

Self-Assembled Monolayer of Thiols on Gold Electrodes Prepared by Gold Electro-chemical Deposition on Platinum Wire

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Abstract: The gold electrodes modified with organic compounds (frequently organic thiols and their derivatives), represent a new category of devices which are widely used in molecular recognition, in special in case of biomolecules analysis. Alkanethiols are spontaneously adsorbed on the gold surface and form a monomolecular film, with a highly ordered structure, called a self-assembled monolayer (SAM). This represents a promising approach which offers the possibility of design and assembling desired structures at molecular level. One of the main disadvantages in the utilization of these kinds of electrodes at large scale is the relative high cost of gold electrodes manufactured on specialized companies. Starting from these, we try to obtain the gold electrodes by electro-chemical deposition of gold, on platinum wire. These electrodes can be easily obtained in laboratory, with common laboratory equipments and are not so expensive. The obtained electrodes have been characterized with cyclic voltammetry and electrochemical impedance spectroscopy (EIM). The experimental results have show that the analytical performances of these electrodes (quantity of thiol retained on surface, permeability degree, stability in time of obtained monolayer, etc.) are comparable with those obtained in case of manufactured gold electrodes. The electrodes have show higher reproducibility in their electrochemical behaviour as well as in their modification, and was prepared to be utilized in the detection of humic acid molecules from environmental samples.

Keywords: gold electrodes, electro-deposition, self-assembled monolayer, thiol, cyclic voltammetry, electrochemical impedance spectroscopy

1. Introduction

In the last years, chemical modified electrodes by self-assembled monolayer of alkanethiols have been extensively used because their simplicity and efficiency [1]. The functionalization of such self-assembled monolayer is important issue today because molecular architecture can be build which confer new surface properties [2, 3]. The design and construction of such novel molecular devices is opening a huge number of applications in areas such as corrosion protection, wetting, microelectronics, optics, chemical, biochemical and electrochemical sensors [4-8].

The development of electrochemical sensors is one of the areas of great and faster growth in analytical electrochemistry that led to an increasing search for cheaper devices with improved reproducibility, sensitivity and stability. Despite the great versatility and perspectives show by electrochemical sensors, the utility of an electrode is limited by gradual degradation of its surface. From this point of view, the gold surface is a preferred one, because has the third best electrical conductivity of all metals at room temperature and its inertness prevent the formation of insulating surface oxides [5, 7].

The gold surface modification with organic thiols compounds opens numerous opportunities for the construction of modified electrodes by using a well known and efficient reaction. In generally, such modified electrodes are obtained in two ways [9-11]: (i) adsorption of thiols on gold surface, followed by the adsorption of specific receptor on thiols monolayer (embedment procedure), or (ii) adsorption of functionalized thiols on gold surface, where the functional groups of thiols have the receptor role. In both cases, the performances of the obtained modifications are significant dependent by the gold surface quality. If the gold surface is the smooth-faced one, its cover degree is higher, the obtained monolayer is well ordered, and the electrodes have great analytical performances. For to attain such performance, the specialized manufactures have develop several screen-printing techniques [12-14], most at very low pressures, by which are obtained gold deposits with higher purity, controlled roughness and very good adhesion to the substrate. But, these modalities for gold surfaces obtaining are laborious, request special attention and equipments, and these can be easily seed in the price of gold electrodes. Due to their high cost, they cannot be used at large scale.

In this paper, to overcome these problems and with the purpose of designing adequate surfaces for sensor development, we present a new modality to obtain gold electrodes, by electrochemical deposition of gold on platinum wires. These electrodes can be easily obtained in laboratory, with common equipments and are cheaper. The obtained electrodes have been characterized by cyclic voltammetry and electrochemical impedance spectroscopy. The experimental results have show that the analytical performances of these electrodes (quantity of thiol retained on surface, permeability degree, stability in time of obtained monolayer, etc.) are comparable with those obtained in case of manufactured gold electrodes. The electrodes have show higher reproducibility in their electrochemical behaviour as well as in their modification, and was prepared to be utilized in the detection of humic acid molecules from environmental samples.

2. Experimental

2. 1. Materials

The platinum wires (purchased from Merck) were cut-up and incorporated in a glass tube, thus their area to be close by 1 cm^2 . A cooper conductor was used for to ensure the electrical connection. Before utilization, the platinum wires have been cleaned in air / acetylene flame. The $\text{KAu}(\text{CN})_2$ salt (from Aldrich) from electro-deposition bath was analytical degree reagent, and was used without further purifications. The n-dodecanthiol and humic acid reagents were purchased from Fluka and were used as received. All other reagents were analytical degree. All aqueous solutions were prepared with double distilled water, obtained from a commercially distillation system.

The behaviour of each electrode was compared with a polycrystalline gold wire electrode (area= 1 cm^2), purchased from BAS-Bioanalytical System.

The 1 mM solution of $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ redox couple was used as marker, because is well known for its capacity of detecting even the small defects in the self-assembled monolayer [15].

2. 2. Gold electro-deposition

A common electrolysis cell was used for gold electro-deposition. The gold electro-deposition bath was composed by 15 mg/mL $\text{KAu}(\text{CN})_2$ salt and 115 mg/mL citric acid. The final pH of the mixture was adjusted to be 4, with KOH. A current of 5 mA/cm^2 was applied through the cell, during of 6 hours with magnetic shaking of 100 rpm. After, this time the electrodes were washed with double distilled water and electrochemical cleaning, by cycling in 0.5 M KOH solution in 3 steps [16]. When the cleaning step was verified, the electrodes were used in the experiments.

2. 3. n-dodecanthiol adsorption on gold surface

Modification of gold electrodes was carried out in a glass tube, where only the gold surface is in contact with organic reagent. Thus, the gold clean electrodes were immersed separately in 20 mM of fresh n-dodecanthiol alcoholic solution. After 24 hours, they were washed by several times with pure ethanol and then with double distilled water. The modified gold electrodes were kept in double distilled water.

2. 4. Cyclic voltammetry measurements

The electrodes were mounted in a conventional three-electrode cell. Before the measurements, the solutions are degassed with N_2 for 15 min. All potential values are reported with respect to a saturated calomel electrode (SCE). The potentiostatic apparatus consist in an AMEL 5000 Potentiostat / Galvanostat driven by Corrware Software.

2. 5. Impedance spectroscopy measurements (EIS)

EIS measurements were performed using an AUTOLAB impedance analyser. The cell used in these experiments has the same construction as we described above. The Randles modified equivalent circuit [17] was used to fit the impedance spectroscopy results and to determine the electrical parameters values for each case. The circuit includes the electrolyte resistance between working and reference electrodes (R_s), electron-transfer resistance (R_{et}), Warburg impedance (W) and the constant phase element (Q) which takes into account the frequency dispersion, direct correlated with the electrode roughness [18].

3. Results and discussion

For gold electro-deposition, the platinum wires were immersed in an electrolysis bath. The six working electrodes are connected in parallel to the potentiostat. This gold electro-deposition was studied with the purpose of reaching the desired electrodes properties: good appearance, mechanical resistance, controlled roughness, deposit uniformity and good adhesion on gold deposit to substrate. The electro-deposit method turned out to be simple, fast and inexpensive, permit the obtaining of reproducible electrodes surfaces, and the required time for a suitable gold deposit is not so long. In table 1 are presented surface characteristics of the gold electrodes obtained in different experimental conditions.

TABLE 1 The characteristics of gold electrodes obtained by electro-deposition on platinum wires.

	Without flame cleaning of platinum wires	With flame cleaning of platinum wires
Adherence	Adequate *	Excellent **
Roughness factor	7.176	5.521

* After 4 days, detachment of gold by mechanical action is observed; ** Here is not detachment of gold, even after 15 days.

On the basis of these characteristics, in the further experiments the gold electrodes was prepared only after a preliminary flame cleaning of platinum wires.

In order to check roughness and cleanness of the electrode surfaces and the reproducibility among them, cyclic voltammograms of the 6 gold electrodes were performed in 1 M HClO₄, at 50 mV/s and a potential domain between 500 and 1700 mV. Fig. 1 shows a typical voltammogram indicating a clean gold surface.

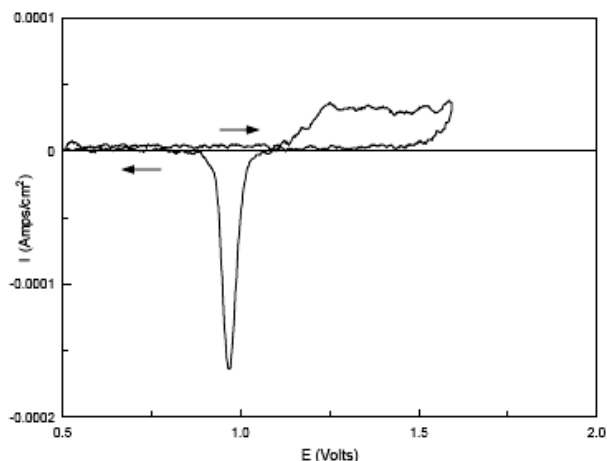


Figure 1. Cyclic voltammogram for one of six gold electrodes in 1 M HClO₄, at 50 mV/s

For all the six electrodes, the voltammetric responses are almost identical. The reproducibility of the procedure used in the electrode construction was evaluated by comparing the charge of the gold oxide reduction peak, and the result was $907.14 \pm 16.5 \mu\text{C}/\text{cm}^2$ ($n = 6$).

The hexammineruthenium complex ($\text{Ru}(\text{NH}_3)_6^{3+/2+}$) was used to investigate the electron transfer behaviour of a reversible redox couple in solution. $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ is commonly used as electrochemical marker since it has great electrochemical properties: stable in both oxidation states, electrochemically reversible and present a fast electron-transfer rate. The cyclic voltammogram with $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ were performed in 1M NaNO₃, for the electrodes obtained by gold electro-deposition on platinum wires (Fig. 2).

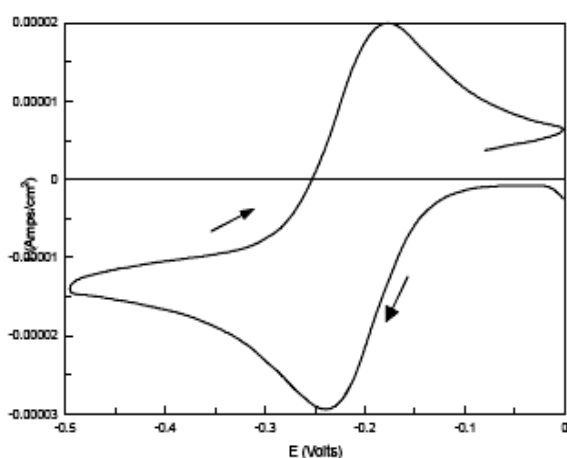


Figure 2. Cyclic voltammogram for one of the six electrodes obtained by electro-deposition with 1 mM $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ in 1 M NaNO₃ at 50 mV/s

At it can see from Fig. 2, the gold electrodes obtained by electro-deposition showing a typical Nernstian behaviour. The values of relevant parameters $E^0 = 310.98$ mV, $\Delta E_p = 79.08$ mV and $i_p^a/i_p^c = 1.019$ ($n = 6$) clearly reflect that the response of the electrodes is reproducible and similar with the manufactured gold electrodes [19].

In order to underline the performances of obtained gold electrodes and to show the applicability of such devices, its chemical modification was studied.

It is well known that organic thiols and their derivates spontaneously adsorb onto gold surface to form a close-packed oriented monolayer (SAM) [20]. In literature are described many aspects related to the adsorption of thiols on gold surface [21, 22].

In this study, the gold electrodes were modified with n-dodecanthiol (T10C). For the evaluation of the T10C adsorption on electrodes surface, we used the method proposed by Walczak et al. [23], based on reductive desorption of thiols at basic pH. After modification, the electrodes were rinsed with absolute ethanol and double distilled water. Cyclic voltammograms were obtained sweeping the applied potential between -0.4 V and -1.2 V/SCE at 100 mV/s in 0.5 M KOH solution, previously degasses with nitrogen. The obtained cyclic voltammograms are presented in Fig. 3.

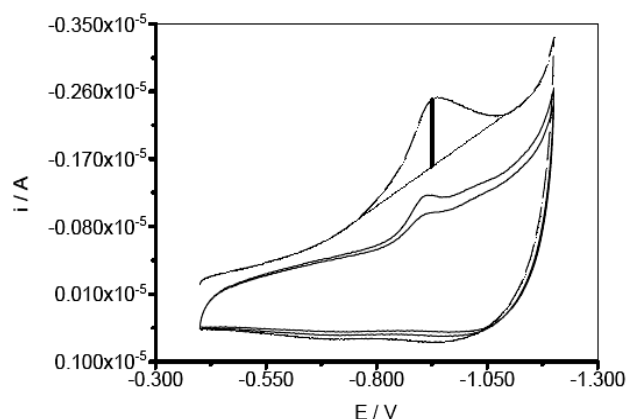


Figure 3. Cyclic voltammogram of immobilized n-dodecanthiol on gold electrodes obtained by electro-deposition, in 0.5 M KOH at 100 mV/s

In this figure, three peaks can be observed due to the reductive desorption of the self-assembled T10C. The height of the first peak is $12.534 \cdot 10^{-7}$ A, which means that around 55.7 molecules of T10C was adsorbed of each mm^2 from electrode surface.

In addition, the changes of the interfacial properties of electrodes by thiol adsorption were evaluated using $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ redox couple, by EIS experiments. Electrochemical impedance spectroscopy (EIS) is a sensitive and non-destructive technique, widely used for the characterization of functionalized electrodes. The thiols adsorption on electrode has as result the alteration of capacitance and interfacial transfer resistance of the conductive surface; and thus EIS is an adequate tool for the analysis of interfacial property change on modified electrodes [24, 25]. On the other hand, the electron transfer behaviour of a redox couple on SAM modified electrodes

give the important information's on the surface morphology and defects [23].

Fig. 4 illustrates the results obtained by adsorption of n-dodecanthiol (T10C) on electrode surface. In absence of T10C, the impedance plot show a negligible semicircle domain, which means that a very fast electron-transfer process with a diffusion limiting step occurs.

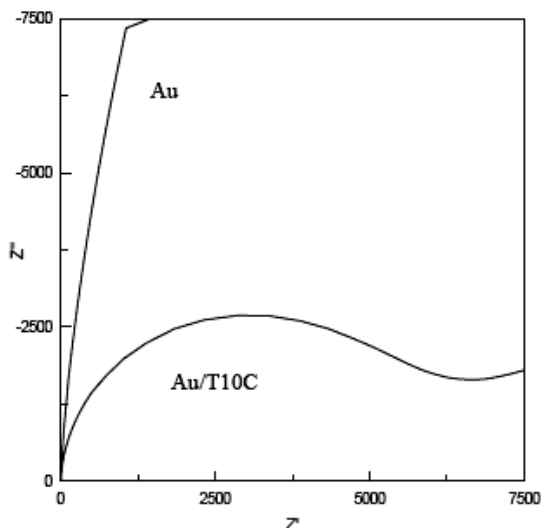


Figure 4. Impedance spectroscopy of gold electrodes obtained by electrochemical deposition immobilized with T10C, in presence of 1 mM $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ as marker in 1 M NaNO_3 . Frequency range: $1 - 10^5$ Hz. The amplitude of the alternative voltage was 10 mV.

When, T10C is immobilized on electrode surface, the semicircle domain is enlarged and indicated a high transfer resistance due to the increased thickness and compactness, as well as the fewer pinhole defects on the electrode surface.

One of the promising applications of this type of modified electrodes is the molecular recognition. To achieve this purpose, we try to use the gold electrodes modified with T10C for the detection of humic acids.

The humic acids are natural macromolecules, and are one of the main constituents of soils, which have a strong hydrophobic character (due to their huge molecular mass) and numerous functional groups ($-\text{COOH}$, $-\text{OH}$, $-\text{C}=\text{O}$, NH_2 , etc). Starting from these characteristics, is expected that humic acids molecules from solution to be adsorbed onto thiol monolayer from gold surface, and this to facilitated the electron-transfer reaction of $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ redox marker.

In order to check the viability of this hypothesis, the gold electrodes obtained by electro-deposition were modified with T10C and then used for humic acids detection. In this case, the experiments were performed in acetate buffer ($\text{pH} = 4$), which ensure a high ionization degree of functional groups from humic acids molecules and will facilitated the interaction with positive ion marker.

The cyclic voltammograms recorded at different concentrations of humic acids are presented in Fig. 5. It can be observed from Fig. 5, an increasing of peaks height with the increasing of analyte concentration. Even, in this

moment, cannot be establish a precise linear dependence between cyclic voltammogram characteristics and the concentration of humic acids from solution, these results show that by using proposed procedure we can obtain a very reproducible surface, suitable for sensors development.

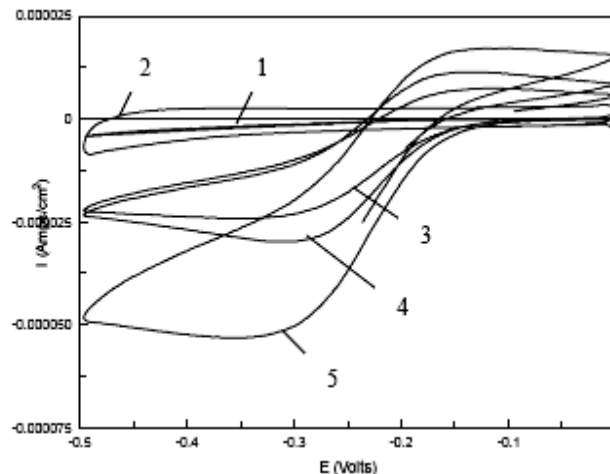


Figure 5. Cyclic voltammograms of gold electrodes obtained by electro-deposition immobilized with T10C, at different concentrations of humic acids with 1 mM $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ in acetate buffer ($\text{pH} = 4$) as supporting electrolyte; scan rate = 50 mV/s. (1: 0 M humic acids; 2: 10^{-5} M humic acids; 3: 10^{-4} M humic acids; 4: 10^{-3} M humic acids; 5: 10^{-2} M humic acids)

Fig. 6 show the results obtained by EIS, performed in mentioned experimental conditions, for T10C modified gold electrodes, in absence and in presence of humic acids.

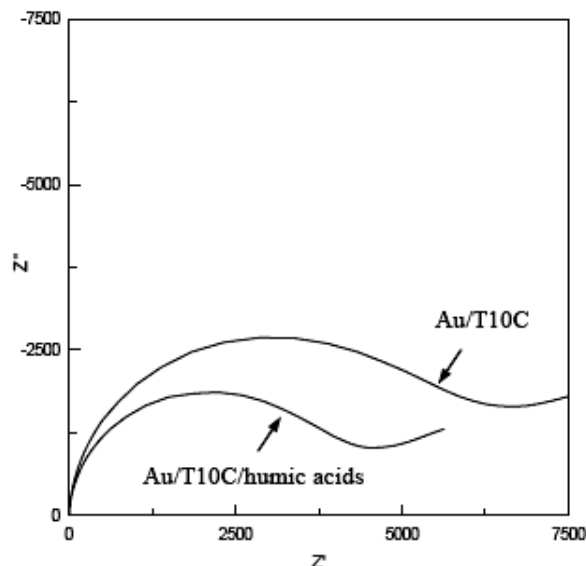


Figure 6. Nyquist representation for Au/T10C/electrolyte and Au/T10C/humic acid/electrolyte in 1 mM $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, acetate buffer ($\text{pH} = 4$). Frequency range: $1 - 10^5$ Hz. The amplitude of the alternative voltage was 10 mV.

The values of relevant parameters determined using Randles modified equivalent circuit, are presented in Table 2. The values of determined parameters indicate that the obtaining procedure of gold electrodes (gold electro-

deposition, thiol adsorption) can be carried out with great reproducibility.

TABLE 2. The values of the equivalent circuit elements

	R_s (Ω)	R_{ct} (Ω)	W (10^{-3})
Au/T10C	109.2	2359	2.09
Au/T10C/humic acids	72.6	2098	3.19

4. Conclusions

In this paper we have described a simple and inexpensive method to obtain disposable gold electrodes. The electro-deposition of gold on platinum wires produces clean surfaces with an electrochemical performances comparable to manufactured gold electrodes; therefore, the results can be straight forward analyzed with well known theoretical models for the electron transfer process on electrodes.

Also, the gold electrodes obtained by electro-deposition have demonstrated to provide a suitable support for the thiol immobilization, the chemical modification of surface can be carried out with a very good reproducibility, suitable for the sensor development.

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REFERENCES

- Ulman, A., Formation and structure of self-assembled monolayer. *Chem. Rev.*, **1996**, Vol. 96, pp 1533 – 1554.
- Schwartz, D. K., Mechanisms and kinetics of self-assembled monolayer formation. *Annu. Rev. Phys. Chem.*, **2001**, Vol. 52, pp 107 – 137.
- Gooding, J.J., A simple model for an amperometric channel biosensor. *Electrochem. Comm.*, **1999**, Vol. 1, pp 119 – 123.
- Radi, A.E., Sanchez, J.L.A., Reusable impedimetric aptasensor. *Anal. Chem.*, **2005**, Vol. 77(19), pp 6320 – 6323.
- Rodgers, P.J., Shigeru, A., Cyclic voltammetry at micropipet electrodes for the study of ion-transfer kinetics at liquid-liquid interface. *Anal. Chem.*, **2007**, Vol. 77(24), pp 9276 – 9285.
- Raj, C.R., Ohsaka, T., Analytical applications of functionalized self-assembled monolayer on gold electrode: voltammetric sensing of DOPAC at the physiological level. *Electroanalysis*, **2002**, Vol. 14(10), pp 679 – 684.
- Yang, N., Wang, X., Thin self-assembled monolayer for voltammetrically monitoring nicotinic acid in food. *Coll. Surf. B*, **2008**, Vol. 61, pp 277 – 281.
- Zhao, W., Xu, J.J., Chen, H.Y., Electrochemical biosensors based on layer-by-layer assemblies. *Electroanalysis*, **2006**, Vol. 18(18), pp 1737 – 1748.
- Dalmia, A., Liu C.C., Savinell, R.F., Electrochemical behaviour of gold electrodes modified with self-assembled monolayers with an acidic end group for selective detection of dopamine. *J. Electroanal. Chem.*, **1997**, Vol. 430(1-2), pp 205 – 214.
- Esplndiu, M.J., Hagenstrom, H., Kolb, D.M., Functionalized self-assembled monolayers on Au(111) electrodes: Surface structures and electrochemistry. *Langmuir*, **2001**, Vol. 17, pp 828 – 838.
- Uosaki, K., Sato, Y., Kita H., Electrochemical Characteristics of a Gold Electrode Modified with a Self -Assembled Monolayer of Ferrocenylalkanethiols. *Langmuir*, **1991**, Vol. 7, pp 1510 – 1514.
- Menard, E., Bilhaut, L., Zaumseil, J., Rogers, A.J., Improved Surface Chemistries, Thin Film Deposition Techniques, and Stamp Designs for Nanotransfer Printing. *Langmuir*, **2004**, Vol. 20, pp 6871-6878.
- Liu, J., Duan, J.L., Toimil-Molaes, M.E., Karim, S., Cornelius, T.W., Dobrev, D., Yao, H.J., Sum, Y.M., Hou, M.D., Mo, D., Wang, Z.G., Neumann, R., Electrochemical fabrication of single-crystalline and polycrystalline Au nanowires: the influence of deposition parameters. *Nanotechnology*, **2006**, Vol. 17, pp 1922 – 1926.
- Priano, G., Gonzales, G., Gunther, M., Battagliani, F., Disposable gold electrode array for simultaneous electrochemical studies. *Electroanalysis*, **2008**, Vol. 20(1), pp 91 – 97.
- Zerulla, D., Uhlig, I., Szargan, R., Chasse, T., Competing interaction of different thiol species on gold surface. *Surf. Sci.*, **1998**, Vol. 402-404, pp. 604 – 608.
- Krysinski, P., Moncelli, M.R., Tadini-Buoninsegni, F., A voltammetric study of monolayers and bilayers self-assembled on metal electrodes. *Electrochim. Acta.*, **2000**, Vol. 45(12), pp. 1885 – 1892.
- Bard, A.J., Faulkner, L.R., *Electrochemical Methods: Fundamentals and Applications*, 2nd ed. Wiley, New York, **2001**, pp 213 – 245.
- de Levie J., Fractals and rough electrodes. *J. Electroanal. Chem.*, **1990**, Vol. 281(1-2), pp 1 – 21.
- Rondinini, S., Vertova, A., Pilan, L., The use of hexaamineruthenium (III) redox marker for the characterization of SAM-Au amperometric sensors. *Electroanalysis*, **2003**, Vol. 15(15-16), pp 1297 – 1301.
- Subramanian, R., Lakshminarayanan, V., A study of kinetics adsorption of alkanethiols on gold using electrochemical impedance spectroscopy. *Electrochim. Acta.*, **2000**, Vol. 45, pp 4501 – 4509.
- Wang, Y.Q., Yu, H.Z., Cheng, J.Z., Zhao, J.W., Cai, S.M., Liu, Z.F., End-group-dominated electrochemical kinetics of azobenzene self-assembled monolayers on gold. *Langmuir*, **1996**, Vol. 12(22), pp 5466 – 5471.
- Brett, C.M.A., Kresat, S., Hianik, T., Brett, A.M.O., Studies on Self-assembled alkanethiol monolayers formed at applied potential on polycrystalline gold electrodes. *Electroanalysis*, **2004**, Vol. 15(5-6), pp. 557 – 565.
- Walczak, M.M., Popenoe, D.D., Deinhammer, R.S., Lamp, B.D., Chung, C., Porter, M.D., Reductive desorption of alkanethiolate monolayers at gold a measure of surface coverage. *Langmuir*, **1991**, Vol. 7, pp 2687 – 2693.
- Ding, S.J., Chang, B.W., Wu, C.C., Lai, M.R., Chang, H.C., Electrochemical evaluation of avidin-biotin interaction on self-assembled gold electrodes. *Electrochim. Acta.*, **2005**, Vol. 50(18), pp. 3660 – 3666.
- Long, Y.T., Li, C.Z., Suther, T.C., Kraatz, H.B., Lee, J.S., Electrochemical detection of single-nucleotide mismatches: application of M-DNA. *Anal. Chem.*, **2004**, Vol. 76(14), pp 4059 – 4065.