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## Electrochemical Activity of Glutathione at a Graphite Electrode Modified with Gold Nanoparticles

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### ABSTRACT

The electrochemical activity of the glutathione (GSH) at the graphite electrodes modified with gold nanoparticles (AuNP-GCE) is formed under the ratio of reactants and in solutions of supporting electrolytes of 0, 1 M NaOH, 0,1 " phosphate buffer (pH 6.86), 0,1 M HCl, 0,1 M NaClO<sub>4</sub> is studied by the method of cyclic voltammetry. The dependence of the electrochemical activity of GSH on ratio of reagents H<sub>2</sub>AuCl<sub>4</sub>:Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>:NaBH<sub>4</sub>, used to the preparation of sols, and the modification time of the GE surface with gold nanoparticles have been studied. The "inverse" cathodic peak of GSH at AuNP-GCE formed in the reaction mixture H<sub>2</sub>AuCl<sub>4</sub>:Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>:NaBH<sub>4</sub> = 1:1:4 is observed on the cathodic branch of cyclic voltammogram at E<sub>c</sub> = 0.05 V in 0.1 M NaOH. The mechanism of electrochemical oxidation of the GSH on the surface of AuNP-GCE in 0.1 M NaOH is proposed.

**Key words:** graphite electrode, gold nanoparticles, cyclic voltammetry, glutathione.

### INTRODUCTION

GSH (2-amino-5-[[2 - [(carboxymethyl) amino] - 1 - (mercaptometil)-2-oxoethyl] amino]-5-oksopentanoic acid) is a water-soluble tripeptide of <sup>3</sup>-glutamylcysteinilglycine. GSH plays an important role in protecting the organism from disease, toxins, viruses, environmental hazards, radiation and the oxidative stress (free radicals). The GSH level in the cells determines the lifetime (Garaeva S.N. at

all, 2009). Therefore the development of highly sensitive methods for the determination of GSH in the different biological matrices is an important task of analytical chemistry. Traditionally, the determination of GSH in a clinical investigations is carried out by chromatography (McDermott G.P., Francis P.S., 2011), optical methods (Hormozi-Nezhad M.R. at all, 2012), capillary electrophoresis (Wang X. at all, 2014), enzymic method (Tietze F., 1969). Disadvantages of these methods are the

long time of sample preparation and analysis and high costs of the equipments. At the same time, electrochemical methods are essentially simpler and cheaper, than most of other methods, used in biochemistry, molecular biology, and medical diagnostics. The main limitation of the use of electroanalytical methods in biochemical analysis is a non-selectivity with respect to the substance to be determined. The components are generally found in low concentration in the presence of a wide range of substances that may obscure the results of analysis, or the presence of masking amino acids. GSH at a mercury dropping electrode is determined by polarographic method (Huska D. at all, 2007). This method is based on the formation of mercaptide of mercury on the surface of the electrode. The detection limit of GSH was  $15 \times 10^{-3}$  M. However, the toxicity of mercury does not allow the use of these electrodes in laboratories. Solid electrodes are used to expand the opportunities of voltammetric analysis of GSH (Budnikov G.K. at all, 2007; Zaharchuk N.F. at all 2008). However, the use of solid electrodes also does not allow to decrease the GSH detection limit due to adsorption of the products of electrochemical oxidation of GSH on the electrode surface. The detection limit of the voltammetric determination of GSH at a platinum electrode is  $1,9 \times 10^{-5}$  M (Zaharchuk N.F. at all 2008). Recently, chemical modified electrodes are used to a voltammetry determination of GSH. There are carbon electrodes modified with different materials such as graphite, microspheres and nanotubes (Apetrei I. at all (2011); Ensafi A.A. at all, 2010), cobalt phthalocyanine (Luz C.S. at all, 2007), ferrocene (Raof J.B. at all, 2009), metal nanoparticles, its oxides and hydroxides (Chee S.Y. at all, 2011; Safavi A. at all, 2009; Raof J.B. at all, 2009) in the voltammetric analysis of GSH. The detection limit of GSH at the carbon paste electrode modified with carbon microspheres was  $6,4 \times 10^{-6}$  M (Apetrei I. at all, 2011). The detection limit of GSH at the carbon paste electrode modified with carbon nanotubes is  $5 \times 10^{-6}$  M (Apetrei I. At all, 2011). The detection limit of GSH at the glass carbon electrode modified with cobalt phthalocyanine in poly-L-lysine film was 15 nM (Luz Cassia Silva at all, 2007). The modification of carbon paste electrode with 2,7-bis (ferrocenyl ethyl) fluoren-9-on allows to determine GSH with a detection limit equal to  $2,1 \times 10^{-6}$  M (Raof J.B. at all, 2009). The modification of the glass carbon

electrode surface with oxide nickel allows to determine the GSH with a detection limit equal to  $1 \times 10^{-4}$  M (Chee S.Y. at all, 2011). The detection limit of GSH at carbon paste electrode modified with hydroxide copper (II) consists  $3 \times 10^{-8}$  M (Safavi A., 2009). The detection limit of GSH at carbon paste electrode modified with oxide titanium (IV) and ferrocene acid consists  $7 \times 10^{-4}$  M (Raof J.B. at all, 2009). The modification of the indicator electrode with metal nanoparticles improves detection sensitivity and reduces detection limits of amino acids. Due to their specific properties the use of nano-sized metal particles as modifiers can decrease the limit of detection of organic substances (Perevezentseva D.O. , Gorchakov E.V., 2012; Compton R.G., 2006). Therefore, modification of the surface carbon electrode with metal nanoparticles is actual task.

**The purpose of this work** is to investigate the electrochemical activity of GSH at the AuNP-GCE in aqueous solution by cyclic voltammetry, and to propose a mechanism of the electrochemical oxidation of GSH.

## Experimental part

### Materials and methods of investigation

Gold nanoparticles were prepared by chemical reduction of  $\text{HAuCl}_4$  with  $\text{NaBH}_4$  and sodium citrate described in the work (Perevezentseva D.O., Gorchakov E.V., 2012). The morphology of the gold nanoparticles was characterized by scanning electron microscopy (JSM-5500). pH values of sol were measured with a PH-150 instrument. Cyclic voltammetric measurements were carried out with the voltammetric analyzer TA-2 (Tomsk) with a two electrode cell having the working electrode and a Ag/AgCl/KCl reference electrode at a temperature of 20°C. The working electrodes were either a graphite electrode (GE), a GE modified with gold film electrode (Au-GE), or a AuNP-GCE.

### Preparation of the AuNP-GCE

Cleaning the surface of the carbon electrode was carried out mechanically by dense filter paper, followed by an electrochemically cleaning. Modification of the surface of the graphite electrode was carried out as follows: The electrode was placed in an electrochemical cell filled with 10

ml of 0,1 M HCl solution with the addition of 0.1 ml of gold sol prepared as described above. The gold nanoparticles were electrochemically deposited on the surface of the graphite electrode at the accumulation potential  $E_{acc} = -1,0$  V during the accumulation time  $t_{acc} = 30 - 300$  s. Then the electrode was removed from the solution, rinsed with double distilled water and placed in the supporting electrolyte 0,1 M NaOH for the voltammetric determination of GSH.

#### Preparation of the GE modified with gold (Au-GE)

Cleaning the surface of the carbon electrode was carried out mechanically by dense filter paper, followed by an electrochemically cleaning. Modification of the surface of the GE was carried out as follows: The electrode was placed in electrochemical cell filled with 10 ml of 10 mg·L<sup>-1</sup> HAuCl<sub>4</sub>. The gold were electrochemically deposited on the surface of the GE at the accumulation potential  $E_{acc} = -1,0$  V during the accumulation time  $t_{acc} = 60$  s. Then the electrode was removed from the solution, rinsed with double distilled water and placed in supporting electrolyte 0,1 M NaOH for the voltammetric determination of GSH.

#### Analytical procedures

A volume 10 ml of the supporting electrolyte was placed in the electrode cell. The

following supporting electrolytes were used: 0,1 M NaOH, 0,1 M phosphate buffer (pH 6.86), 0,1 M NaClO<sub>4</sub>, 0,1 M HCl. The voltammograms of the supporting electrolyte were recorded by cyclic voltammetry under the following conditions: scan rate 0.100 V·s<sup>-1</sup>, potential range  $E = -1,0$  to  $+1,0$  V. Then 20 μl of a GSH solution of unknown concentration were added to the solution. The obtained solution was stirred for 1 minute and then the cyclic voltammogram of GSH was recorded. The solutions of GSH were prepared in double distilled water before voltammetric measurements.

## RESULTS AND DISCUSSIONS

#### The electrochemical activity of the GSH at the Au-GE, AuNP-GCE

Gold nanoparticles have a spherical shape. The average size of gold nanoparticles is 5-15 nm (Figure 1). The size of the gold particles depends on the nature of the reducing agent and conditions of the formation and storage (Perevezentseva D.O., Gorchakov E.V., 2012).

At a GE, GSH does not show an electrochemical signal at a concentration of  $1,3 \times 10^{-12}$  M in 0.1 M NaOH (Curve 1, figure 2). GSH is electrochemical active at AuNP-GE, Au-GE. In the presence of  $1,3 \times 10^{-12}$  M GSH at the AuNP-GCE two

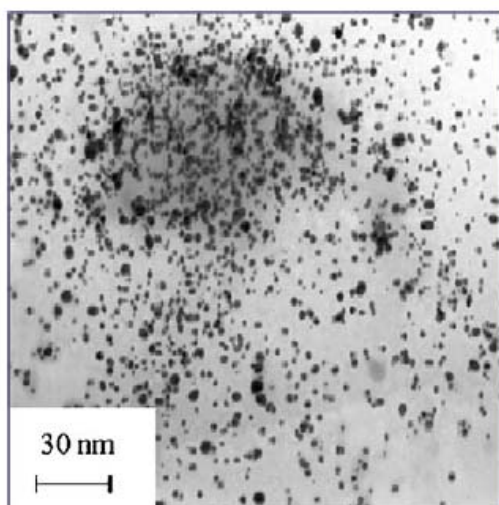


Fig. 1: SEM-image of gold nanoparticles

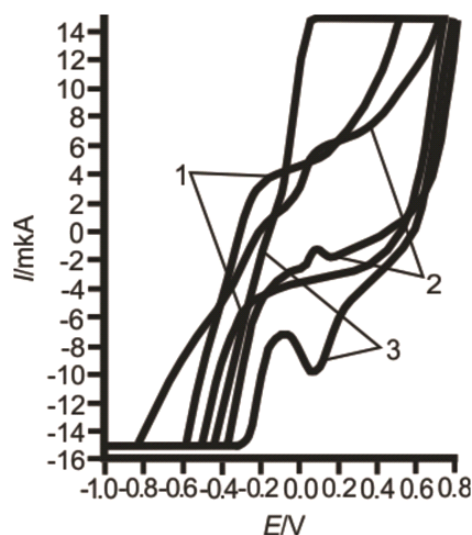


Fig. 2: Cyclic voltammograms GSH at: GE (1), AuNP-GCE (2), Au-GE (3) in solution 0,1 M NaOH,  $C_{GSH} = 1,3 \cdot 10^{-12}$  M; scan rate 100 mV·s<sup>-1</sup>

wave are observed at  $E_{o_1} = -0,2$  V and  $E_{o_2} = 0,15$  V on the anodic branch of the cyclic voltammogram (Curve 2, figure 2). There is "inverse" cathodic peak in the presence of  $1,3 \times 10^{-12}$  M GSH at  $E_c = 0,05$  V on the cathodic branch of the cyclic voltammogram at the AuNP-GCE (Curve 2, figure 2). The "inverse" cathodic peak of GSH at the AuNP-GCE formed in the reaction mixture  $\text{HAuCl}_4:\text{Na}_3\text{C}_6\text{H}_5\text{O}_7:\text{NaBH}_4 = 1:1:4$  is observed at  $E_c = 0,05$  V in 0.1 M NaOH on the cathodic branch of cyclic voltammogram. There are not peaks on the anodic branch of this cyclic voltammogram at the Au-GE in the presence of  $1,3 \times 10^{-12}$  M GSH (Curve 3, figure 2). In the presence of  $1,3 \times 10^{-12}$  M GSH at the Au-GE the cathodic peak is observed at  $E_c = 0,05$  V on the cathodic branch of the cyclic voltammogram (Curve 3, figure 2).

To choose optimal conditions in which GSH shows the greatest electrochemical activity were investigated the following dependences: the heights of the maxima of GSH from the nature of the supporting electrolyte, the ratio of reagents  $\text{HAuCl}_4:\text{Na}_3\text{C}_6\text{H}_5\text{O}_7:\text{NaBH}_4$ , used to the preparation of sols, and of the modification time of the GE surface with gold nanoparticles.

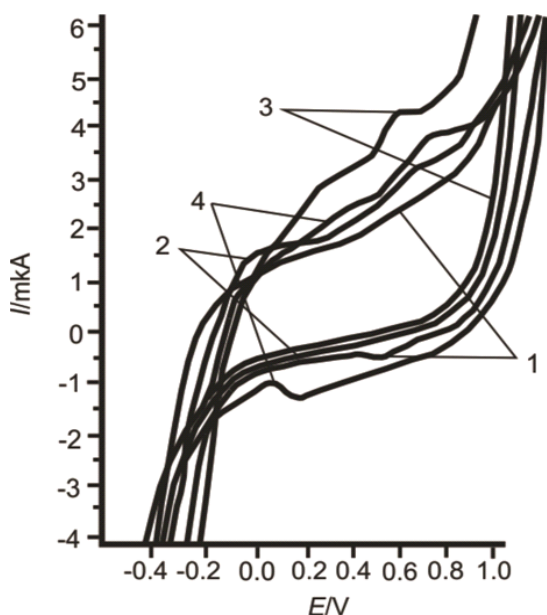


Fig. 3: Cyclic voltammograms GSH at AuNP-GCE in: 1) 0,1 M phosphate buffer pH 6,86, 2) 0,1 M  $\text{NaClO}_4$ , 3) 0,1 M HCl, 4) 0,1 M NaOH.  $C_{\text{GSH}} = 1,3 \times 10^{-12}$  M; scan rate  $100 \text{ mV}\cdot\text{s}^{-1}$

### The electrochemical activity of the GSH at AuNP-GCE in the solution of different electrolytes

Firstly, the electrochemical activity of GSH was investigated at the AuNP-GE in solutions of follows supporting electrolyte: 0.1 M HCl, 0.1 M NaOH, 0.1 M  $\text{NaClO}_4$ , 0.1 M phosphate buffer (pH 6.86). In the presence of  $1,3 \times 10^{-12}$  M GSH at the AuNP-GE on the anodic branch of the cyclic voltammogram in 0.1 M phosphate buffer (pH 6.86) peaks are not observed (Curve 1, figure 3). The maximum is observed at  $E_c = 0,5$  V on the cathodic branch of this cyclic voltammogram at the AuNP-GCE (Curve 1, figure 3). Two waves are observed at  $E_{o_1} = 0,0$  V and  $E_{o_2} = 0,8$  V on the anodic branch of the cyclic voltammogram in 0.1 M  $\text{NaClO}_4$ . There is not maximum on the cathodic branch of this cyclic voltammogram (Curve 2, figure 3). Two waves are observed at  $E_{o_1} = 0,2$  V and  $E_{o_2} = 0,6$  V on the anodic branch of cyclic voltammogram in 0.1 M HCl (Curve 3, figure 3). The maximum at  $E_c = 0,1$  V is observed on the cathodic branch of cyclic voltammogram (Curve 3, figure 3).

The electrochemical activity of the GSH at AuNP-GCE formed in the reaction mixture

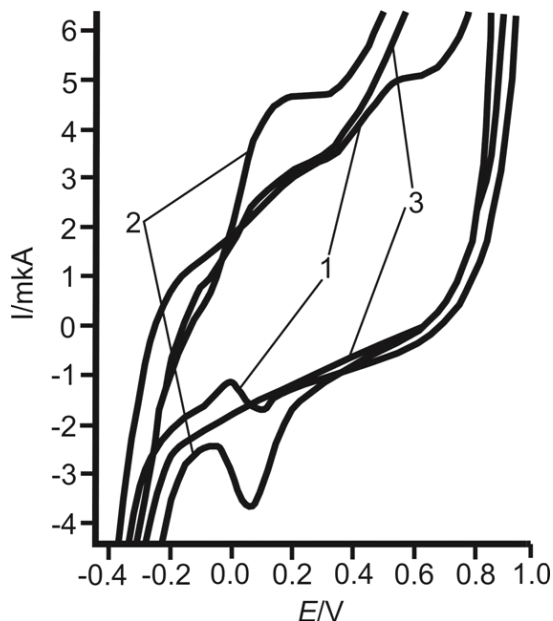


Fig. 4: Cyclic voltammograms of  $1,3 \times 10^{-12}$  M GSH at AuNP-GCE formed in the reaction mixture  $\text{HAuCl}_4:\text{Na}_3\text{C}_6\text{H}_5\text{O}_7:\text{NaBH}_4$ :  $\text{HAuCl}_4:\text{Na}_3\text{C}_6\text{H}_5\text{O}_7:\text{NaBH}_4 = 1:1:4$  (1),  $\text{HAuCl}_4:\text{Na}_3\text{C}_6\text{H}_5\text{O}_7:\text{NaBH}_4 = 1:1:6$  (2),  $\text{HAuCl}_4:\text{Na}_3\text{C}_6\text{H}_5\text{O}_7:\text{NaBH}_4 = 1:1:6$  (3)  $\omega = 100 \text{ mV}\cdot\text{s}^{-1}$

**Table 1. The magnitudes of height of “inverse” cathodic peaks of gold nanoparticles at GE on time of accumulation, supporting electrolytes 0,1 M NaOH**

t, [s]	30	60	90	120	150	180	210	240	270	300
I, [ $\mu$ A]	0,2	0,3	0,4	0,22	0,2	0,2	0,18	0,18	0,5	0,5

$\text{HAuCl}_4:\text{Na}_3\text{C}_6\text{H}_5\text{O}_7:\text{NaBH}_4$  under the different molar ratio and the time modification of the GE surface with gold nanoparticles

The dependence of the electrochemical activity of GSH on ratio of reagents  $\text{HAuCl}_4:\text{Na}_3\text{C}_6\text{H}_5\text{O}_7:\text{NaBH}_4$ , used to the preparation of sols, and the modification time of the GE surface with gold nanoparticles have been further studied.

In the presence of  $1,3 \times 10^{-12}$  M GSH the “inverse” cathodic peak at the AuNP-GCE formed in the reaction mixture  $\text{HAuCl}_4:\text{Na}_3\text{C}_6\text{H}_5\text{O}_7:\text{NaBH}_4=1:1:4$  only is observed at  $E_c = 0,05$  V on the cathodic branch of cyclic voltammogram in 0,1 M NaOH (Figure 4, curve 1). There is not the “inverse” cathodic peak of GSH at the AuNP-GCE formed in the reaction mixture  $\text{HAuCl}_4:\text{Na}_3\text{C}_6\text{H}_5\text{O}_7:\text{NaBH}_4=1:1:6$ . The anodic peak is observed at  $E_a = 0,2$  on the anodic branch of cyclic voltammogram at the AuNP-GCE formed in the reaction mixture  $\text{HAuCl}_4:\text{Na}_3\text{C}_6\text{H}_5\text{O}_7:\text{NaBH}_4=1:1:6$  (Curve 2, figure 4). The cathodic peak is observed at  $E_c = 0,1$  V on the cathodic branch of cyclic voltammogram at the AuNP-GCE formed in the reaction mixture  $\text{HAuCl}_4:\text{Na}_3\text{C}_6\text{H}_5\text{O}_7:\text{NaBH}_4=1:1:6$  (Curve 2, figure 4). When the ratio of reactants  $\text{HAuCl}_4:\text{Na}_3\text{C}_6\text{H}_5\text{O}_7:\text{NaBH}_4 = 1:1:10$  and  $\text{HAuCl}_4:\text{Na}_3\text{C}_6\text{H}_5\text{O}_7:\text{NaBH}_4 = 1:1:40$  gold particles at the GE are not electrochemically active, consequently GSH has not electrochemical activity.

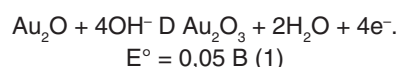
It was found that the electrochemical activity of GSH at the AuNP-GCE depends on the accumulation time of gold nanoparticles at GE. As seen from table 1, with the increase of accumulation time of gold nanoparticles from 30 to 90 s, the height of “inverse” cathodic peak of gold nanoparticles is increasing. With further increase of accumulation time from 90 to 240 s, the height of “inverse” cathodic peak of gold nanoparticles is decreasing. With further increase of accumulation time to 300 s, the height of “inverse” cathodic peak reaches its

maximum value. Based on this dependence the optimal time of GE modification by gold nanoparticles is 90 s.

#### The mechanism of the electrochemical oxidation of GSH at the AuNP-GCE

The electrochemical behavior of gold electrodeposited at the GE from the solutions and gold sols obtained by chemical reduction, it is difficult and involves the formation on the surface of the GE-Au oxo- and hydroxi- compounds of metal in different oxidation states:  $\text{Au}(\text{OH})$ ,  $\text{Au}(\text{OH})_3$  or  $\text{Au}_2\text{O}_3$  (Burke L, Nugent P, 1997; Burke L.D., Nugent P.F., 1998; Meretukov M.A. 2008; Perevezentseva D.O., Gorchakov E.V., 2014).

During the recording of the cathodic branch of this cyclic curve at GE modified with gold nanoparticles in 0,1 M NaOH (Curve 1, figure 4) is observed “inverse” maximum that can be described by the following scheme of the reaction equation (1):

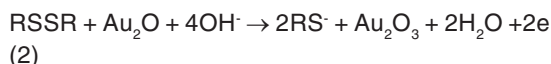


The cause of the appearance of “inverse” peak at the AuNP-GCE can be associated with a gold oxide from lower to higher oxidation states (e.g.  $\text{Au}_2\text{O}$  to  $\text{Au}_2\text{O}_3$ ), similar at mercury film to the process electrode of oxidation of  $\text{Ag} \rightarrow \text{Ag}_2\text{O}$  in alkaline solution (Brainina H.Z., 1988),  $\text{NaClO}_4$  (Korshunov A., Heyrovsky M., 2009) or to the process electrode of oxidation of  $\text{Cu}_2\text{O} \rightarrow \text{CuO}$  (Korshunov A., Heyrovsky M., 2009), to the process  $\text{OsO}_2 \rightarrow \text{OsO}_4$  in  $\text{H}_2\text{SO}_4$  (Kolpakova N.A., Kaminskaya O.V. at all, 1998), to the process of electroreduction of oxygen, catalyzed by the gold deposition (Korshunov A.V., Yosypchuk B. at all, 2011).

In the presence GSH the height of “inverse” cathodic peak at  $E = 0,05$  V is increased.



The process taking place at the AuNP-GE in the presence of GSH can be referred to electrocatalytical process of GSH oxidation by scheme of the reaction equation (2):



### CONCLUSION

In this work an electrochemical activity of GSH is investigated at the GE, Au-GE, AuNP-GCE by cyclic voltammetry.  $1,3 \cdot 10^{-12}$  M GSH shows no electrochemical activity at the graphite electrode. It is shown that GSH is electrochemically active on the AuNP-GCE surface and the Au-GE in the supporting electrolyte of 0,1 M NaOH. It was first shown that the "inverse" cathodic peak of GSH at the graphite electrode modified with gold nanoparticles is observed at  $E_c = 0,05$  V on the cathodic branch of cyclic voltammogram in 0,1 M NaOH. The effect of the ratio of reagents  $\text{HAuCl}_4:\text{Na}_3\text{C}_6\text{H}_5\text{O}_7:\text{NaBH}_4$ , used for gold sols and time modifying gold nanoparticles of the graphite electrode and the nature of the supporting electrolyte on electrochemical activity of GSH has been studied.

It was first shown that the presence of the "inverse" cathodic peak of GSH depends on the amount of sodium borohydride was consumed for

obtaining the gold nanoparticles. The "inverse" maximum of GSH is observed at the graphite electrode modified with gold nanoparticles formed in the reaction mixture  $\text{HAuCl}_4:\text{Na}_3\text{C}_6\text{H}_5\text{O}_7:\text{NaBH}_4 = 1:1:4$ . The time modifying the graphite electrode by gold nanoparticles was experimentally determined and is equal to 90 s.

The electrochemical activity of GSH at the graphite electrode modified with gold nanoparticle in the solution of some supporting electrolytes has been investigated by method cyclic voltammetry. They are as follows 0,1 M NaOH, 0,1 M  $\text{NaClO}_4$ , 0,1 M HCl, 0,1 M phosphate buffer (pH 6.86).

It is found that in the presence of GSH the height of the "inverse" maximum is observed on the cathode branches of cyclic voltammogram at graphite electrode modified with gold nanoparticles in 0,1 M NaOH. The mechanism of the electrocatalytic oxidation of GSH at the graphite electrode modified with gold nanoparticles is proposed.

There are further developments to investigate the mechanism of the electrochemical oxidation and reduction of GSH. The dependence of the height of "inverse" cathodic peak on the concentration of GSH will be investigated in biological objects.

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