Modification of carbon containing electrodes by aryldiazonium iodate salts for electroanalysis

In the work the method of spontaneous chemical modification of a glassy carbon electrode (GCE) with aryl diazonium iodate salts was studied. The adsorption of modifier from the solution was applied for GCE modification. The modification effectiveness assessment was performed for different modifiers under the conditions of modifier concentration varying and the time of electrode keeping in the solution. The cyclic voltammograms of the reversible pair $[\text{Fe(CN)}_6]^{3-}/^{4-}$ were recorded in the background KCl 0.5 M electrolyte. Modifier surface layers form spontaneously without the application of potentials. The control of thickness and the conductive characteristics of the modified electrode were performed by the adjusting of concentration and the keeping time of the electrode in modifier solution. It has been established that the oxidation and reduction currents of $[\text{Fe(CN)}_6]^{3-}/^{4-}$ are maximum for the 4-carboxybenzodiazonium iodate modifier of GCE with a concentration of 10 mg·l$^{-1}$ when the time of keeping the electrode in its solution is for 5 seconds. The increasing of the reversible pair $[\text{Fe(CN)}_6]^{3-}/^{4-}$ current in the indicated conditions after the modification of 4-carboxybenzodiazonium iodate is associated with an increase in the area of the electroactive electrode surface, by almost 2.5 times. The study of the morphology of the electrode surface of the GCE by the method of scanning electrode microscopy confirmed the presence of a polylayer modifier with a carboxy substituent on the surfaces of a glassy carbon electrode. To confirm the presence of organic functional groups of the 4-carboxybenzodiazonium iodate modifier on the surfaces of the GCE, the reflection spectra of the electrode surfaces were obtained by IR spectroscopy. The method of modifying the GCE with iodate salts of aryldiazonium is simple, rapid, has low costs, and can be used to increase the sensitivity of determining a number of analytes in electroanalyses.

Keywords: aromatic diazonium salts, modifiers, glassy carbon electrode, cyclic voltammetry, IR spectroscopy, SEM (scanning electron microscopy), potassium ferrocyanide, spontaneous formation of modifier layer.

Introduction

The search for novel electrode materials and surface modifiers, which provide the necessary level of analytical and metrological characteristics, is on cutting edge of electroanalytical chemistry. One of such materials are the aromatic salts of diazonium (ASD), because as a result, materials with desired properties are formed, which are used in various fields of activity (medicine, analytical chemistry, polymer chemistry, biochemistry, etc.) [1–9].

Therefore, ASD are promising electrode modifiers for electroanalysis [9]. As a result of the modification, new electrode materials are used both for the electrochemical biosensors formation, where the ASD serves as a linker [10], and as organo-modified electrodes for the quantitative determination of biologically active substances in different objects [11, 12].

Currently, there are two fundamental approaches to modifying the ASD electrode surfaces: the adsorption method with the formation of weak physical bonds [13–17] and the method of strong covalent bond formation between the surface and the organic molecule [18–21], which simplifies the control of modification process and provides the higher selectivity of further surface transformations of functional groups [22, 23]. It is known that the implementation of the second modification method is carried out using two approaches: the electrochemical modification [24] and the chemical or spontaneous modification [25].

Electrochemical reduction of ASD [26] is an attractive method that was implemented for carbon electrode materials [27]. However, the issue of controlling the thickness of an organic modifier layer while maintaining the conductive properties is controversial, since in most cases, electrochemical modification results in the rapid formation of ASD multilayer, which reduce the activity of the electrode surface. The electrographing mechanism of diazonium salts is well known and detailed described in the work [28]. The mechanism involves the generation of aryl radicals, followed by the binding of these radicals to the surface via carbon-carbon bonds [29].

There is a number of works concerned with the spontaneous modification of carbon-containing electrodes. The authors note the simplicity of the spontaneous method of modifying carbon-containing electrodes...
Modification of carbon containing electrodes …

with obtaining thinner and conductive mono [28] or poly [30] layers of ASD modifiers. Generally, the procedure for modifying the electrodes of an ASD consists of simply immersing the electrode for a certain time in the solutions of the ASD. However, the issue of controlling the thickness of the modifier layer depending on the concentration of the modifier and the time the electrode is kept in the appropriate solution remains controversial.

In the work, the electrochemical properties of GCE when modifying aryldiazonium iodate salts with different functional groups are studied. For the selection of optimal conditions for the spontaneous chemical modification of the GCE, a series of concentrations of 10, 30, 60 mg\textper百万\textper cent and a holding time of 2, 5, 10, 30, 60, 120 seconds were chosen. In order to assess the optimal conditions for modifying the GCE in various modifiers, under conditions of varying their concentration and time of maintaining the GCE, cyclic voltammograms of the reversible pair [Fe(CN)$_6$]$^{3-/-4-}$ were recorded in a background KCl electrolyte of 0.5 M. on the electrically conductive properties of the electrode surface of the GCE. With respect to each modifier, the conditions for spontaneous chemical modification, such as time and concentration, are different. To characterize the surfaces of the electrodes before and after modification, the methods of scanning electron microscopy and IR spectroscopy were used.

**Experimental**

The following iodate salts of aryldiazonium were chosen as modifiers of the electrode surfaces of the GCE: [HOOC$_6$H$_4$N$_2$]IO$_3$, [NCC$_6$H$_4$N$_2$]IO$_3$, [O$_2$NC$_6$H$_4$N$_2$]IO$_3$, [C$_6$H$_5$N$_2$]IO$_3$, [H$_3$C$_6$N$_2$C$_6$H$_4$N$_2$]IO$_3$, [H$_2$C$_6$N$_2$C$_6$H$_4$N$_2$]IO$_3$. Their structures are depicted in Figure 1. All reagents were of analytical grade. The water was obtained by water purification system Milli-Q Direct; water resistivity was 18.2 M\Omega cm. Silver chloride electrodes were used as auxiliary electrode and reference electrode.

To select the optimal conditions for the spontaneous modification of GCE with aryldiazonium iodate salts, the concentration of the modifier (mg\textper million\textper cent) and the time of aging of the GCE in the solutions of the corresponding modifiers (sec) were varied. The working concentrations of diazonium salt solutions for modification were 10, 30, 60 mg\textper million\textper cent. The holdup time of GCE in the solutions of the modifiers was 2, 5, 10, 30, 60, 120 seconds. To evaluate the reversibility of electrode processes on the GCE, cyclic voltammograms of hexacyanonferrate salts [Fe(CN)$_6$]$^{3-/-4-}$ of concentration 0.25 M (background 0.5 M KCl) were recorded before and after chemical modification.

![Figure 1. Structural formulas of aryldiazonium salts](image)

A universal electrochemical workstation TA-2 (Tomanalyt, Tomsk, Russian Federation) with a three electrode cell was used. Silver chloride electrodes and glassy carbon electrodes for modification were purchased from LLC Tomanalyt (Tomsk, Russian Federation). Investigations of the cutoffs of the electrode were carried out using a scanning (raster) electron microscope JEOL JSM-7500FA. To confirm the presence of organic functional groups on the glassy carbon electrode surface, IR reflection spectra were obtained. The investigations were carried out using the Cary 660 IR spectrometer (manufactured by Agilent).

**Results and Discussion**

To assess the effectiveness of modifying GCE with different modifiers under the conditions of changing the concentration of the modifier and the time of aging of the GCE, the value of \(\Delta I(\%)\) was calculated:

\[
\Delta I = \left( \frac{I_1 - I_0}{I_0} \right) \times 100,
\]

where \(I_0\) is current of [Fe(CN)$_6$]$^{3-/-4-}$ without modifier; \(I_1\) is current of [Fe(CN)$_6$]$^{3-/-4-}$ after aging in the solution of the modifier.
In the course of the study (Fig. 2), it was established that the oxidation and reduction currents of 
\([\text{Fe(CN)}_6]^{3-/4-}\) are maximal for 4-carboxybenzodiazonium iodate of the GCE modifier at the time of holding
the electrode in its solution for 5 seconds and the modifier concentration 10 mg∙l\(^{-1}\) (\(\Delta I = 230\% \) cathode scan
and \(\Delta I = 185\% \) anode scan).

To prove the presence of 4-carboxybenzodiazonium iodate on the surface of the GCE, microscopes of
the surfaces of the electrodes were taken before and after the modification by scanning electron micros-
copy (Fig. 3).

The first sample is the surface of pure GCE, before the reversible \([\text{Fe(CN)}_6]^{3-/4-}\) pair is added to the cell.
On the sample surface, selective microporosity is observed (Fig. 3A). The pore size does not exceed 10 \(\mu\)m.
On the surface there is a slight contamination with an extraneous phase, which has the form of globular parti-
cles. Presumably, this phase is a particle of salt, which is part of the background electrolyte. The second sample
is the surface of the GCE after introducing a reversible \([\text{Fe(CN)}_6]^{3-/4-}\) pair into the cell.
Modification of carbon containing electrodes …

A — GCE without a modifier; B — GCE after the addition of the reversible \([\text{Fe(CN)}_6]^{3-/4-}\) pair to the cell; C — GCE after modification of the solution of the 4-carboxybenzodiazonium iodate modifier (10 mg∙l\(^{-1}\)) for 5 sec

Figure 3. Scanning electron microscopy of GCE surfaces and corresponding cyclic voltamograms

On a microscopic photograph, \([\text{Fe(CN)}_6]^{3-/4-}\) aggregates are observed on the surface of the electrode, covering the micropores of glassy carbon. Areas with inclusions of a spherical shape are observed (Fig. 3B). Presumably, this phase corresponds to iron-containing hexacyanoferrate. The third sample is the surface of the GCE after modification of 4-carboxybenzodiazonium iodate (10 mg∙l\(^{-1}\) for 5 seconds).

On a microscopic image (Fig. 3C), laminated aggregates of irregular shape are observed confirming the flow of adsorption on the surface of the electrode substrate, which proves the fact of the chemical reaction on the GCE surface between the carbon and the diazonium modifier. It is obvious that a covalent modification of the GCE is possible without imposing a potential in a very short period of time. In addition, after the
modification, the current-conducting properties of the SEM are increased due to an increase in the currents of the reversible $[\text{Fe(CN)}_6]^{3-/4-}$ pair at the potentials of 0.15 V and 0.35 V under the optimum modification conditions.

From the cyclic voltammograms of the reversible pair $[\text{Fe(CN)}_6]^{3-/4-}$, the electroactive surface areas of the electrodes were calculated before modification and after according to the Randles-Shevchik equation (Table):

$$I_p = \pm 2.69 \times 10^9 \times z^{1/2} \times A \times D \times C \times W^{1/2},$$

$I_p$ — peak current, A; $z$ — the number of electrons ($n = 1$); $A$ — the area of the electroactive surface, cm$^2$; $D$ — the diffusion coefficient ($7.60 \times 10^{-6}$ cm$^2$/s); $C$ — concentration $[\text{Fe(CN)}_6]^{3-/4-}$ in solution ($1 \times 10^{-3}$M).

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<tr>
<th>Square electroactive surface of the GCE before modification, cm$^2$</th>
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<td>0.00452</td>
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As a result of modifying the GCE using the spontaneous chemical modification method with a carboxy substituent (modifier concentration 10 mg·l$^{-1}$, aging time 5 seconds), the area of the electroactive surface increases almost 2.5 times, which leads to an increase in the cathodic and anodic currents of the reversible $[\text{Fe(CN)}_6]^{3-/4-}$ with respect to the unmodified surface of the GCE.

To further confirm the presence of organic functional groups on the GCE surface, IR reflection spectra (Fig. 4) were obtained: 1) 4-carboxybenzodiazonium iodate modifier with a concentration of 10 mg·l$^{-1}$; 2) the initial surface of the GCE; 3) the surface of the glassy carbon electrode after modification. The absorption bands at 3659, 1685, 1590, 1710, 878 cm$^{-1}$, corresponding to the carboxyl group and the phenyl nucleus are observed in the spectrum.

$1$ — modifier 4-carboxybenzodiazonium iodate ($c = 10$ mg·l$^{-1}$); $2$ — the initial surface of the GCE; $3$ — surface of the glassy carbon electrode after modification.

Figure 4. The transmission spectrum of the IR surface of the GCE
If the balance between the concentration of the modifier and the modification time with respect to each modifier is not observed, blocking of the conductive surfaces of the GCE and reduction of the cathodic and anodic currents [Fe(CN)₆]₃⁻⁴⁻ is observed.

The phenomena of uncontrolled growth of polylayer modifiers on carbon-containing electrodes, leading to blocking of conductive surfaces after the application of potentials, are described in the literature [28, 29].

Moreover, the mechanism of the formation of different structures of polylayer modifiers is not fully understood. We noted that the growth of modifier polylayers occurs without the application of potentials under conditions of spontaneous adsorption.

Controlling the thickness and, accordingly, the conductive characteristics of the GCE is possible by adjusting the concentration and the holding time of the electrodes with respect to modifiers of different nature, which is confirmed by the data in Figure 2.

For different nature modifiers having a concentration of 10 mg⁻¹, modification time was: [HOOC-C₆H₄N₂]IO₃ — 5 seconds, [NCC₆H₄N₂]IO₃ — 60 seconds, [O₂C₆H₄N₂]IO₃ — 60 seconds, [C₆H₄N₂]IO₃ — 5 seconds, [H₃C₁₆C₆H₄N₂]IO₃ — 120 seconds, [H₆C₈N₂C₆H₄N₂]IO₃ — 120 seconds.

Conclusions

Thus, it has been established that [HOOC-C₆H₄N₂]IO₃ is used as an electrode modifier for the GEC. The optimal modification conditions are a concentration of 10 mg⁻¹, a holding time of 5 seconds. As a result of the modification of a GCE using the method of spontaneous chemical modification with salts of an ASD with a carboxyl substituent, the area of the electroactive surface increases almost 2.5 times. The presence of organic functional groups of the 4-carboxybenzodiazonium iodate modifier on the surfaces of the GCE has been confirmed by SEM IR spectroscopy. Controlling the thickness and, accordingly, the conductive characteristics of the GCE is possible, by adjusting the concentration and the holding time of the electrodes with respect to modifiers of different nature. The method of modifying the GCE with iodate salts of aryl diazonium is simple, rapid, economical, and can be used to increase the sensitivity of the determination of a number of analytes in electroanalysis.

References

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Модификация углеродсодержащих электродов посредством йодистых солей арилдиазония для электроанализа

В статье изучен способ спонтанной химической модификации стеклоуглеродного электрода (СУЭ) йодатными солями арилдиазония. Модификация СУЭ проводилась адсорбцией из раствора соответствующих солей. Для оценки эффективности модификации СУЭ разными модификаторами в условиях изменения их концентрации и времени выдерживания СУЭ были записаны циклические вольтамперограммы обратимой пары $[\text{Fe(CN)}_6]^{3-/4-}$ в фоновом электролите КСІ 0.5 М. Рост полислоев модификаторов происходит без наложения потенциалов в условиях спонтанной адсорбции. Управление толщиной и соответственно токопроводящими характеристиками СУЭ возможно путем регулирования концентрации и времени выдерживания электродов в отношении разных по природе модификаторов. Установлено, что токи окисления и восстановления $[\text{Fe(CN)}_6]^{3-/4-}$ максимальны для модификатора 4-карбоксибензодиазониум йодата СУЭ с концентрацией 10 мг·л⁻¹ при времени выдерживания электрода в его растворе в течение 5 с. Увеличение токов обратимой пары $[\text{Fe(CN)}_6]^{3-/4-}$ в указанных условиях после модификации 4-карбоксибензодиазониумом йодата связано с увеличением площади электроактивной поверхности электрода почти в 2.5 раза. Исследования морфологии электродной поверхности СУЭ методом сканирующей электродной микроскопии подтвердили наличие полислоев модификатора с карбоксизаместителем на поверхностях стеклоуглеродного электрода. Для подтверждения наличия органических функциональных групп модификатора 4-карбоксибензодиазониум йодата на поверхностях СУЭ получены спектры отражения электродных поверхностей методом ИК спектроскопии. Способ модификации СУЭ йодатными солями арилдиазония прост, экономичен и может быть использован для увеличения чувствительности определения ряда анализов в электроанализе.

Ключевые слова: ароматические соли диазония, модификаторы, стеклоуглеродные электроды, циклическая вольтамперометрия, ИК-спектроскопия, СЭМ (сканирующая электронная микроскопия), декациноферрат калия.