

## **Applicability of Electrodes Modified with Composite Layers of Conducting Polymers in Electro- and Bioelectroanalysis**

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**Abstract:** Obtaining modified electrodes is a response of electrochemistry to continuous development in areas such as technology, electronics, medicine, biology and many others. Modifying layers allow scientists to build electrodes with required properties such as for example: selectivity, stability, precision, durability, range of potentials etc. The aim of the studies was to modify the surface of gold and platinum with the layer of poly(3,4-ethylenedioxythiophene) (PEDOT) and polyaniline (PANI) doped with various organic acids and their salts. Additives such as *p*-toluenesulfonic acid (PTSA), dodecylbenzene-sulfonic acid (DBSA), poly(4-styrenesulfonic acid) (PSSH) and poly(4-lithium styrenesulfonic acid) (PSSLi) were used. The main application of these electrodes was the determination of ascorbic acid, uric acid and catecholamines (dopamine, epinephrine). Another modification covered the preparation of PEDOT/polyacrylic acid (PAA)/PSSLi layer with available free carboxyl groups and afterwards the immobilization of glucose oxidase via covalent bond through *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide (WSC). The purpose of the research on selected modifications was to find electrodes that could be applied in electroanalysis as sensors to determine chosen biologically active compounds. Low capacity current, wide range of potentials, the ability to work in the broadest pH range, especially physiological pH was required. The third modification gave rise to the honeycomb structure with the increased area of electrode surface and the use of PEDOT/PAA/PSSLi allows us to immobilize enzyme.

**Keywords:** Conducting polymer; Polyaniline; poly(3,4-ethylene-1,4-dioxythiophene) (PEDOT); Modification; Doping; Immobilization; Honeycomb structure.

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## Introduction

One of the main aspects in modern electrochemistry is to modify electrode's surface and apply such electrodes in different areas, not only in chemistry but also in biology, medicine, industry etc. That is why each year the number of published papers on modified electrodes is growing, describing thousands of electrodes and their applications. Regardless of the type, a conductive phase is basic for each modified electrode. The most typical materials to build it are noble metals, usually gold and platinum, but also carbon (pyrolytic graphite, carbon nanotubes) and ITO (indium thin oxide). The influence of the substrate on the properties of the modified electrode increases with decreasing thickness of the modifying layer. On the other hand, at the same time the influence is insignificant when the potential range is limited to the area of electrical double layer.

Papers of MacDiarmid, Diaz et al. on obtaining conducting polymers and their properties gave rise to the new paths in electrochemical studies [1, 2]. One of them has been laid out by modifications of electrodes with conducting polymers. One can distinguish modifications by layers of polymers, copolymers, composite materials on the basis of conducting polymers, materials with nanostructure and layers with immobilized enzyme. All various techniques of electrodes' modifications with conducting polymers can be divided into three main types. We can distinguish chemical and electrochemical methods or synthesis in plasma. Moreover, a multilayer can be obtained with different techniques. However, only electrochemical synthesis and synthesis in plasma allow to obtain conducting layer directly on the surface of the electrode and eliminate dip coating or spin coating method step to transfer polymer from chemical synthesis on electrode [3].

Electrochemical techniques to obtain conducting polymer are convenient and widely used. Polymer can be acquired by applying potentiostatic or galvanostatic conditions or by using cyclic voltammetry. There are several reasons to apply electrochemical methods. First of all, obtained layers are free of residual oxidant, secondly, the ability to control layer properties is greater. The activity of electrode modified with conducting layer is mainly based on electrocatalysis and mediation in redox processes [4].

In this paper, we would like to present examples of electrodes modified by different techniques and its applications. We have distinguished three types of modifications using conducting polymers (PANI and PEDOT). There are electrodes modified with layers of doped polymers and copolymers, layers with immobilized enzymes and 'honeycomb structures. All layers have been prepared according to our elaborated procedure and tested during electrochemical measurements.

## **Conducting Polymers**

Conducting polymers are macromolecular compounds capable of conducting electrical current, where charge carriers are electrons and electron holes. The most popular and the best examined conducting polymers of this type are polyaniline, polypyrrol, polythiophene and poly(p – phenyl) [3, 5]. There are many advantages of using conducting polymers, amongst them for example: wide range of conductivity, quite simple polymerization, stabilization of noble metal electrode, and various applications.

### **Polyaniline (PANI)**

Polyaniline (PANI) is one of the earliest studied conducting polymer. It can be synthesized by chemical and electrochemical methods. Changing the type of polymerization different polymer properties can be obtained, from insulator to a conductor [6]. Polyaniline conducts current when synthesized from acidic solution ( $\text{pH} < 3$ ), which ensures that nitrogen atoms are protonated. The second requirement is doping at the level of at least 30 %. Polymer obtained in this manner is partially oxidized, protonated, doped and shows high electrical conductivity. Polyaniline occurs in several redox forms. There can be partially oxidized emeraldine, reduced leucoemeraldine and oxidized pernigraniline [6, 7]. The application of polyaniline is quite broad and diverse. Basing on polyaniline, other polymers for electrode modification can be obtained. One possibility is to polymerize aniline derivatives which lead to formation of appropriate derivative of polyaniline, for example. poly(o-toluidine) [8]. Another option is the copolymerization of aniline and its derivatives, for example, copolymerization of aniline with o-aminosulphonic acid [9]. Polyaniline is also a component of conducting composite materials. [4]

### **Poly(3,4-Ethylene-1,4-Dioxythiophene) (PEDOT)**

Poly(3,4-ethylene-1,4-dioxythiophene) (PEDOT) is a relatively new polymer developed by a group of scientists from Bayer's laboratories in the second half of the eighties [10,11]. This is one of the most durable conducting polymers with very good stability and high conductivity (low GAP level). In the state of complete oxidation its conductivity decreases and polymer behaves like a semiconductor. Moreover, PEDOT demonstrates electrochromic effect. It is dark blue in reduced state and colourless when oxidized [12]. PEDOT is usually obtained from non-aqueous solutions, for example, acetonitrile.

Synthesis from aqueous solutions is also possible, but because of the limited solubility of (3,4-ethylene-1,4-dioxythiophene) (EDOT) in water, obtained polymer layers are mainly thin. Apart from applications in electrochemistry, such as batteries, fuel cells, sensors and biosensors, PEDOT is widely used in optoelectronics [4].

## Measuring Equipment

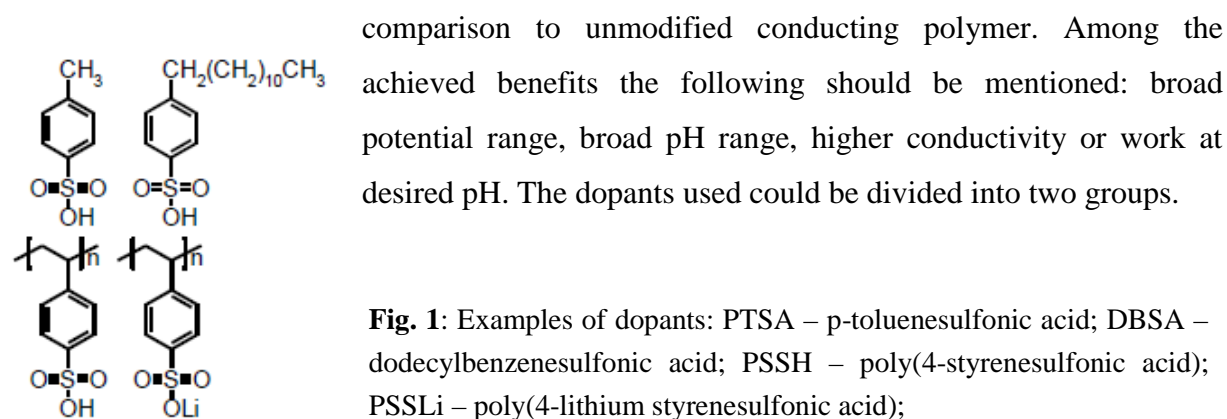
The measurements were carried out using constant-potential electrolysis, cyclic voltammetry (CV), and differential pulse voltammetry (DPV). The measuring equipment incorporated a potentiostat (model PAR 273A, EG&G Princeton Applied Research, USA) connected to a PC with CorrWare 2.9, CorrView 2.9 software (Scribner Associates, USA) and the three-electrode cell that consisted of modified metallic electrode (platinum or gold) as the working electrode, Pt-wire as the counter and a saturated calomel electrode (SCE, with NaCl as the inner solution) chosen as the reference electrode.

## Types of Modifications and Its Applications

Nowadays, for modern electrochemistry, standard electrodes are not simply enough. The key to the development are more and more sophisticated modifications and searching for new materials like, for example, graphene [13]. Therefore, in this part of paper three examples of electrode modification are presented. Selected examples are modifications by doping, immobilization and microstructure such as ‘honeycomb’ arrangement.

### Doping

Doping process means introducing into conducting polymer structure other compounds for the purpose of modulating its chemical properties. This allows to obtain certain advantages in



comparison to unmodified conducting polymer. Among the achieved benefits the following should be mentioned: broad potential range, broad pH range, higher conductivity or work at desired pH. The dopants used could be divided into two groups.

**Fig. 1:** Examples of dopants: PTSA – p-toluenesulfonic acid; DBSA – dodecylbenzenesulfonic acid; PSSH – poly(4-styrenesulfonic acid); PSSLi – poly(4-lithium styrenesulfonic acid);

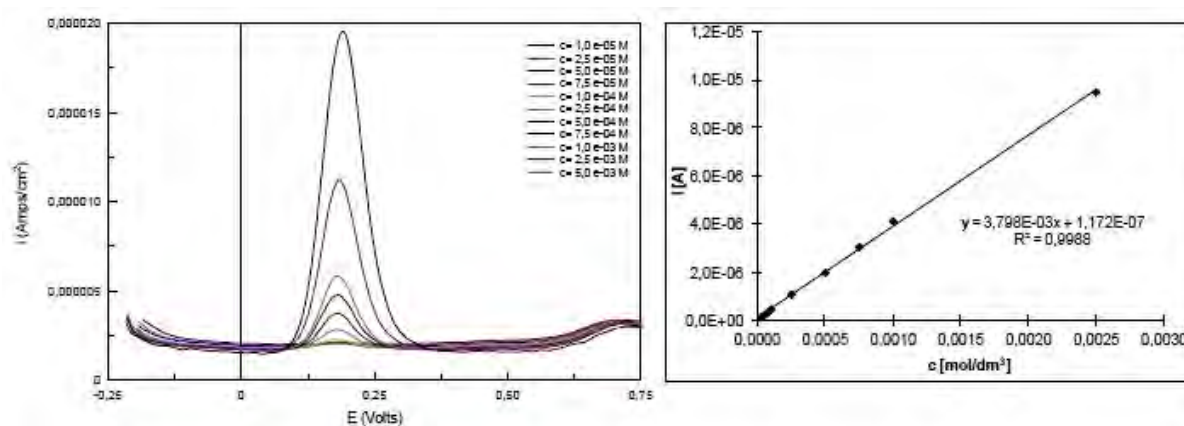
One group consists of compounds that are added just to change electrical properties providing charge carriers (p-toluenesulfonic acid (PTSA), dodecylbenzenesulfonic acid (DBSA)). The other group not only provides charge carriers but also creates polymer on its own giving composite conducting layers (poly(4-styrenesulfonic acid) (PSSH), poly(4-lithium styrenesulfonic acid) (PSSLi); see Fig. 1. The doping process takes place during electro-polymerization from one solution. The electrochemical formation of the composite layers of PEDOT was conducted by electrolysis at constant potential  $E = 1$  V from solutions containing EDOT in appropriate electrolyte (PSSLi, PSSH, PTSA, and DBSA) for required time (usually 5 s) [14]. Polymerization of polyaniline was conducted via cyclic voltammetry (CV) in potential range 0.0 – 0.8 V with scan rate  $v = 200$  mV/s for appropriate number of scan from solution containing aniline in an appropriate electrolyte ( $H_2SO_4$ ,  $HClO_4$ ,  $HCl$ ) [13]. The first stage before each polymerization was the cleaning of working electrode's surface.

#### **Determination of Ascorbic Acid [14]**

Ascorbic acid (AA) is one of the very significant compounds in analytical chemistry and biochemistry as such, being incorporated into many food and beverages [15] and present in various human and animal biological fluids [16,17]. Therefore, due to the modern nutrition standards, there is a great need to determine precisely the concentration of ascorbic acid additives in foodstuffs. Furthermore, it has been proved that the level of ascorbic acid in physiological fluids can be used to assess oxidative stress that is connected with many diseases such as Parkinson's disease, Alzheimer's disease, heart failure and carcinogenicity. The process of oxidation of ascorbic acid is used in electrochemical determination of ascorbic acid [18,19,20]. The EC mechanism of ascorbic acid oxidation is well - known and described in conjunction with specific substrates adsorption [21,22]. Electrode surface condition has a considerable impact on oxidation process. To the best of our knowledge, there are no published results with using the electrode modified with PEDOT/PSSLi composite. The application of modified electrodes gives the opportunity to improve the parameters of electrochemical oxidation of ascorbic acid.

Electrodes modified with PEDOT/PSSLi composite synthesized by electrolysis at constant potential at  $E = 1$  V during 5 seconds from solution containing 0.01 M EDOT in 0.1 M PSSLi turned out to be the best for determination of AA. Layers obtained in shorter time did not produce repeatable results in measurements of ascorbic acid determination.

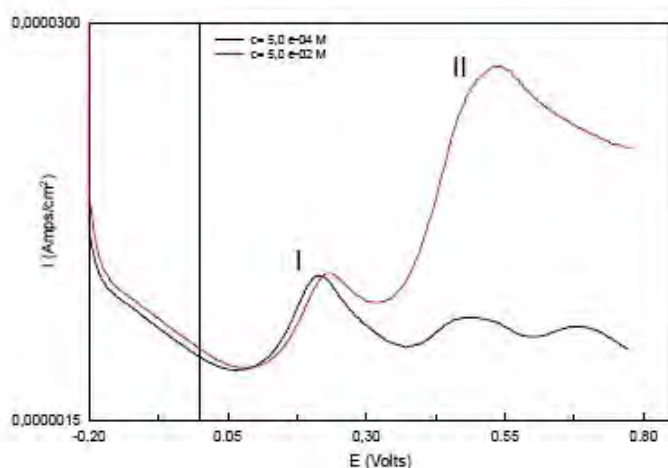
Layers obtained in longer time produced repeatable results but the lower detection limit was shifted towards higher concentration with the increase of the layer's thickness. That was caused by the higher background value of the current for those electrodes. The research was conducted in three different supporting electrolytes: potassium chloride, potassium chloride with ascorbic acid and PBS solution at pH = 7.4.



**Fig. 2.a.** DPV curves of ascorbic acid oxidation in KCl+citric acid on platinum electrode modified with PEDOT/PSSLi layer.

**b.** Calibration curve for ascorbic acid oxidation in KCl+citric acid on platinum electrode modified with PEDOT/PSSLi layer. [14]

According to the obtained results (Fig. 2a) the best of the investigated method for analysis of ascorbic acid is the determination in the potassium chloride solution with addition of citric acid with the different pulse voltammetry (DPV). Comparison of the results obtained in the mixture medium to the results coming from analysis only in potassium chloride shows the influence of the addition of citric acid. It works like a buffer and stabilizes pH of the solution which was confirmed by very good correlation coefficient (Fig. 2b).

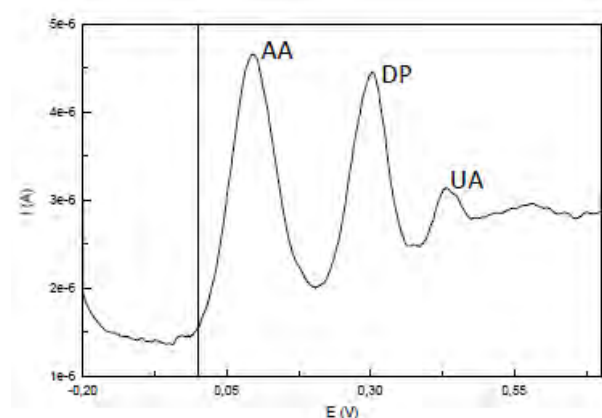


**Fig. 3.** DPV curve of ascorbic acid oxidation in 1 M HClO<sub>4</sub> on electrode modified with polyaniline layer obtained from 0,1 M aniline in 0.1 M PSSH solution by cyclic voltammetry; E = 0-0.8 V; v = 200 mV/s; n = 20 (according to [14]).

Obviously, not only PEDOT layers are appropriate for electrode modification and compounds determination. Another object that can be shown is the determination of ascorbic acid on electrode modified with polyaniline. In the presented example (see Fig. 3) electrode is modified by cyclic voltammetry from solution containing 0.1 M aniline in 0.1 M PSSH (when  $E = 0 - 0.8$  V;  $v = 200$  mV/s;  $n = 20$ ). Measured ascorbic acid solutions ( $5.0 \times 10^{-4}$  M and  $5.0 \times 10^{-2}$  M) are prepared in 1 M HClO<sub>4</sub>. In both curves, we can distinguish two peaks, (i) the first one of comparable size is characteristic for polyaniline layer and it is connected with change of redox forms (leucoemeraldine – emeraldine), (ii) the second indicates the actual current intensity for the oxidation of ascorbic acid. Therefore, as the concentration of ascorbic acid is increased, the peak height also increases, which reflects the higher value of the current. Unfortunately, as mentioned above, the work with electrodes modified with PANI has one major disadvantage – it is electroactive only in acidic medium.

#### Determination of Neurotransmitters [23]

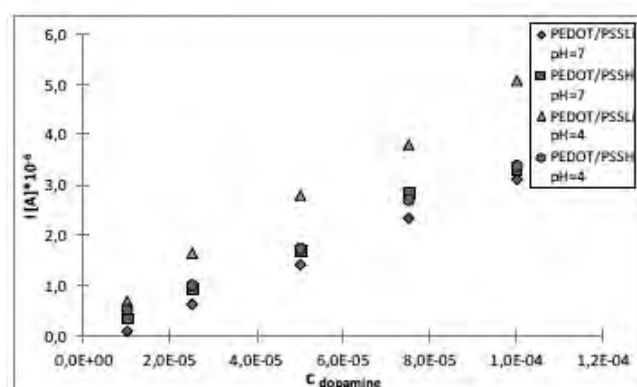
Neurotransmitters are endogenous chemical compounds that are released by neurons and travel through synapse to a target cell to excite or inhibit chosen actions. Many neurotransmitters are produced by biosynthetic conversion of amino acids (for example tyrosine). The first discovered neurotransmitter was acetylcholine in 1921 but the most common neurotransmitters present in human body are epinephrine, norepinephrine and dopamine. Half-life of neurotransmitters in human blood is less than a minute. Neurotransmitters cause response of the body such as blood pressure raise, accelerated action of heart, raise of glucose level in blood. Moreover, they have specific acid – base properties and could occur in form with different charges. The importance of neurotransmitters in biochemical processes is so important that these compounds for years have been the subject of interest of chemists and biochemists.



**Fig. 4.** DPV curve of ascorbic acid (AA,  $c = 10^{-3}$  M), dopamine (DP,  $c = 10^{-4}$  M) and uric acid (UA,  $c = 5 \times 10^{-5}$  M) oxidation in phosphate – citrate buffer pH=4.0 on electrode modified with PEDOT/PSSLi layer (after [23]).

Electrodes modified with conducting composite layer of PEDOT/PSSLi under the same condition as for the determination of ascorbic acid are an effective and appropriate tool for neurotransmitters determination. DPV technique allows to determine the concentration of dopamine or epinephrine also in the presence of very common interfering compounds like ascorbic acid and uric acid (see Fig. 4 and [23]).

Another interesting aspect is change of dopamine oxidation current value in solutions of different pH while different doping agents are used (Fig. 5). It turned out that the best results at pH = 7 were received while working with electrode modified with PEDOT/PSSH layer. At the same time electrode modified with PEDOT/PSSLi layer gave better results in solution of pH = 4. The above mentioned example exhibits how important is the process of doping agent selection. It depends not only on the determined compound nature but also on the medium of the determination.



**Fig. 5.** *The influence of dopant on the value of the oxidation current of dopamine at different values of pH (taken from [23]).*

## Enzyme Immobilization [24]

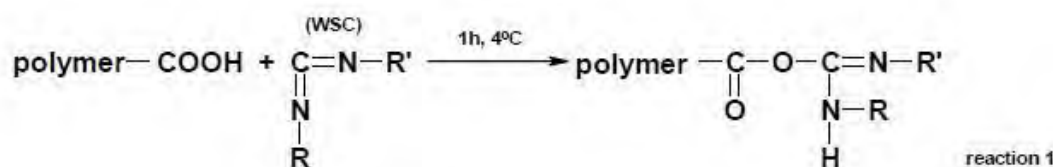
The immobilization of enzymes on electrodes has several advantages like the possibility to reuse enzyme for several times due to longer lives, lower degradation level, and improved stability. Other benefits are the possibility to control reaction rate, starting and finishing point of the reaction and to prevent the final product or measured solution from contamination. Examples of using various enzymes for immobilization can be multiplied. There are, for instance glucose biosensors immobilized on surface modified with carbon nanotubes [25], hydrogen peroxide biosensor using  $\gamma$ -aluminium trioxide nanoparticles and horseradish peroxidase on chitosan film [26]. There are several techniques of enzymes immobilization such as: adsorption [27], covalent attachment [28], entrapment [29] and cross linking [30]. Enzyme immobilization by covalent bonding is the most often used technique.



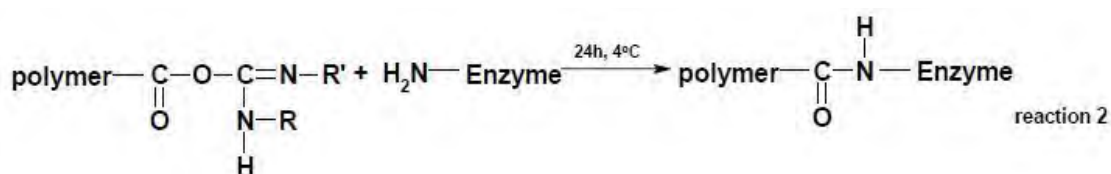
An undoubted advantage is the stable nature of the bond which prevents the enzyme from leakage into solution during measurement but, on the other hand, this type of immobilization is quite expensive and also difficult to conduct.

During the research composite material as a basis for immobilization has been developed. The concept of layer for immobilization was elaborated based on the work of Raitman et al. [31] and it assumes creating conducting layer with free carboxylic groups as a support for immobilization. Composite material was obtained during electrochemical synthesis of PEDOT in the presence of polyacrylic acid on platinum electrode using electrolysis at constant potential with applied potential  $E = 1 \text{ V}$  and time 3 s respectively. Solution for polymerization contained 15 mg/ml PAA, 0.1 M EDOT and 0.1 M PSSLi as a supporting electrolyte. The final product of this stage was (PEDOT+PAA)/PSSLi conducting layer with available carboxyl groups on the surface.

The chemical immobilization of GOD on obtained support layer was the second step. Our procedure of immobilization has been elaborated as a combination of methods described by Li et al. [32] and Kulik et al. [33] and based on chemical covalent bonding of GOD with carboxyl groups via *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide (WSC). The WSC acted as activator for COOH groups of the copolymer layer.



**Fig. 6:** Forming of a covalent bond between the free carboxyl groups of composite layer and carbodiimide (WSC), during 1 hour at 4 °C. (According to [24]).



**Fig. 7:** Enzyme immobilization by forming a covalent bond between the free carboxyl groups of composite layer with carbodiimide (WSC) and the enzyme, during 24 hours at 4 °C [24].

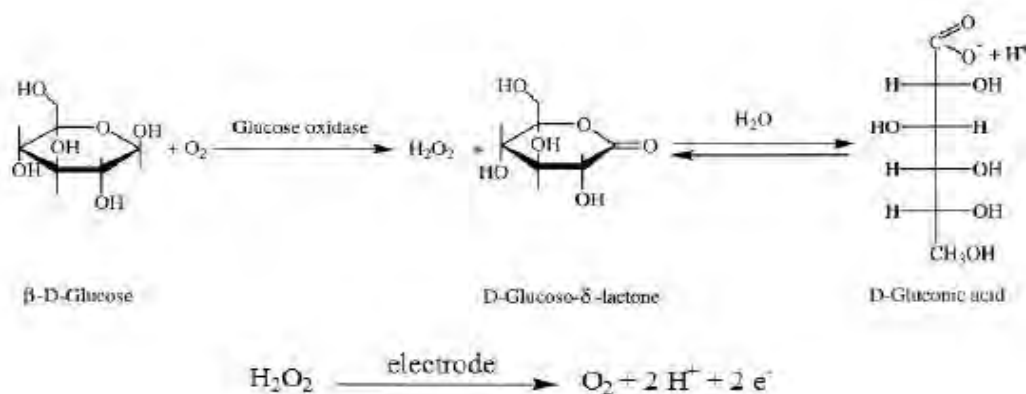
The activation has been reached by soaking the modified electrode in WSC (5 mg/ml) in PBS solution at 4 °C during 1 h (see Fig. 6). After the preactivation the electrode was transferred to solution containing GOD (4 mg/ml) in PBS with added CaCl<sub>2</sub> (0.02 M); the immobilization then proceeded at 4 °C during 24 h (see Fig. 7). In the final phase the electrode was soaked in PBS solution with added CaCl<sub>2</sub> at room temperature during 1 h to desorb reversibly bound GOD and to stabilize the electrode.

## Determination of Glucose [24]

It was crucial for the immobilization that the composite layer had free carboxyl groups on its surface and to prove it Toluidine Blue O (TBO) technique was applied. The procedure was developed according to Tiraferri and Elimelech paper [34]. Tests in order to confirm the chemical activities of the obtained electrodes were carried out as well [35]. There are several factors like: layer thickness, appropriate doping agent or WSC and GOD concentration having impact on glucose determination.

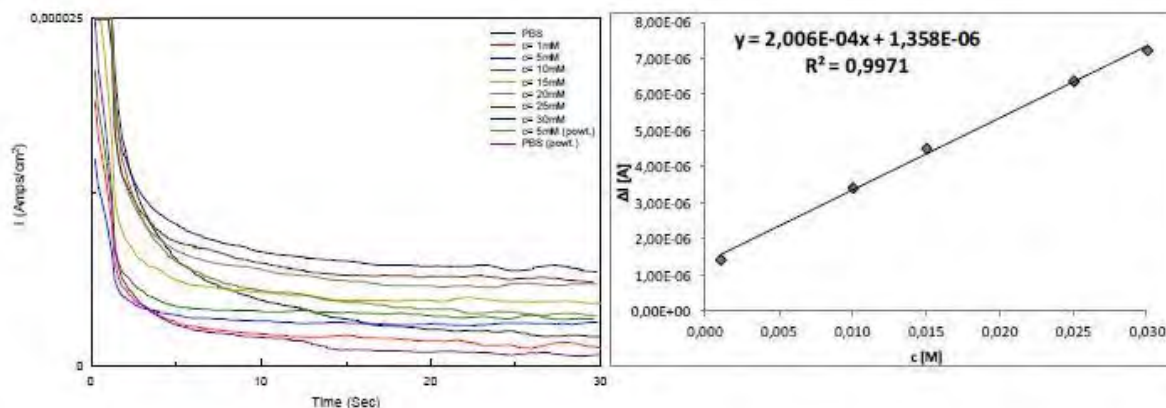
Electrode was modified with PEDOT and polyacrylic acid doped with PSSLi, had free carboxyl groups, (as it was proven) and the enzyme immobilization occurred via covalent bond between free carboxyl groups, WSC and GOD. The elaborated procedure reduces reagents consumption and hence, the cost. Moreover, another advantage is maximum simplicity excluding complicated chemical transformations and sophisticated equipment. The electrode was active over a period of 1 month. During this time, a daily measurements of glucose oxidation in PBS solution (pH = 7,4) were carried. The obtained results revealed that the electrode modified with immobilized glucose oxidase exhibited good stability, low errors, satisfactory repeatability, as well as the acceptable relative standard deviation.

According to the mechanism (see Fig. 8), the determination of glucose can be accomplished by amperometric detection (see Fig. 9a, overleaf)



**Fig. 8:** Reactions occurring on the surface of electrode while amperometric detection of glucose.

Elaborated procedure of receiving biosensor stands out because of low cost of single polymerization, simplicity, long-term activity, activity at physiological pH and covering glucose level in blood.



**Fig. 9:** a) Amperograms of glucose analysis in PBS solution (pH = 7,4) for electrode modified with PEDOT/PAA/GOD doped with PSSLi. (b) Calibration curve for different glucose concentration in PBS solution measured with electrode modified with PEDOT/PAA/GOD doped with PSSLi. Both images according to [24].

As seen in the inset (9b), the calibration curve obtained can be characterized by a very good linearity with a correlation coefficient,  $r^2 = 0,9971$

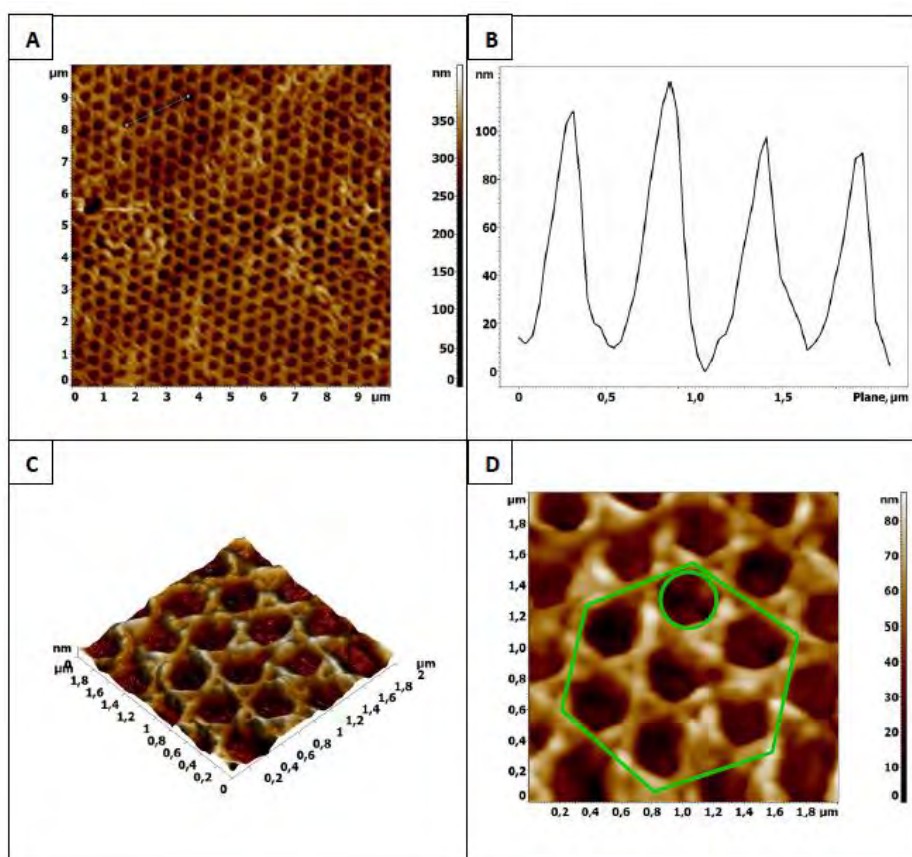
### Honeycomb Structure [36]

In recent years microstructure electrodes have been of interest to many research centres due to their properties and applicability. One of these forms of microstructure is so called honeycomb structure basing on hexagonal close-packed organization. Electrodes modified with honeycomb structure are characterized by several times greater effective surface area than geometric one, thus the capacity is also higher [37]. This type of electrodes has been applied in such areas as energy storage devices [38], capacitors [39], solar cells [40], sensors and biosensors [41], for electrocatalysis [42].

There are several techniques for honeycomb structure manufacturing that can be divided into two basic groups: techniques without and with use of a template. The procedure presented below needs polystyrene template deposition, polymerization and template removal. During template deposition proper electrode preparation is crucial, therefore gold surface must be chemically pure. Afterwards template is deposited with dip-coating technique from concentrated polystyrene in sodium dodecylsulphate (SDS). The key role in the process of template deposition is fulfilled by anionic surfactant – SDS. Its concentration in 4% polystyrene solution as well as in flooding solution should be exactly 0.04 M and any departure from this value would cause interfering in the structure of arranged monolayer.

Moreover, important factors are inclination angle during decantation and the decantation rate. All the layers have been prepared via electro-polymerization from appropriate solutions. The first electrode was modified with PEDOT/PSSLi manufactured via electrolysis at constant potential from solution of 0.01 M EDOT in 0.1 M PSSLi with applied potential of  $E = 1 \text{ V}$  during 5 seconds.

The second composite material for electrode modification was obtained during electrochemical synthesis of PEDOT in the presence of polyacrylic acid (1.5 mg/ml PAA, 0.01 M EDOT and 0.1 M PSSLi) on gold electrode with template using electrolysis at constant potential with applied potential  $E = 1 \text{ V}$  and time 5 s respectively. After the polymerization, polystyrene template was dissolved in toluene during 24 hours. The surface of obtained electrodes has been characterized with AFM (atomic force microscope) (Fig.10). The structure contains close-packed hexagonally arranged pores.



**Fig. 10:** *Microstructure of electrode modified with PEDOT/PSSLi layer.* A – AFM image of microstructure; B – cross section; C – AFM 3D image of microstructure; D – hexagonal arrangement of microstructure. Electrode obtained by electro-polymerization at constant potential  $E = 1 \text{ V}$ ,  $t = 5 \text{ s}$  from solution containing 0.01 M EDOT in 0.1 M PSSLi. (After [36]).

In the case of PEDOT/PSSLi electrode there is a possibility of encapsulation. Electrode with (PEDOT+PAA)/PSSLi has free carboxyl groups on its surface, that is why the immobilization via covalent bonding will be possible. The described procedure for microstructure electrodes manufacturing is relatively simple and quick especially in comparison with evaporation techniques and the ones involving the use of controlled humidity chambers. Moreover, the used equipment is not sophisticated and the level of reagent consumption is low which makes the process quite inexpensive. Regular and comparable microstructure is present on the entire surface of polycrystalline gold electrode, even despite surface irregularities or scratches.

## Conclusions

In this paper, we have presented three different elaborated modifications of electrode with conducting polymers. There are many possibilities to improve electrode properties and amongst them doping, copolymerization, immobilization and creating honeycomb structure. Many factors like the type of the polymer, the nature of determined compound, medium of the determination can affect the modification procedure.

We have already obtained electrode modified with PEDOT/PSSLi for determination of ascorbic acid and neurotransmitters (dopamine, epinephrine). The other electrode with immobilized glucose oxidase on PEDOT/PAA copolymer layer can be used for glucose determination. Finally, electrode with 'honeycomb' structure is ready for further research on enzyme immobilization.

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