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Electrochemical Study of Modified Glassy Carbon Electrode with Carboxyphenyl Diazonium Salt in Aqueous Solutions

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Abstract: The covalent grafting of carboxyphenyl functionalities to planar carbon substrates by reaction with 2-carboxybenezenediazonium salt has been studied in aqueous acid solution. The surface was characterized, before and after the functionnalization process, by cyclic voltammetry, electrochemical impedance spectroscopy and linear sweep voltammetry (LSV) in order to control and to prove the formation of a coating on the carbon surface. The results indicate the presence of substituted phenyl groups on the investigated surface. Electrochemical impedance measurements show that the slowing down of the electron transfer kinetics was more evident by increasing the number of cycles resulting to higher ΔEp and R_{CT} parameters. Besides, the effect of the pH on the electron transfer processes of the $Fe(CN)_6^{3-/4-}$ at the modified electrode is studied. By changing the solution pH the terminal group's charge state would vary, based on which the surface pKa value is estimated. *Copyright © 2014 IFSA Publishing, S. L.*

Keywords: Diazonium salts, Glassy carbon (GC), Cyclic voltammetry, Impedance spectroscopy Surface pKa.

1. Introduction

The field of chemically modified electrodes in electrochemistry has been a very attractive research area in the recent years. These electrodes are often prepared by modification of carbon or metal substrates to produce an electrode which carried out specified reactions or processes [1]. The modification of conductive substrates is also one important objective in electrochemistry and material science as well as molecular electronics [2]. Various methods are necessary for the modification of metal surfaces with organic based materials [3].

Aromatic diazonium salts $ArN_2^+X^-$ have been known for a long time as being a basis for the production of dyes [4]. One of their important reactions is dediazonation, the loss of dinitrogen with the formation of an aryl radical $Ar^{\bullet}$ or cation Ar+. As far as electrografting is concerned we will be interested in the homolytic pathway [5] and the formation of radicals. Back in 1992, in a pioneering paper, Pinson and co-workers described the reaction mechanism for the modification of carbon electrodes by aryl diazonium salts. Since then, Pinson and several other research groups rushed into the fundamental and applied aspects of the surface chemistry of aryl diazonium salts [6]. The interest in using aryl diazonium salts lies in being easy to prepares rapid (electro) reduction, large choice of reactive functional groups, and strong aryl–surface covalent bonding [7, 8].The covalent bond between the modifier and the electrode surface is particularly attractive for the construction of chemical-sensor or bio-sensor and due to its expected stability in several measurement conditions such as temperature and pH. The attractiveness of aryl diazonium salts are enhanced further by recent studies showing that they can also be grafted to a variety of metal [9] and semiconductor [10] surfaces as well as carbon nanotubes [11]. This feature raises the exciting possibility of one monolayer forming system being suitable for a large range of electrode materials needed in a variety of applications. Additionally, the grafting procedure offers the opportunity of multilayer formation resulting in the integration and condensation of recognition sites on the electrode surface [12]. This is in contrast to the self assembly of alkanethiols on Au where a single bonding functionality is solely available [13]. The purpose of this work is to examine the multilayer formation via electrochemical reduction of the in situ generated diazonium cation of 2-aminobenzoic acid (2-ABA) at glassy carbon electrode surfaces in an aqueous acid solution. The degree of multilayer formation was controlled by the number of potential cycling during the grafting procedure. Cyclic volammetry (CV), electrochemical impedance spectroscopy (EIS) and Linear Sweep Voltammetry (LSV) were used to characterize the grafted electrodes. Also, we estimated the surface pKa value of the CBD modified glassy carbon electrode.

2. Experimental

2.1. Reagents

2-aminobenzoic acid (2-ABA), hydrochloric acid, sodium nitrite ($NaNO_2$), potassium chloride. The solutions of diazonium salt were freshly prepared for each modification. Ferricyanide ($K_4Fe(CN)_6$) and ferrocyanide ($K_3Fe(CN)_6$) were purchased from Sigma-Aldrich (Germany). Phosphate buffer solutions (PBS) at different pH values were prepared from 0.1M H_2NaPO_4 + HCl (pH 2-3) and (0.1 M) HK_2PO_4+ H_2NaPO_4 (pH 4-9). Aqueous solutions were prepared using double-distilled deionised water and purged with nitrogen gas prior to each experiment.

2.2. Synthesis of 2-COOH-PD

2-aminobenzoic acid (17mM) was dissolved in 20 mL of 50 % w/w aqueous hydrochloric acid solution. After the solution was cooled to 0 °C, 2.4 g (34 mM) of $NaNO_2$ dissolved in cold water was slowly added to the mixture [14]. The temperature was kept at 0-4 °C while stirring the solution for an additional 0.5 h. The diazonium salt was kept in a desiccator at 4 °C.

2.3. Electrode Preparation and Modification

Working electrode was glassy carbon (GC) (3 mm diameter) with a geometric area (A) of 0.07 cm^2. The surface of glassy carbon (GC) was first polished with 0.05 µm alumina slurry. After each polishing the electrode was carefully washed with distilled water and allowed to dry in air. The covalent attachment of 2-carboxyphenyl (CP) groups to the GC surface was performed by electrochemical reduction of the corresponding diazonium salt (Fig. 1).

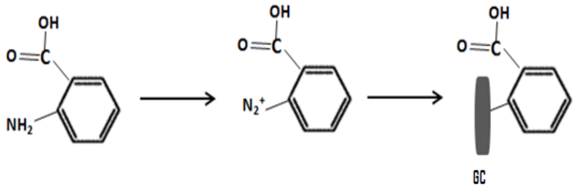

Fig. 1. Schematic illustration of the grafting of the GC electrode by the electrochemical reduction of in *situ* generated 2-carboxyphenyl diazonium cation.

The electrochemical modification of GC surface was carried out in situ in the mixture of diazonium salt solution. In order to vary the surface coverage of CP groups, the potential was cycled between 0.6 and -0.4 V (vs.SCE) for 1, 5 and 10 scans using a sweep rate of 100 mVs^{-1}. The electrodes modified with 2-carboxyphenyl groups are designated as [n]GC/CP where there is the number of potential cycling during grafting procedure.

The solution containing électroactive probe was ferricyanide/ferrocyanide (1 mM, 0.1M KCl, adjusted at pH 7 with a 1 M NaOH solution) was used for the various films. The electrode coverage is related to the charge-transfer resistance and is given by the following equation [15].

$$\Theta(\%) = 1 - \frac{R_{CT}^{O}}{R_{CT}} \times 100, \quad (1)$$

where θ is the apparent electrode coverage, assuming that all the currents are passed via bare spots on the electrode, and R_{CT}^{0} and R_{CT} represent the charge-transfer resistance measured on a bare and on a modified glassy carbon electrode, respectively. $[Fe(CN)_6]^{3-/4-}$ redox couple was used also as a probe molecule to investigate the apparent acid dissociation constant (pKa') of the carboxylic acid group on the [1] GC/CP.

2.4. Instrumentation and Procedure

Cyclic voltammetry were done in a one-compartment cell with a three electrode configuration consisting of a working glassy carbon electrode (0.07 cm^2), a saturated calomel reference electrode (SCE) and platinum wire as a counter electrode. All electrochemical experiments were performed using a Voltalab 40, model PGZ 301, controlled by Voltamaster 4 software. Electrochemical impedance spectroscopy (EIS) was performed in the frequency range between 100 mHz and 100 kHz. Measurements were done using $[Fe(CN)_6]^{3-/4-}$ as redox probe. The measured impedance spectra were analyzed in terms of electrical equivalent circuits using the analysis program Z.

The permeability of CP films was studied on bare GC and aryl-modified GC electrodes using a rotating disk electrode (RDE) voltammetry (Gough and Leypoldt, 1979; Saveant, 1991). The electrode rotation rate was varied between 100 and 500 rpm.

3. Results and Discussion

3.1. Electrografting of in Situ Generated Diazonium Salt

Fig. 2 shows the CVs for the reduction of diazotized CPD. A broad irreversible cathodic peak is observed at around +0.0 V in the first cycle. The peak current gradually disappeared during subsequent scans, reflecting the formation of the CP layer on the GC surface, indicating a complete blocking by aryl layers [16].

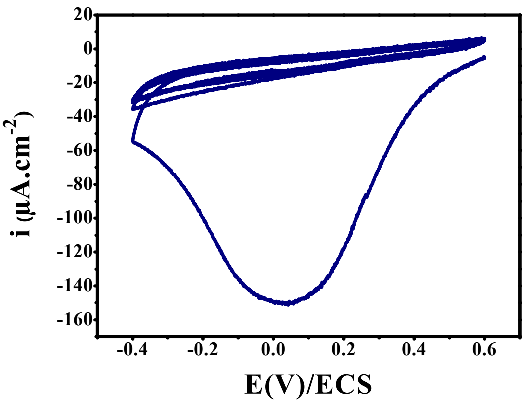

Fig. 2. Cyclic voltammograms at a GC electrode immersed in the reaction mixture of diazonium salt. Scan rate = 0.1V.s^{-1}. Temperature = 4 °C, n = 10cycles. The inset shows cyclic voltammograms of [1] GC/CP; [5] GC/CP and [10] GC/CP.

Based on the area of the reduction peak during the modification of the GC electrode with the diazonium salt, the surface concentration (Γ) of carboxyphenyl groups for GC/CP electrode was estimated by charge integration under voltammetric peaks according to:

$$\Gamma = \frac{Q}{nFS}, \qquad (2)$$

where Q is the charge under the peak, n is the number of electrons involved (n =1) [17, 18]. Table 1 shows that the surface coverage increased with increasing the number of the scanning cycles. The surface modification by cycling the potential once (n =1) between 0.6 and -0.4 V, resulted in the value of 6.23×10^{-10} mol.cm^{-2} modification with 5 full cycles and 10 cycles gave surface concentrations of 9.2×10^{-10} and 9.57×10^{-10} mol.cm^{-2} respectively.

The theoretical monolayer coverage is 12.5×10^{-10} mol.cm^{-2} [19], thus the surface concentration of CP groups is less than a monolayer.

Table 1. Values of the surface concentration (Γ) obtained for aryl modified glassy carbon electrode in aqueous solution at different potential scanning number.

n	Q (C.cm^{-2})	Γ (mol.cm^{-2})
1	-6.015×10^{-5}	6.23×10^{-10}
5	-8.88×10^{-5}	9.2×10^{-10}
10	-9.24×10^{-5}	9.57×10^{-10}

3.2. Characterization of the Grafted Layers by Cyclic Voltammetry Measurements

Fig. 3 shows the cyclic voltammograms before and after modification of the GC electrode with COOH functionnalized layer in aqueous solutions.

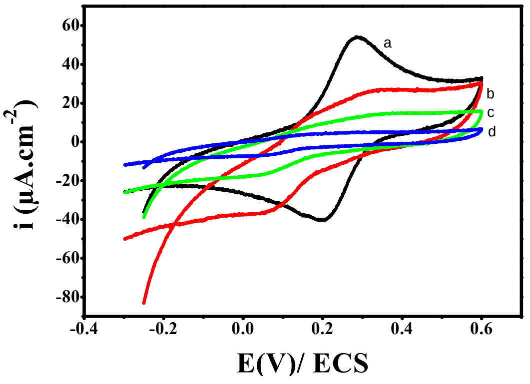

Fig. 3. Cyclic voltammograms corresponding to the various layers grafted onto the glassy carbon electrode: (a) Bare GC, (b) GC/CP (1cycle), (c) GC/CP (5cycles), (d) GC/CP (10cycles), Scan rate of 0.1 V/S.

0.1 M KCl buffered at pH = 2, in the presence of 1 mM $[Fe(CN)_6]^{3-/4-}$, a negatively charged redox couple was used. In this experiment, the Ph of solutions is 2, so this weak acidic condition was employed to exclude the contribution of charge-charge repulsion between the surface COO^- groups and $[Fe(CN)_6]^{3-/4-}$ as discussed later.

The voltammograms of $[Fe(CN)_6]^{3-/4-}$ redox system presents a reversible behaviour at the bare electrode where small peak separation ΔEp (84 mV) is recognized, indicating fairly rapid electron transfer.

Subsequent cycles number 1, 5 and 10 during the grafting procedure have a significant effect on ΔEp values 257, 385 and 490 mV, respectively. The increase in the ΔEp value reflects an important decrease in the electron transfer rate due to the blocking effect induced by the grafted CP layer.

3.3. Electrochemical Impedance Spectroscopy of Phenyl Modified GC Electrode

Electrochemical impedance spectroscopy measurements can be used to evaluate the effect of 2-carboxyphenyl on the kinetics of redox reaction at GC electrode. Fig. 4(a) presents the complex impedance plots for a bare electrode at a potential of 0.190 V in the presence of 1 mM $[Fe(CN)_6]^{3-/4-}$.

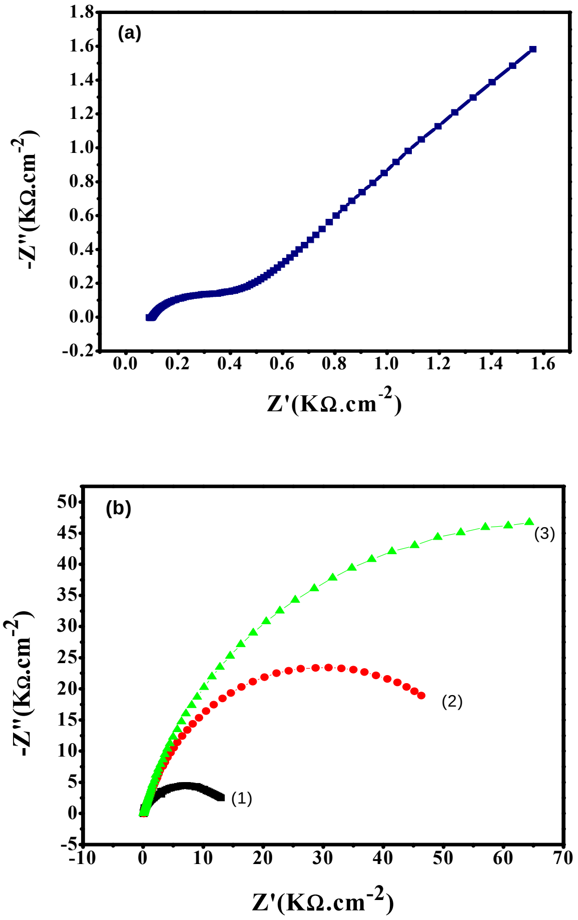

Fig. 4. EIS plots for (a) the bare and (b) the 2-carboxyphenyl modified GC electrodes (1) 1cycle, (2) 5 cycles, (3) 10 cycles in aqueous 1 mM $[Fe(CN)_6]^{3-/4-}$, 0.1 M KCl, at various scanning potential number. Spectra were obtained between 100 mHz–100 KHz and with amplitude of alternative voltage of 170 mV.

The Nyquist plot for a bare glassy carbon electrode presents a typical shape with a semicircle in the high-frequency domain characteristic of an interfacial charge-transfer mechanism and a straight Warburg line with a slope near unity in the low-frequency domain characteristic of a semi-infinite diffusion phenomenon. The charge-transfer calculated from the semicircle diameter is 338 Ω. After modification (Fig. 4b) the diameter of the semicircle increases and the Warburg line was not observed for the modified electrodes in the frequency range 100 kHz - 100 MHz used here. Qualitatively, the increase of the semicircle indicates that the electrode kinetics become slower as the GCE is modified with a substituted phenyl group. An electrical equivalent circuit for both modified and bare GC electrode is shown in Fig. 5 which comprises the solution resistance, the charge-transfer resistance, the resistance and the capacitance of the coated layer [20].

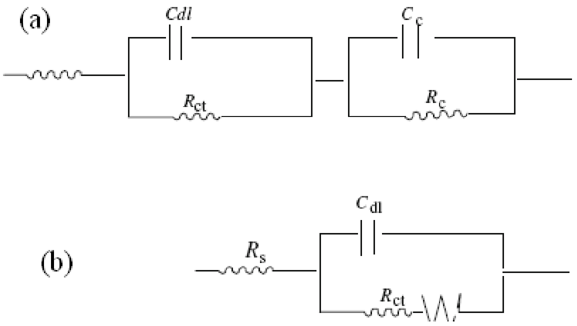

Fig. 5. Equivalent circuits used for the analysis of the electrochemical impedance data for (a) the modified and (b) the bare electrodes.

Besides a constant phase element (CPE) characterized by the pseudocapaciatance T and the exponent φ were incorporated [21].

The CPE was used instead of a pure capacitor in the equivalent circuit that represents the electrochemical system due to microscopic surface roughness and inhomogeneity in surface and kinetics. Impedance data were analyzed using the electrical equivalent circuit.

The charge-transfer resistance of the modified electrode varies from 16.5 to 324 KΩ (Table 2), which represents a significant increase compared to the bare GCE and is in consistent with the cyclic voltammetry data.

The blocking effect of the grafted layer can have two sources: (i) the physical barrier of the grafted layer prevents the access of $[Fe(CN)_6]^{3-/4-}$ to the underlying glassy carbon electrode and (ii) the electrostatic repulsion, particularly important for CP.

Based on the treatment of the relationship between R_{CT} and the heterogeneous electron transfer rate constant (K^0), an increase in R_{CT} from 0.338 to 324 KΩ implies a decrease in K^0. The higher R_{CT} values intermingles also with the coverage of more electrodes leading to a high compact and less permeable layer.

Table 2. R_{CT} (Ω), K° and θ (%) obtained for GC electrodes modified with 2-carboxyphenyl for different scanning number.

n	R_{CT} (KΩ)	K^0 (cm.s^{-1})	θ (%)
0	0.338	$4.55.10^{-3}$	0
1	16.5	$9.67.10^{-5}$	87.75
5	120	$3.03.10^{-5}$	98.31
10	324	$1.2.10^{-5}$	99.30

3.4. RDE Resultants of $Fe(CN)_6^{4-}$ Oxidation on Aryl Modified GC Electrode

Representative RDE voltammetry curves for $Fe(CN)_6^{4-}$ oxidation on a bare GC electrode at pH= 5 are shown in Fig. 6. Current variations are observed on unmodified GC in the range of potential between 0.2 and 1.2 V. The oxidation current is equal to the theoretical diffusion-limited current calculated by the Levich equation [22]:

$$I_d = 0{,}62 nFAC^o D^{2/3} v^{-1/6} \omega^{1/2}, \qquad (3)$$

where I_d represents the diffusion-limited current, n is the number of electrons involved (n=1), F is the Faraday constant (96485 Cmol^{-1}), A is the electrode area (0.07 cm^2), C° is the concentration of $Fe(CN)_6^{4-}$ in the bulk (10^{-6} mol.cm^{-3}), D is the diffusion coefficient of $Fe(CN)_6^{4-}$ (0.65×10^{-5} cm^2.s^{-1} [23]), υ is the kinematic viscosity of the solution (0.01 cm^{2}s^{-1} [24]) and ω is the electrode rotation rate.

The rotating disk voltammograms were recorded for different modified diazonium electrodes at different rotation rates in an aqueous solution of a charged molecule, ferrocyanide as electroactive permenant and compared to results obtained from a bare glassy carbon. Based on the typical equations introduced by Gough and Leypoldt (Gough and Leypoldt, 1979; Gough, 1980), relating the variation of limiting current i_{lim} with the mass transport for a rotating disk electrode functionalized with aryl films:

$$1/i\lim = 1/0{,}62 nFAD_s^{2/3} C^O v^{-1/6} \omega^{1/2} + \frac{\delta}{nFAC^O KDm} \qquad (4)$$

$$Pm = \frac{KDm}{\delta} \qquad (5)$$

$$1/i\lim = 1/0{,}62 nFAD_s^{2/3} C^O v^{-1/6} \omega^{1/2} + \frac{1}{nF} P_m AC^O, \qquad (6)$$

where terms *D*s and *D*m are the diffusion coefficients for the substrate in the bulk solution and in the film, δ the thickness of the aryl film and *K* the partition equilibrium constant of the substrate between solution and film. Eq. (4) is consisting on two terms that characterize the current flow with or without the layer. The first term represents the diffusion of the substrate in the bulk solution and the second term accounts for the diffusion of the substrate in the aryl film. Only the first term of the equation is dependent upon the rotation rate of the RDE. To assess the permeability value (*P*m), a plot of $1/i_{lim}$ versus $\omega^{-1/2}$ refer to a linear behavior with the same slope as for a bare electrode with a positive intercept that depends on the permeability *P*m of the film, Eq. (6).

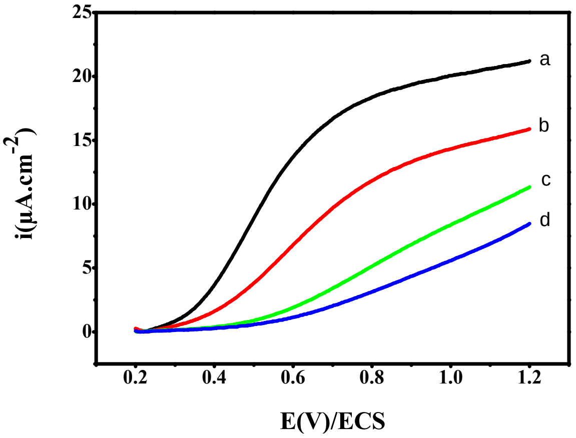

Fig. 6. RDE voltammetry curves for $Fe(CN)_6^{4-}$ oxidation on a bare GC electrode (a) and GC/CP (b) n=1, (c) 5 and (d) 10 cycles in 10^{-3}M $Fe(CN)_6^{4-}$ containing 0.1 M KCl. ω= 500 rpm, υ= 10 mVs^{-1}

The estimated permeability of the three electrodes coated with carboxyphenyl groups (n=1; 5; and 10) were 1.46×10^{-2}, 3.47×10^{-3} and 2.02×10^{-3} cm/s, respectively. The RDE results demonstrated that the electrons transfer process of the $Fe(CN)_6^{4-}$ was not completely suppressed on [1]GC/CP , however, the largest blocking effect towards ferrocyanide was observed for [10] GC/CP which was also similar to the CV results.

As discussed in Section 3.3, besides electrostatic interactions the barrier properties are strongly influenced by surface coverage of the modifier film. Previous investigations have shown that the blocking properties of aryl films depend on the modification conditions and even on the post-grafting [25]. In addition, the presence and distribution of pinholes in the film may considerably influence in barrier properties. All these sides are important for the practical application of diazonium modified electrodes in electroanalysis.

3.5. Determination of pKa for Grafted CP Groups

As compared to the bare GC electrode, results are obtained at pH 3 and 4 for aryl-modified electrodes grafted by one cycle compared to the solutions of other pH (Fig. 7). The oxidation and reduction peaks of $[Fe(CN)_6]^{3-/4-}$ ions was clearly visible at pH 3 and 4, while at pH 5, the electrochemical responses of the redox system was more suppressed and even more at pH 6-8. Hence, observed pH dependant redox responses can be ascribed to the electrostatic repulsion between $[Fe(CN)_6]^{3-/4-}$ and the negatively charged CP groups on the electrode surface.

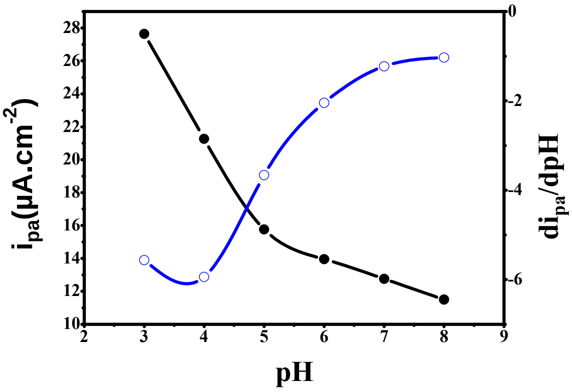

Fig. 7. Relationship between peak current and pH values of buffer solutions. (●) Experimental curve and (○) differential curve of experimental data.

A similar bahaviour has been reported by Saby et al. [26] by studying the origin of the electron transfer inhibition to the solution pH by studying the blocking effect of 4-nitrophenyldiazonium salt. This blocking behaviour could be explained by the surface pKa value of the COOH groups. Fig. 7 shows that the apparent pKa of the 2-carboxyphenyl grafted layer is estimated to be about four from dI_p/dpH vs. pH. This result is consistent to that of the solution based benzoic acid (pKa = 4.2) [27]. For these experiments, the pH of the $[Fe(CN)_6]^{3-/4-}$ solution is adjusted between appropriate values around the pKa of the corresponding acid to obtain a variation in the ratio of charged and neutral forms of the molecule grafted on the electrode surface.

Several factors can be invoked to explain the shift of the pKa value of an immobilized molecule on a substrate surface compared to its pKa in bulk solution and their possible combinations as well as the unknown structure of the surface grafted layer make it difficult to provide a definitive explanation for the phenomenon observed in the present work.

4. Conclusion

In this study, we have described, the electrochemical reduction of 2-carboxyphenyl diazonium salt on GC surface yielded stable monolayer. Ability of the modified surfaces for blocking redox reaction was estimated using $Fe(CN)_6^{3-/4-}$ probe and showed important differences depending on the potential scan number. The electrochemical behaviour of $Fe(CN)_6^{3-/4-}$ has been studied employing the CV, SI and RDE methods. An increase in R_{CT} indicates that the permeability of the films to the redox probe becomes low. Our observations on comparing CV curves at various pHs exhibited that the blocking effects of the surface by CP groups was significant at higher pH values. This effect can be described according to the electrostatic repulsion between the COO^- groups and the $Fe(CN)_6^{3-/4-}$ probe.

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