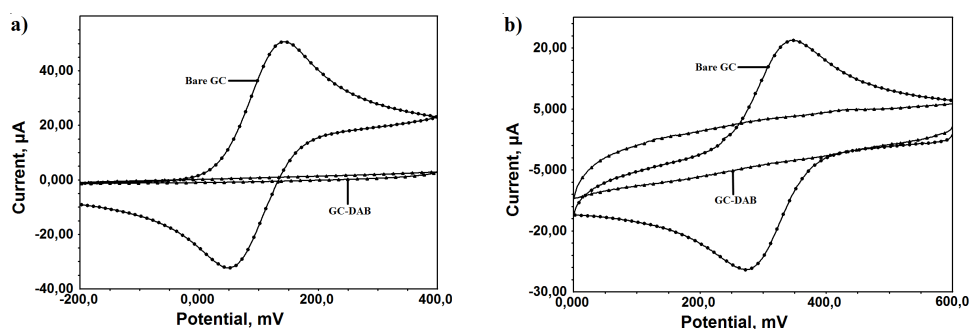


Fig. 2. Surface characterization voltammograms for bare glassy carbon electrode and glassy carbon electrode-3,3'-diaminobenzidine surfaces using (a) 1 mM ferrocene redox probe in 0.1 M TBATFB versus Ag/Ag^+ (0.01 M) reference electrode (b) 1 mM $\text{Fe}(\text{CN})_6^{3-}$ redox probe in 0.1 M H_2SO_4 solution versus $\text{Ag}/\text{AgCl}/\text{KCl}$ (sat) reference electrode. Scan rate is 100 mV s^{-1}

To determine the probability of the surface modification of 3,3'-diaminobenzidine only between -500 and +1500 mV, multiple cycles were performed by cycling back from the last peak in the voltammogram. As it is clear from Fig. 3a, there is no modification to the glassy carbon electrode surface between -500 and +600 mV. This case was stated by using ferrocene redox probe in Fig. 3b. This case is an important reference point in order to suggest a reaction mechanism of binding of 3,3'-diaminobenzidine to the glassy carbon electrode surface.

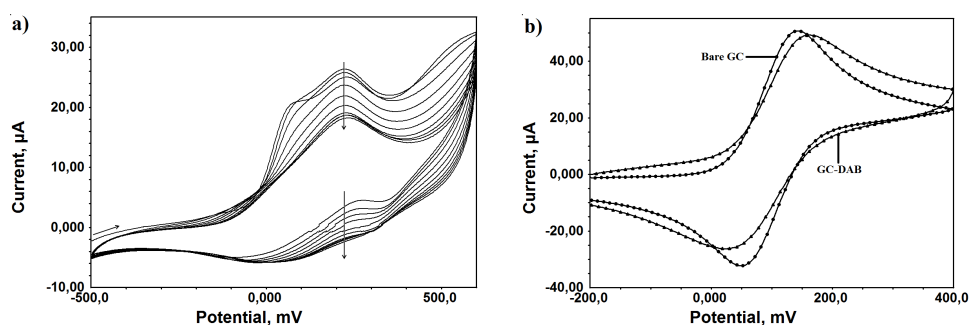


Fig. 3. (a) Cyclic voltammogram of glassy carbon electrode-3,3'-diaminobenzidine in acetonitrile containing 0.1 M TBATFB, -500 and +600 mV potential range on glassy carbon electrode using 100 mV s^{-1} with 10 cycle. (b) Surface characterization voltammograms for bare glassy carbon electrode and glassy carbon electrode-3,3'-diaminobenzidine surfaces using 1 mM ferrocene redox probe in 0.1 M TBATFB versus Ag/Ag^+ (0.01 M) reference electrode

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

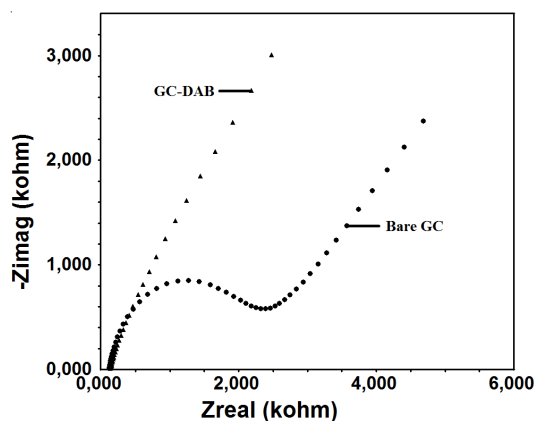


Fig. 4. Nyquist plot for (a) bare glassy carbon electrode and (b) glassy carbon electrode-3,3'-diaminobenzidine. Electrochemical impedance spectra of the redox couple $\text{Fe}(\text{CN})_6^{3-/4-}$ solution in 0.1 M KCl at the frequency range of 100.000-0.050 Hz at 10 mV wave amplitude

in 0.1 M KCl at the bare glassy carbon electrode and after modification of glassy carbon electrode with 3,3'-diaminobenzidine. The bare glassy carbon electrode exhibits a low frequency straight line with a very small semi-circle. 3,3'-Diaminobenzidine 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.

In order to find out the transfer of molecule to the GCE surface whether it is a diffusion controlled process or not, 10, 25, 50, 100, 200, 300, 500 and 1000 mV s^{-1} scanning rates were used in the -500 and +1500 mV potential range with one cycle^{10,11}. The obtained voltammograms are depicted in Fig. 5a. The plots in Fig. 5b were drawn by using the peak current obtained from Fig. 5a. $\log I_p$ versus $\log v$ plot in Fig. 5b gives a straight line. Having a straight line plot of $\log I_p$ versus $\log v$ prove that 3,3'-diaminobenzidine was carried to the glassy carbon electrode surface by a diffusion controlled process.

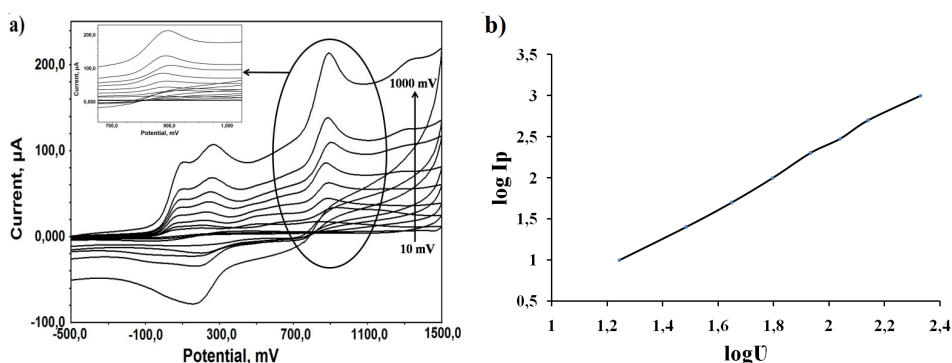


Fig. 5. (a) Overlying cyclic voltammograms of different scanning rate for 10, 25, 50, 100, 200, 300, 500 and 1000 mV s^{-1} and -500 and +1500 mV potential range. (b) Plot of logarithm of peak current versus logarithm of scan rate, dependence of the cyclic voltammetric response at a modified glassy carbon electrode on scanning rate in 0.1 M TBATFB in acetonitrile

Conclusion

Electrochemical mechanism is suggested for the binding reaction of 3,3'-diaminobenzidine to the glassy carbon electrode surface through amine oxidation method. Here, amine was oxidized in the solution (electrochemical, E) and then chemically (chemical, C) binded to the glassy carbon electrode surface through covalent binding. It can be concluded from Fig. 2, peak at lower potential belongs to oxidation of amino group and peak at higher potential belongs to the binding of 3,3'-diaminobenzidine to the glassy carbon electrode surface.

The important question at this point, after the modification was completed, glassy carbon electrode surface was expected to be active due to three amino groups on the 3,3'-diaminobenzidine. However, Figs. 3(a-b) and 4 show that the glassy

carbon electrode surface is inactive after the completion of modification process. This case can be explained as the binding of the cation radicals that were produced from the oxidation process at the first cycle to the glassy carbon electrode surface. At the second cycle, the amino groups on the monolayer were oxidized and then the formed radicals in the solution dimerized with the formerly produced cation radicals thus formed second layer. At the third cycle, the amino groups at the second layer were oxidized and the dimerization took place. This process continued by dimerization until obtaining a certain thickness. The decrease in the first peak depended on it. As the layer got thicker, the amino groups at the surface were hardly oxidized and the current got lowered and eventually became zero at the end. In other words multiple layers formed at the glassy carbon electrode surface. Thus the glassy carbon electrode surface became inactive. The result of this study also supports the situation explained above.

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