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Investigation of Nitrite Detection with Electrochemical Impedance Spectroscopy

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***Abstract*— An electrochemical impedance spectroscopy study is described for the determination of nitrite. A screen printed carbon electrode (SPCE) was modified with biocompatible gold nanoparticles stabilized by a polymer (branched polyethyleneimine). The modified SPCE exhibits high electro catalytic activity toward nitrite oxidation, typically at a working potential at around 0.5 V (vs. Ag/AgCl). Sensitive impedimetric detection of nitrite is demonstrated. The studied detection range extends from 1 to 10000 µM. Based on found results, the sensor's performances will be calculated (limit of detection, sensitivity, linear range...) and further studies like stability and selectivity test will be continued.**

Keywords*— *Nitrite detection, Electrochemical sensors, Gold nanoparticles, Screen Printed Electrodes, Electrochemical Impedance Spectroscopy

I. INTRODUCTION

Nitrite (NO_2^-) is a dangerous inorganic contaminant which gets awareness because of its significant risk to public health and the environment [1]. There is NO_2^- in food as preservatives or as natural substance in vegetables for examples. It also occurs in water as a result of chloramination, which can lead to the formation of nitrites in the water supply network. Nitrite concentration can have a tendency to increase as the water moves towards the extreme ends of the system. The World Health Organization (WHO) has classified nitrite as a Carcinogen substance with critical values ranging from 8.7 µM to 28.3 µM [2]. Several approaches can be used to determine nitrite ion levels, such as capillary electrophoresis, chemiluminescence, ion chromatography, spectrophotometry, high performance column chromatography and electrochemical techniques [3][4][5][6][7][8][9].

Among all existing detection techniques, electrochemical techniques are widely applied for the detection of nitrites due to their ease of use, speed, high sensitivity and low cost, etc. [10]. The performances of the electrochemical system can be affected by the electrode type, the nanomaterials for functionalization and the combination of both [11]. The electrochemical nitrite detection process is either based on the oxidation or reduction of NO_2^- on the surface of electrodes [12]. The oxidation potential of nitrite is found very high at non modified electrodes, which will be hard to distinguish it from other interfering substances that oxidises more easily. From here came the way to solve this problem with the use modified electrodes with nanomaterials [13]. Accordingly, the exploitation of several modified materials makes a significant contribution to the detection of nitrite. In electrochemistry, research has always aimed to investigate new functional materials to enhance the electrocatalytic capabilities of nitrite sensors. Many functional nanomaterials showed great potential in nitrite detection. Carbon-based materials like graphene, carbon nanotubes has received significant interest throughout recent decades in electrochemical non-enzymatic detection due to their low cost, high efficiency and good catalytic activity [14]. Also metallic (Au, Ag, Sn, Cu etc.) functionalized electrodes have been applied for nitrite detection for their tremendous characteristics such as their high electrical conductivity, high surface area, and greater number of active sites [15]. Among them, gold nanoparticles have attracted scientists for their stability and especially their biocompatibility. For example, gold nanoparticles-multi-walled carbon nano- tubes (MWCNTs) modified carbon paste electrode (GNP/MWCPE) were developed for nitrite electro-oxidation. Thus, a synergistic reaction has occurred in the GNP/MWCPE hybrids to provide their improved electrocatalytic abilities [16]. Also, a β-cyclodextrin capped gold nanoparticles based GCE electrode was realized. This sensor is applied in food samples and drinking water [17]. Moreover, a sensor based on α-Fe2O3 NRAs on fluorine-doped tin oxide (FTO) conductive glass, then gold nanoparticles (with 3-5 nm diameter) were modified onto the surface of α-Fe2O3 nanorods with HAuCl4 reduction to finally give rise to AuNPs-Fe2O3 NRAs [18]. Due to this high interest in gold nanoparticles application, this work is based on developing a screen printed carbon electrode modified with capped cold nanoparticles with polyethyleneimine. The sensor performances were studied by using Electrochemical Impedance Spectroscopy (EIS). Advantages of EIS technique over other traditional techniques that it is very sensitive, accurate and reproducible technique suitable for highly resistive environments.

The findings strongly validated that the modified electrode can be implemented as a simple and easy tool for the detection of nitrite in real samples at low levels.

II. EXPERIMENTAL SECTION

A. Chemicals and Instruments

Standard nitrite solutions were prepared with sodium nitrite. Ferri/ferrocyanide redox probe solution was prepared with potassium ferrocyanide and potassium ferricyanide salts.

NPs-PEI were photochemically synthesized according to the procedure described in [19]. Carbon screen printed electrodes working electrodes were purchased from PalmSens BV, Houten, Netherlands. All electrochemical measurements were carried out using PalmSens 4 potentiostat also purchased from PalmSens BV.

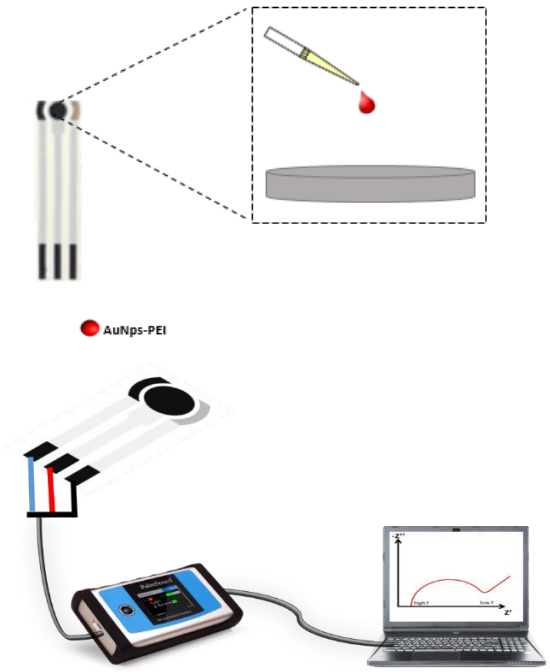

Fig.1: Graphical illustration of GSPE modification and setup

B. Sensor Preparation

The sensor preparation consists of the functionalization of the electrode with the nanomaterial. It was performed by dropping an amount of AuNPs-PEI solution into the working electrode of SPE (Fig.1). Then, letting it dry for 24 hours in room temperature.

III. RESULTS AND DISCUSSION

The electrochemical behavior of the electrodes is studied. The electron transfer kinetics of the bare and modified electrodes were investigated by EIS in 5mM ferri/ferrocyanide solution. The semicircle diameter in high frequency part shows the electron transfer resistance R_{cT}, that its value describe the electron transfer kinetics of the electrochemical reaction on the electrode. The EIS curves of both bare and modified electrodes are illustrated in fig.2, showing that the bare electrode has a larger semicircle diameter than the modified electrode, giving rise to the suggestion that the electron transfer kinetics of the gold nanoparticles modified electrode is faster than the bare.

Phosphate buffer solution was prepared with sodium phosphate dibasic heptahydrate and sodium phosphate monobasic monohydrate. All chemicals were purchased from Sigma-Aldrich and used without additional purification. Au-

These results could be explained as the gold nanoparticles own a very high electrical conductivity due to their high surface area to volume ratio. Also, using gold nanoparticles with other nanomaterials could potentially offer a conductive nanocomposite to improve the electrons transfer in electrochemical reactions.

The sensibility of the gold modified electrode toward nitrite ions was then examined. The Nyquist diagram in Fig.4 illustrates the impedimetric response of the modified electrodes following the addition of various nitrite concentrations from 10^{-6} M to 10^{-2} M in 0.1 M of phosphate buffer (PBS) at pH=6.. The increase of the diameter of the semicircles was observed at lower frequencies range following an ionic concentration increase, which could be due to the charge transfer resistance variation.

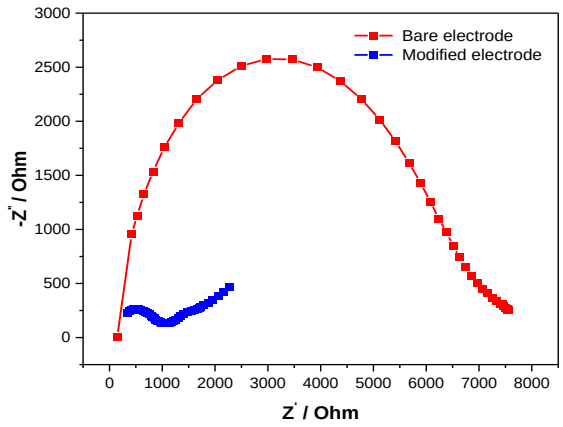

Fig.2: Impedance spectra in Nyquist presentation of bare and modified electrodes

Obtained curves could be fitted by the Randles equivalent circuit (figure3).

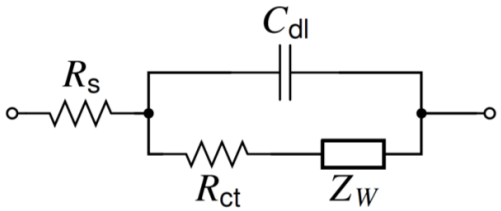

Fig.3: Randels equivalent circuit [20]

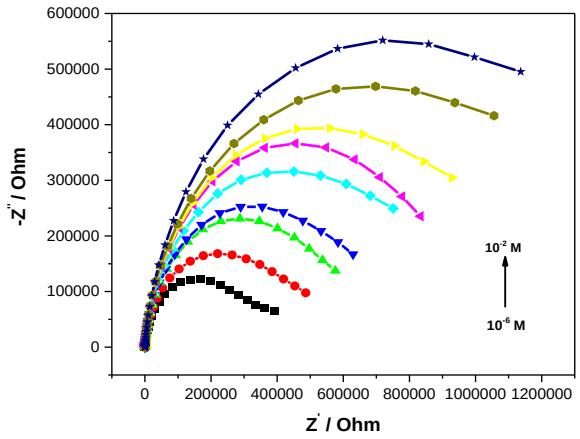

Fig.4: Impedance spectra in Nyquist presentation of the modified electrode in different nitrites concentrations between 10^{-6} and 10^{-2} M in 0.5 M of phosphate buffer at pH=6.

We conclude that the charge transfer resistance (R_{CT}) is proportional to the nitrite concentration. This effect can be assigned to the increase of the ionic strength in the medium when nitrite concentation is stonger.

Further test was experienced with electrodes. A stability test was done as follows. The prepared sensor was examined for 365 cycles as a daily measurement cycle to evaluate its performance (fig.5) in 10^{-3} M of nitrite concentartion and 0.1M PBS at pH=6.

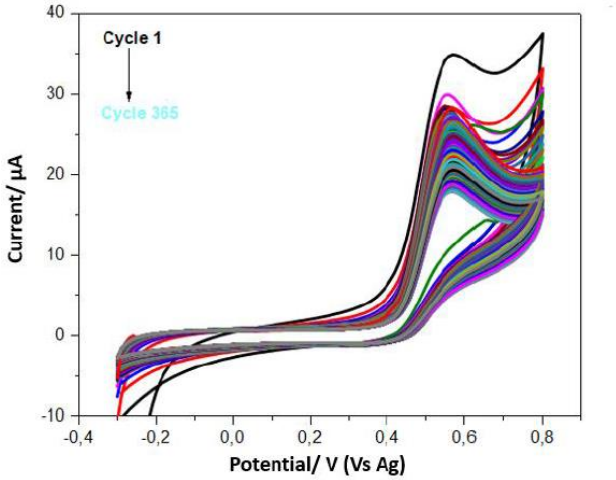

Fig.5: Stability test (365 cycles) at 0.001M of nitrite and 0.1M PBS at pH=6

It can be seen that the current decreases over time, but the condition and performance of the electrode was not affected. In addition, the conductivity of the electrode is very stable.
Second test consists of measuring 10^{-3} M of nitrite, then washing the electrode and making a PBS measurement, then washing the electrode again and making a measurement of the same nitrite concentration. This type of test showed that the electrode response is almost the same even after washing and that the PBS measurement does not affect the oxidation current and the electrode did not absorb other species of the PBS buffer solution. Therefore, these results indicate good stability and repeatability of the prepared sensor.

IV. Conclusion

The feasibility of an electrochemical sensor based on gold nanoparticles coated with polyethyleneimine on carbon screen printed electrodes for phosphate detection was studied. It shows an ability for detection in wide range of concentrations for nitrite detection from 10^{-6} to 10^{-2} M. Based on these results, further sensor's figures of merit will be calculated (LOD, sensitivity ..). The improvement of the work will be based on other sensitive techniques such as voltammetry techniques. Also, the sensor will be tested with interfering and in different real samples.

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