

## THE NEW METHOD OF COVALENT GRAFTING OF ORGANIC FUNCTIONAL GROUPS ON THE GRAPHITE/GC ELECTRODES USING ARENEDIAZONIUM TOSYLATES

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### Abstract

*The new method of spontaneous covalent functionalization of graphite/glassy carbon surface using arenediazonium tosylates is shown. Found that spontaneous functionalization of electrode surface increases the sensitivity of quercetin voltammetric determination.*

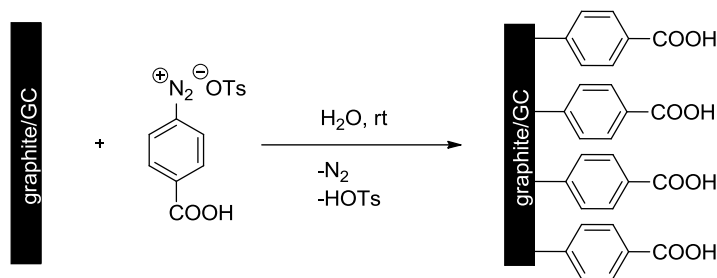
### 1 Introduction

The possibility of a carbon surface modification via diazonium chemistry was demonstrated by Delamar and co-workers [1]. The method of surface modification consisted in electrochemical reduction of diazonium tetrafluoroborates in MeCN solution in appropriate buffer (usually  $\text{Bu}_4\text{N}^+\text{BF}_4^-$ ). This method also used by other investigators for obtaining a new generation of sensors for metal ions determination and other purposes [2, 3, 4]. The modification of metal surface via electrochemical reduction of diazocations has been shown later [5, 6, 7].

The described method has some disadvantages due to diazonium tetrafluoroborates usage. First, arenediazonium tetrafluoroborates have a poor solubility in water and low stability at storage. Second, surface organic layers cause blocking effect in voltammetric determinations because high layer thickness [8, 9].

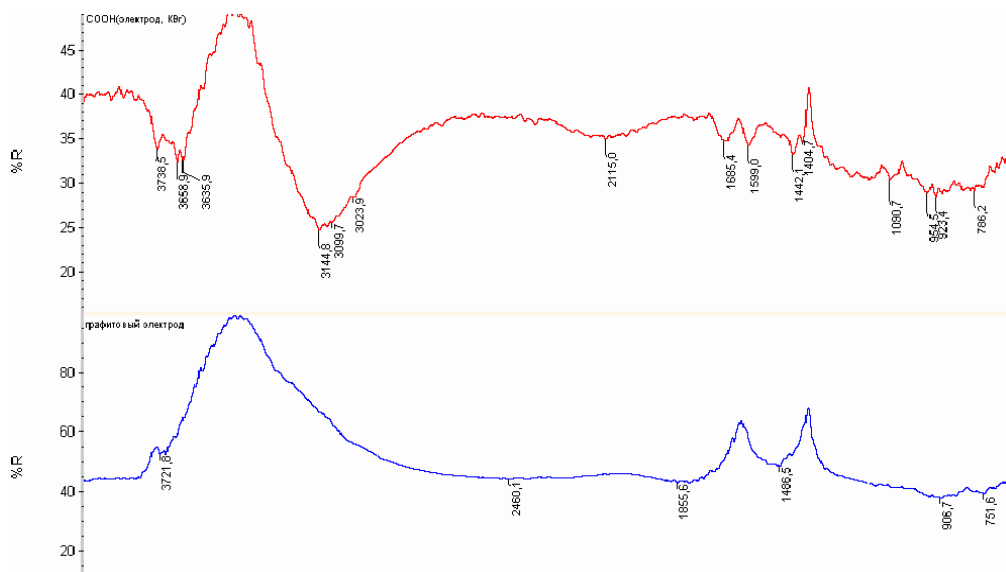
Previously we reported about synthesis and synthetic applicability of new diazonium salts – arenediazonium tosylates (ADT) [10]. ADT have a good solubility in water and some organic solvents, high stability at storage and non-explosion properties. Also, we found, that ADT can spontaneously react with surface of carbon-coated metal nanoparticles [11]. It became a basis for studies of interactions between water solution of ADT and graphite/glassy carbon surfaces.

We found that immersing of graphite electrode in ADT water solution leads to spontaneous reaction between surface and ADT with nitrogen evolving (figure 1).



**Figure 1.** Scheme of graphite/GC surface modification using 4-carboxybenzenediazonium tosylate (4-CBDT).

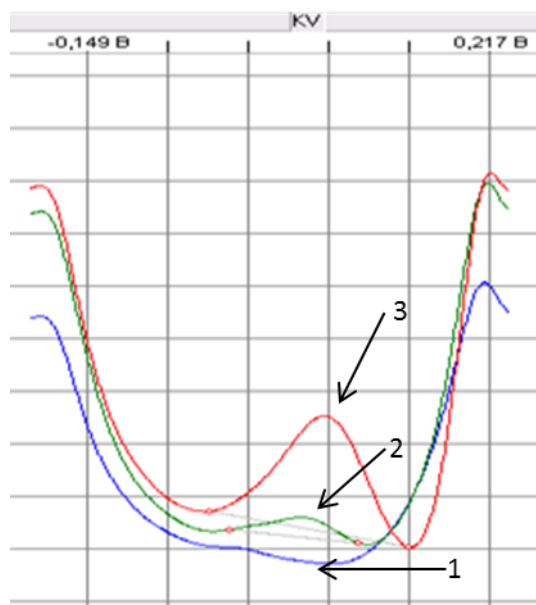
After modification process obtained electrode was investigated by IR-ATR spectroscopy (figure 2).



**Figure 2.** IR-ATR spectra of graphite electrode modified by 4-carboxybenzenediazonium tosylate.

At IR-spectra the vibrational band of C<sub>6</sub>H<sub>4</sub>COOH groups (786-1090 cm<sup>-1</sup>, 1442-1685 cm<sup>-1</sup> and about 3000-3700 cm<sup>-1</sup>) was observed.

The modified electrode also used in model electrochemical reaction of quercetin oxidation. The typical voltammetric curve is represented in figure 3.



**Figure 3.** The voltammetric curves of quercetin oxidation (1 – background electrolyte 0,1 M Na<sub>2</sub>HPO<sub>4</sub>; 2 – quercetin solution 0,2 mg/l, unmodified graphite electrode; 3 - quercetin solution 0,2 mg/l, modified graphite electrode).

Analysis of the voltammetric curves showed that the surface modification significantly increased the sensitivity of quercetin voltammetric determination. It's a new and unique application of carbon electrodes with modified surface.

We observed a correlation between reaction time, ADT concentration and the value of quercetin oxidation current (table 1).

Reactions conditions		Quercetin oxidation current, uA
4-CBDT concentration, mg/l	Reaction time, sec	
30	5	0,49± 0,05
30	10	0,52± 0,06
300	5	0,35±0,09
1000	5	0,26±0,06
1000	10	0,23±0,05
30	15	0,15±0,03
30	30	0,11±0,02

**Table 1.** The correlation between reactions conditions and quercetin oxidation current (background electrolyte 0,1 M Na<sub>2</sub>HPO<sub>4</sub>; quercetin solution 0,2 mg/l)

The oxidation current decreasing can be explained by blocking effect of surface organic layers. This effect was observed previously in the process of electrochemical reduction of diazocations. It was associated with formation of saturated organic monomolecular or polymolecular layers on the carbon surface [8, 9]. Spontaneous reaction of ADT with carbon surface leads to modification of only active sites and keeping of electrochemical activity.

The detail mechanism of spontaneous reaction between ADT and carbon surface do not fully investigated yet. However, it doesn't diminish the practical and scientific significance of the obtained results. The new generation of high-sensitivity electrochemical sensors for determinations of organic substances has a great application in analysis.

## 2 Materials and testing methods

The 4-carboxybenzenediazonium tosylate was obtained according described procedure [10]. Voltammetric measurements were performed on the voltammetric analyzer STA (LLC "UMX", Tomsk, Russia). Graphite electrode was made of spectrally pure graphite impregnated by paraffin. Water for all voltammetric measurements was distilled twice from all-glass apparatus. The IR-ATR spectra were recorded on FT-IR spectrometer Nicolet 5700 with ATR unit equipped with diamond crystal.

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