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A.O. Gusar, Ye.V. Dorozhko, K.V. Dyorina, Ye.I. Korotkova

Tomsk Polytechnic University, Russia
(E-mail: anngsa@mail.ru)

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 $[Fe(CN)_6]^{3-/4-}$ 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 $[Fe(CN)_6]^{3-/4-}$ are maximum for the 4-carboxybenzodiazonium iodate modifier of GCE with a concentration of 10 $mg \cdot l^{-1}$ when the time of keeping the electrode in its solution is for 5 seconds. The increasing of the reversible pair $[Fe(CN)_6]^{3-/4-}$ 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].

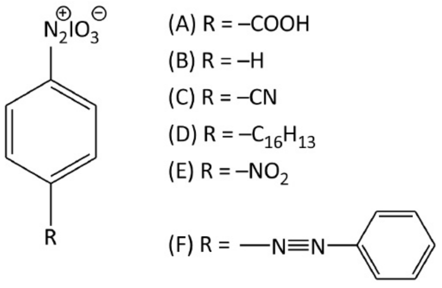
There is a number of works concerned with the spontaneous modification of carbon-containing electrodes. The authors note the simplicity of the spontaneous method of modifying carbon-containing electrodes with obtaining thinner and conductive mono [28] or poly [30] layers of ASD modifiers. Generally, 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·l^{-1} 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: $[HOOCC_6H_4N_2]IO_3$, $[NCC_6H4N_2]IO_3$, $[O_2NC_6H_4N_2]IO_3$, $[C_6H_5N_2]IO_3$, $[H_{33}C_{16}C_6H_4N_2]IO_3$, $[H_4C_6N_2C_6H_4N_2]IO_3$. 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 MΩ 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·l^{-1}) 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·l^{-1}. 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 hexacyanoferrate salts $[Fe(CN)_6]^{3-/4-}$ of concentration 0.25 M (background 0.5 M KCl) were recorded before and after chemical modification.



A — 4-carboxybenzodiazonium iodate;
B — iodate aryldiazonium;
C — 4-cyanobenzodiazonium iodate;
D — 4-hexadecylbenzodiazonium iodate;
E — 4-nitrobenzodiazonium iodate;
F — 4-(phenyldiazenyl)benzodiazonium iodate

Figure 1. Structural formulas of aryldiazonium salts

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).

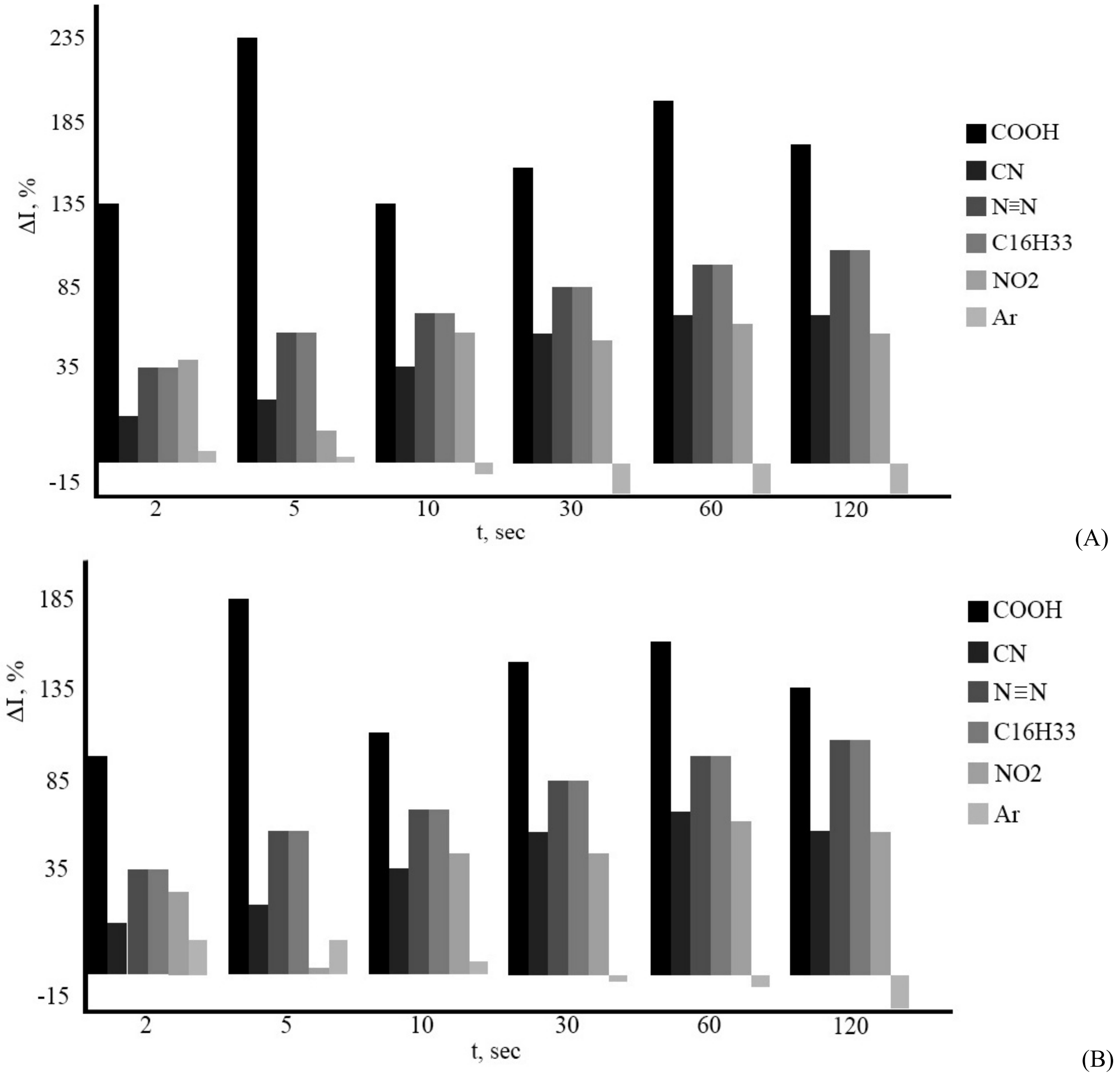
Results and Discussion

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 ΔI (%) was calculated:

$$\Delta I\frac{(I_1 - I_0)}{I_0}\cdot 100\,,$$

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 $[Fe(CN)_6]^{3-/4-}$ 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} (ΔI = 230 % cathode scan and ΔI = 185 % anode scan).

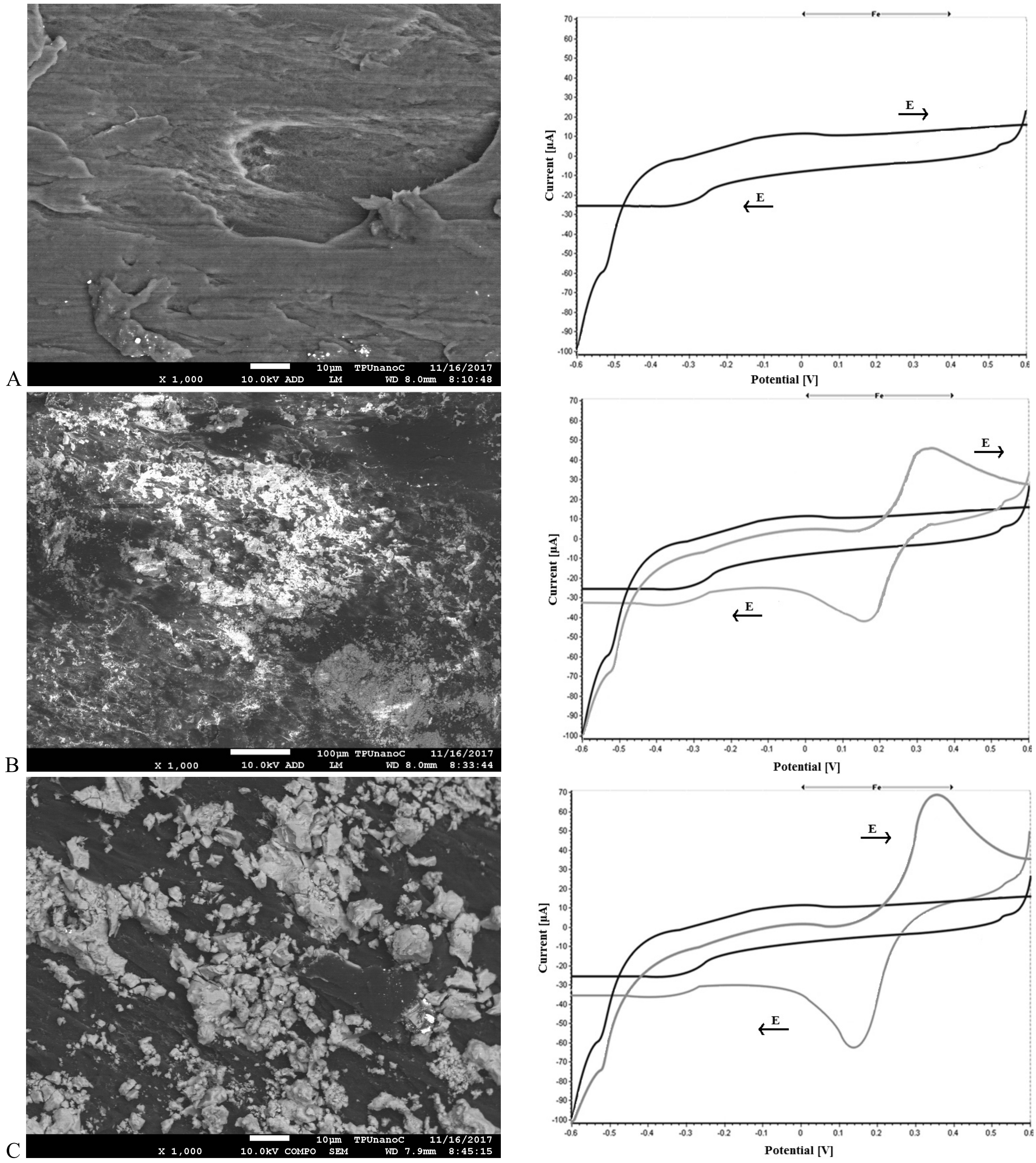


A — cathode currents; *B* — anode currents. The background electrolyte is KCl 0.5 M; scan rate 80 mV·s^{-1}; concentration 10 mg·l^{-1}

Figure 2. Dependence of the change in the currents of $[Fe(CN)_6]^{3-/4-}$ (ΔI, %) on the time of aging of GCE in the solution of the aryl diazonium iodate salts modifiers

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 microscopy (Fig. 3).

The first sample is the surface of pure GCE, before the reversible $[Fe(CN)_6]^{3-/4-}$ pair is added to the cell. On the sample surface, selective microporosity is observed (Fig. 3A). The pore size does not exceed 10 µm. On the surface there is a slight contamination with an extraneous phase, which has the form of globular particles. 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 $[Fe(CN)_6]^{3-/4-}$ pair into the cell.



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

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

On a microscopic photograph, $[Fe(CN)_6]^{3-/4-}$ 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. 3*B*). Presumably, this phase corresponds to iron-containing hexacyanoferrate. The third sample is the surface of the GCE after modification of 4-carboxybenzodiazonium iodate (10 $mg \cdot l^{-1}$ for 5 seconds).

On a microscopic image (Fig. 3*C*), 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 $[Fe(CN)_6]^{3-/4-}$ 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 $[Fe(CN)_6]^{3-/4-}$, the electroactive surface areas of the electrodes were calculated before modification and after according to the Randles-Shevchik equation (Table):

$$Ip = \pm 2.69\times 10^5 z^{3/2} A D^{1/2} C W^{1/2},$$

Ip — peak current, A; z — the number of electrons ($n = 1$); A — the area of the electroactive surface, cm^2; D — the diffusion coefficient (7.60×10^{-6} cm^2/s); C — concentration $[Fe(CN)_6]^{3-/4-}$ in solution ($1\cdot10^{-3}$M).

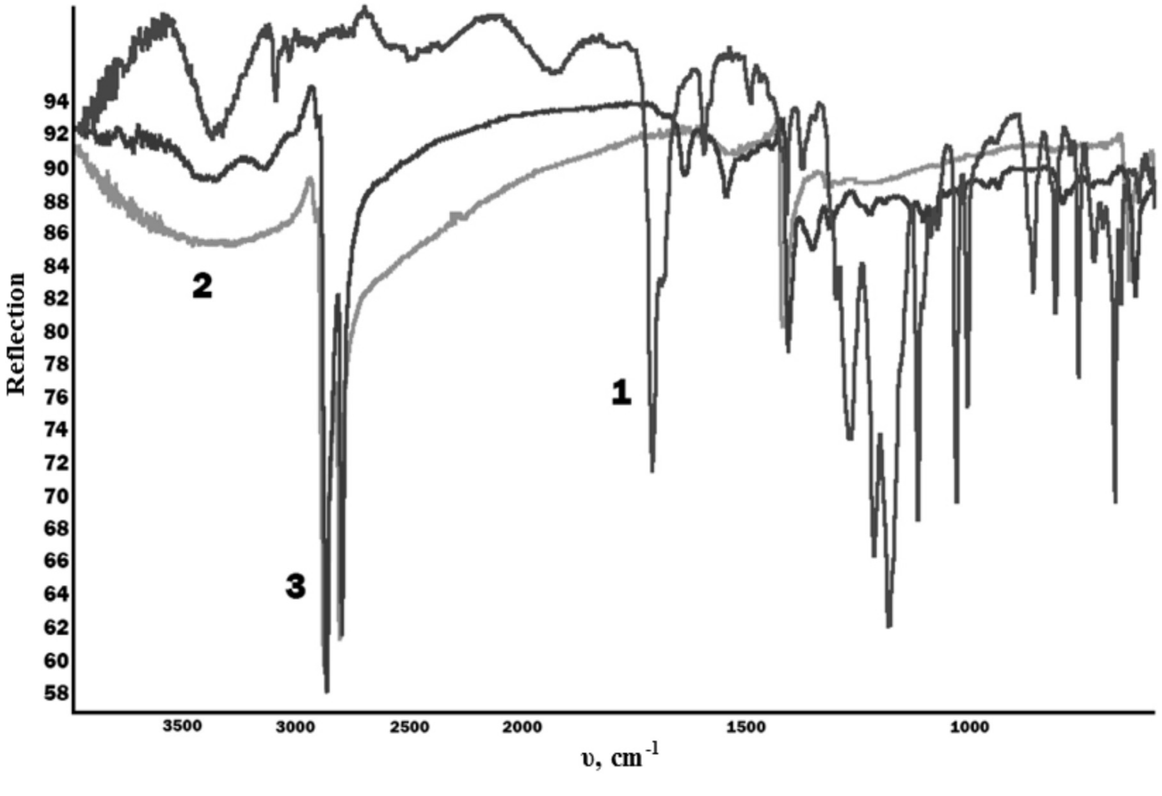
Table

Areas of the electroactive surface of the GCE (cm^2) before modification and after modification

Square electroactive surface of the GCE before modification, cm^2	Square electroactive surface of the GCE after modification, cm^2
0.00452	0.01054

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 $[Fe(CN)_6]^{3-/4-}$ 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 — modifier4-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 $10\ mg \cdot l^{-1}$, modification time was: $[HOOCC_6H_4N_2]IO_3$ — 5 seconds, $[NCC_6H_4N_2]IO_3$ — 60 seconds, $[O_2NC_6H_4N_2]IO_3$ — 60 seconds, $[C_6H_5N_2]IO_3$ — 5 seconds, $[H_{33}C_{16}C6H4N2]IO_3$ — 120 seconds, $[H_4C_6\ N_2C_6H_4N_2]IO_3$ — 120 seconds.

Conclusions

Thus, it has been established that $[HOOCC_6H_4N_2]IO_3$ is used as an electrode modifier for the GEC. The optimal modification conditions are a concentration of $10\ mg \cdot l^{-1}$, 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 carboxy 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 aryldiazonium is simple, rapid, economical, and can be used to increase the sensitivity of the determination of a number of analytes in electroanalysis.

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А.О. Гусар, Е.В. Дорожко, К.В. Дёрина, Е.И. Короткова

Көміртекқұрамды электродтарды арилдиазонийдің йодты тұздары арқылы электрталдау үшін модификациялау

Мақалада шыныкөміртекті электродты (ШКЭ) арилдиазонийдің йодты тұздарымен химиялық модификациялау әдісі зерттелді. ШКЭ модификациялау сәйкес тұздарының ерітінділерінен адсорбциялау арқылы жүргізілді. ШКЭ модификациялаудың тиімділігін бағалау үшін әртүрлі модификаторлармен олардың концентрациялары және ШКЭ ұстау уақыты өзгеруі жағдайларында, KCl 0.5 M фонды электролитінде $[Fe(CN)_6]^{3-/4-}$ қайтымды жұптың циклді вольтамперограммалары жазылды. Модификаторлардың полиқабаттарының өсуі спонтанды адсорбция жағдайларында потенциалдарының қабаттасуысыз жүреді. ШКЭ қалыңдығын және сәйкесінше тоқ өткізетін сипаттамаларым басқару концентрацияларын реттеу және табиғаты әртүрлі модификаторларға қатысты электродтардың ұсталу уақытын реттеу арқылы мүмкін болады. $[Fe(CN)_6]^{3-/4-}$ тотығу және тотықсыздану тоқтары 4-карбоксибензодиазониум йодаты ШКЭ модификаторы үшін оның концентрациясы 10 мг·л$^{-1}$ және оны ерітіндіде ұстау уақыты 5 с болғанда максималды болатыны анықталды. Қайтымды жұптың $[Fe(CN)_6]^{3-/4-}$ тоқтары артқанда көрсетілген жағдайларда 4-карбоксибензодиазониум йодатының модификациялануынан кейін ұдайы электродтың электрбелсенді бетінің аумағы 2,5 есеге дейін артуымен байланысты. ШКЭ электродты бетінің морфологиясын сканерлейтін спонтанды микроскопия әдісімен зерттеу шыныкөміртектік электрод беттерінде карбоксиорынбасушысы бар модификатордың полиқабаттары бар екенін дәлелдеді. Органикалық функционалды топтарының 4-карбоксибензодиазониум йодат модификаторының құрамында болуын дәлелдеу үшін ШКЭ беттерінде ИҚ-спектроскопия әдісімен электродты беттерінің шағылысу спектрлері жазылды. ШКЭ арилдиазонийдің йодатты тұздарымен модификациялау әдісі қарапайым, үнемді және электрталдауда аналиттер қатарын анықтау сезімталдығын арттыру үшін қолданылуы мүмкін.

Кілт сөздер: диазонийдің ароматты тұздары, модификаторлар, шыныкөміртектік электродтар, циклді вольтамперометрия, ИҚ-спектроскопия, СЭМ (сканерлейтін электронды микроскопия), калийдің гексацианоферраты.

А.О. Гусар, Е.В. Дорожко, К.В. Дёрина, Е.И. Короткова

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 модифицирования СУЭ разными модификаторами в условиях изменения их концентрации и времени выдерживания СУЭ были записаны циклические вольтамперограммы обратимой пары $[Fe(CN)_6]^{3-/4-}$ в фоновом электролите KCl 0.5 M. 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 $[Fe(CN)_6]^{3-/4-}$ 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 $[Fe(CN)_6]^{3-/4-}$в указанных условиях после модификации 4-карбоксибензодиазониум йодата связано с увеличением площади электроактивной поверхности электрода почти в 2,5 раза. Исследования морфологии электродной поверхности СУЭ методом сканирующей электродной микроскопии подтвердили наличие полислоя 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 аналитов в электроанализе.

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