Elaboration of Reduced Graphene Oxide Electrodes Functionalized with rGO-ION Composite for Nitrite Detection in Water

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Abstract

In this paper, we propose a novel nitrite sensor based on reduced graphene oxide electrodes elaborated by light scribing. . First, graphene oxide was deposited on flexible substrate, which was previously plasma treated and wetted by a Poly(diallyldimethylammonium chloride) polymer solution. Then, in order to tune and enhance the sensitivity, the working electrode has been modified by layer-by-layer deposition of iron oxide-reduced graphene oxide nanocomposite (ION-rGO). The working electrode has been characterized at different levels of modification by scanning electron microscopy (SEM) and dispersive X-ray spectroscopy (EDX) showing a successful deposition and functionalization. Furthermore, electrochemical characterizations have been carried out by impedance spectroscopy and cyclic voltammetry (CV) and quantitative measurements for nitrite detection by differential pulse voltammetry (DPV). The experimental results demonstrate a good electrochemical response for nitrite with a sensitivity of 0.314 µA/mM. Several successive scans by CV at 50 mV/s in 1 mM nitrite solution show that the electrode remains stable and the sensitivity slightly reduces due to surface contaminations. The proposed fabrication procedure has a significantly better performance in comparison with some reported state-of-the art electrodes [12].

Keywords-component; Electrochemical sensors, Nitrite detection; Light scribe Graphene; Layer-by-Layer Deposition, reduced Graphene Oxide (rGO); Iron-oxide nanoparticles

1   Introduction

Over the last few years, in Germany due to excessive use of fertilizers, ground water is contaminated by nitrite in several regions, so that it has been condemned by the European court of justice for breach of EU law in this respect. Exceeding the allowed level of nitrite in drinking water causes several health problems, such as the "blue baby syndrome". Ingested nitrite can also react with amides and amines then forming potent carcinogens, such as nitrosamines [1-2]. The amount of nitrite in drinking water should therefore not exceed 3 mg/L referring to the World Health Organization (WHO) [3].

Hence, a reliable and accurate method for nitrite detection in water is important and recently received much attention. So far, many techniques have been adopted to detect nitrite, which involve tedious procedures and are time-consuming, such as chromatographic methods, ion spectrophotometry and chemiluminescence 4. Alternatively, electrochemical techniques are widely used because they provide highly selectivity, sensitivity and rapid nitrite determination compared with other traditional methods [5]. The electrochemical determination of nitrite is reported in literature either by oxidation or reduction. However, the oxidative nitrite determination is generally preferred because the nitrite reduction is basically known to suffer from interferences such as reduction of nitrate and molecular oxygen [6].

Recently, the applications of screen-printed electrodes (SPE) have significant advantages, such as simplicity, and low fabrication cost [7]. The whole electrode system, including working, reference and counter electrodes is printed on a substrate. Usually, for bare electrodes, the oxidation of nitrite occurs at high overpotential. Therefore, a modification of the screen printed electrodes is necessary in order to decrease the over potential and thereby to increase its sensitivity.

In this paper, we propose a novel nitrite sensors based on reduced graphene oxide electrodes produced by light scribing (LSG) [8-9]. To realize a high stability of the electrodes, graphene oxide was deposited on flexible substrate, which was plasma treated and wetted by a Poly(diallyldimethylammonium chloride) polymer solution. In order to tune and enhance the sensitivity, the working electrode has been modified by reduced graphene oxide- iron oxide nanoparticle (rGO-ION). The modification was made by layer-by-layer deposition of PDAC polymer and rGO-ION. The development of this modified electrode for nitrite detection is not expensive compared to conventional

electrodes. This novel fabrication technique realizes low-cost sensors able to be used on-site.

2   Material and methods

2.1   Chemicals

The graphene oxide (GO) is commercially available in aqueous solution with a concentration of 4 g/L, prepared by modified Hummers method and it is obtained from Graphenea S.A, Spain. Iron oxide-reduced graphene oxide nanocomposite (ION-rGO) was synthesized as following; 200 mL of GO 0.1 g/L with a pH of 11 was prepared. Under stirring, a solution of 0.5 g of $FeSO_4.7H_2O$ in 10 mL of deionized water was added to GO solution dropwise. The solution was stirred further for 30 m and the mixture was left decanting aided by a magnet. Cleaning steps were carried out by removing the supernatant and adding deionized water and decanting with the magnet. Finally, the particles were suspended NH3 solution (pH 9) using the horn sonicator and then centrifugated.

In this study, all reagents used were of analytical grade and distilled water was used throughout. Sodium nitrite was purchased from Aldrich. Freshly made 0.1 M phosphate buffer solution (PBS) in different pHs, consisting of sodium phosphate dibasic (Na2HPO4) and sodium phosphate monobasic (NaH2PO4) was used during experimental testes as the supporting electrolyte.

2.2   Preparation of the electrodes

The preparation of LSG was done by using a commercially available laser source (LightScribe DVD drive with 788nm) controlled by means of a computer software (Nero Cover Design) to reduce the graphene oxide (GO). For that, GO in an aqueous solution of 0.3 wt. % was casted directly onto polyethylene terephthalate (PET) substrate which was plasma treated. The substrate was already glued to a DVD disc by adhesive spray. GO takes 24 h to dry under ambient conditions. Then, the obtained film was reduced by light scribing method. More than 20 electrodes can be produced on a single DVD disc. The electrodes were prepared by pasting Ag/AgCl to the reference electrode (RE). Working electrodes (WE) were functionalized with the ION-rGO nanocomposite, while counter electrodes (CE) were kept unchanged i.e. only reduced graphene oxide (rGO). Finally, a passivation layer was applied to obtain final electrode as shown in Fig 1a.

rGO working electrodes were functionalized with Layer-by-layer technique using tow oppositely charged materials The first step was drop casting a layer of PDAC polymer on the working electrode WE and washed by deionized water in order to remove unbound material. The same procedure is repeated to deposit ION-rGO nanocomposite as

shown in the figure 1b. This process forms one bilayer. Finally, the functionalized electrode was dried with nitrogen gas and it is ready for the electrochemical testes.

2.3   Characterization and Measurement Setup

The examination of the electrode morphology was carried out by a scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectroscopy (EDX). For the electrochemical experiments, PalmSens 4 (PalmSens BV) was used to perform cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements.
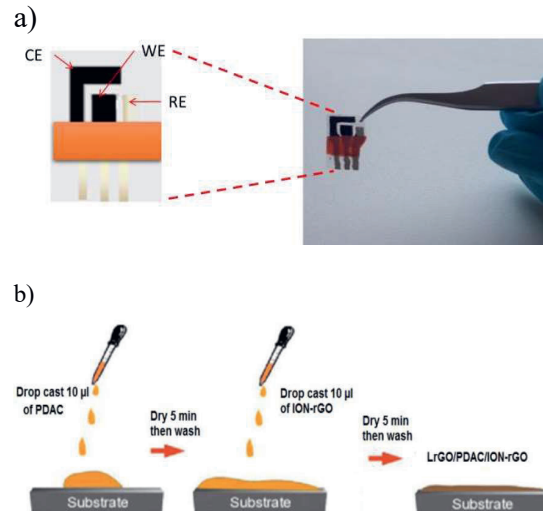
a)

b)

Fig1. a) LSG fabricated electrode configuration and b) Graphical illustration of the electrode functionalization

3   Results and Discussion

3.1   Surface Characterization electrodes

The morphology of electrodes after each preparation step can be clearly seen from the SEM images displayed in in Fig2. In Fig. 2a, the initial GO cast film shows a homogeneous film. After laser-scribing, when GO is photothermally reduced to rGO, the surface becomes rougher . This morphological transformation may be a consequence of a chemical bonds breaking during the reduction process. The lattice defects during the surface reconstruction after removing hydroxyl and epoxy groups may also contributed to change the morphology. The formation of rGO was further confirmed by EDX, which is performed using the same samples. EDX results show that carbon to oxygen relative concentration increase from GO to rGO samples, proving the reduction efficacy of the laser scribing process. . Finally, the last step of modification with PDAC/ION-rGO nanocomposite film is seen in Fig.2c. . It is possible to detect rGO sheets decorate with nearly spherical nanoparticles, which are the ION. EDX measurements detected the presence of iron and confirm the successful functionalization of the working electrode.
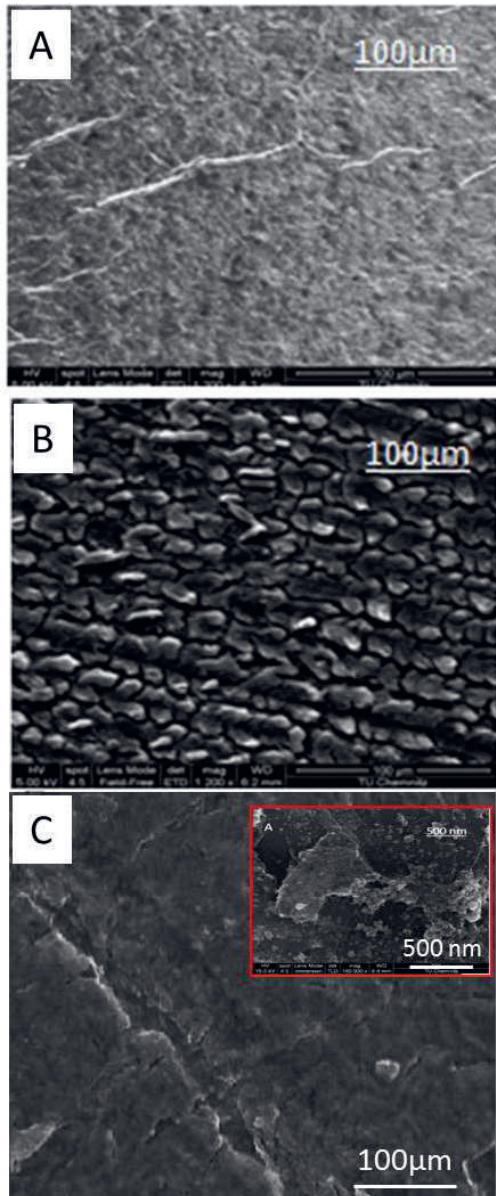
Fig 2. SEM images of (a) graphene oxide on top of the PET substrate, (b) rGO obtained after laser scribing, and (c) PDAC/ION-rGO nancomposite film on top of the laser scribed rGO electrode, Inset: image with higher magnification with noticeable ION nanparticles

3.2 Electrochemical behavior

First of all ,a test of the electrode without target ion with a solution composed of 0.1M of KCl and 10^{-3} M ferri/ferrocyanide [Fe (CN) 6]$^{3-/4-}$ was performed. For both bare and modified (PDAC/ION-rGO) electrodes we tested by CV, Fig.3. For modified surfaces, the [Fe (CN) 6]$^{3-/4-}$ redox couple provides a good electrochemical probe to study, because its oxidation and reduction proceed via a simple one-electron-transfer process. This chemical reaction (1) is the base of this redox-couple's electrochemistry:

$$[Fe(CN)_6]^{3-} + [Fe(CN)_6]^{3-}e^- \leftrightarrow [Fe(CN)_6]^{4-} \qquad (1)$$
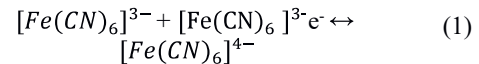
An improvement between bare and modified electrodes in the electrochemical response can be seen in Fig.3 by the increase of the ferri/ferrocyanide oxidation and reduction peak currents after electrode modification with the PDAC/ION-rGO film. This improvement is ascribed to the increase of the surface area provided by the electrode modification.
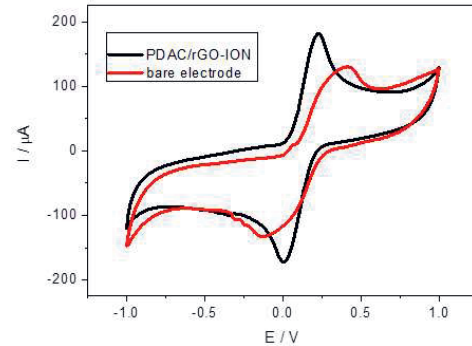

Fig.3.Cyclic voltammograms of Ferri-Ferrocyanide solution 10^{-3} M of bare and modified electrode in 25 mV/s

CV was also performed at different scan rates (25 mV/s, 50 mV/s, 100 mV/s, 150 mV/s, 200 mV/s). It was found a linear relationship between anodic/cathodic peak currents (i_p) and the square-root of the scan rate ($v^{1/2}$), shown in Fig.4.

The electro-active surface area of the electrodes was calculated by using the Randles-Sevcik equation. This equation predicts that the current peak should be proportional to the square root of the scan rate when voltammograms are taken at different scan rates. At 25 °C, the Randles-Sevcik equation can be reduced to the following equation (2) [11]:

$$i_p = 2,69 \ 10^5 \ n^{\frac{3}{2}} AD^{\frac{1}{2}} Cv^{\frac{1}{2}} \qquad (2)$$

in which n is the number of electrons appearing in half reaction for the redox couple (n=1 in our case), A is the active surface of the electrode (cm^2), C represents the concentration of the electroactive species (mol cm^{-3}), v is the speed at which the potential is swept (V/s), and D is the diffusion coefficient of the analytes ($cm^2 s^{-1}$). From this equation, we can directly calculate the electroactive area for bare and modified electrodes.

Before the modification A is 0.2 cm^2, and it increases to 0.29 cm^2 after functionalization with the layer-by-layer assembled PDAC/ION-rGO film.

To choose the proper pH value at which the best detection of nitrite takes place, CV was performed by changing the pH value of the PBS solution: 3.5, 4.5, 5.7, 6.0, 6.5 and 7.4 as shown in in Fig.5a and b. The nitrite concentration is fixed at 1 mM as well as scan rate used is fixed at 50mV/s. It is found that oxidation current of nitrite ions for the modified electrodes has a better peak achieved at pH=5.7.
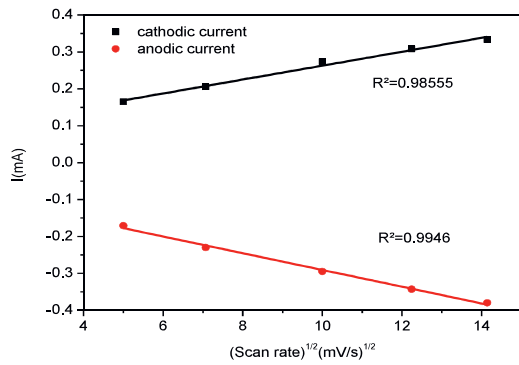
Fig. 4 Anodic and cathodic current of nitrite versus Square root of scan rate Vs

The sensor response to nitrite detection was tested by differential pulse voltammetry (DPV). The DPV curves of the modified electrode following the change in nitrite ion concentration were measured and shown in Fig. 6. The peak oxidation current increases with increasing the nitrite concentrations. This increase is almost linear.
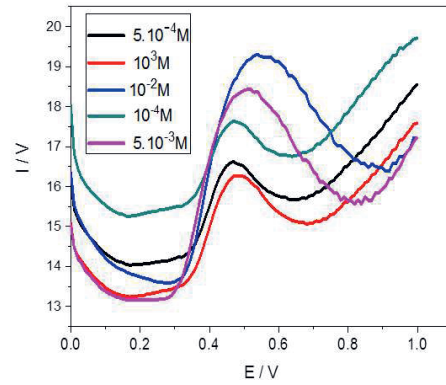

Fig. 6: DPV of modified electrode with RGO-IONs/PDAC for different nitrite concentrations

Fig. 7 illustrates the calibration curve describing the variation of currents as a function of increasing nitrite concentrations. We find that the method has a sensitivity of 0.314 $\mu A/mA$ with (R^2=0.93).

Fig.7 Nitrite calibration curve

Moreover, the reproducibility was studied as an important parameter of sensor characterization. The reproducibility was investigated from the current and potential response from CV using four electrodes independently prepared in the same way as seen in Fig. 8. Furthermore, the electrodes show stability of the oxidation peak current even after tens of cycles. Several successive scans by cyclic voltammetry of with a rate of 50 mV/s in 1 mM nitrite solution show that the electrode remains stable and using plasma and PDAC wetting make the electrode more stable.
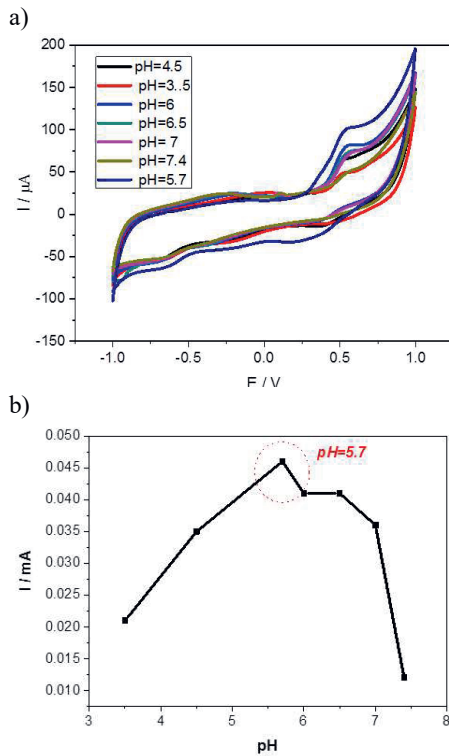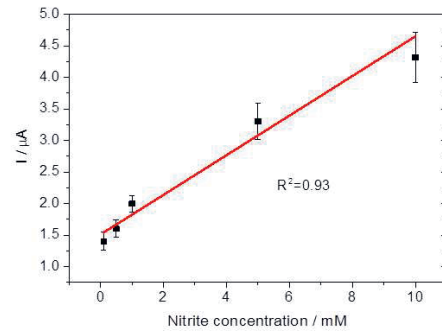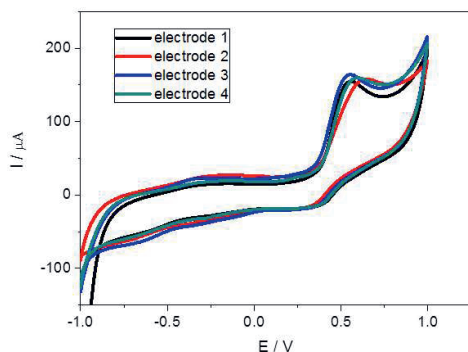

Fig. 5. (a) Cyclic voltammograms of detection of nitrite in different pHs and (b) Variation of nitrite oxidation peak current value with the pH. All measurements performed with the LSG PDAC/ION-rGO electrode.

Fig. 8 Cyclic voltammograms of nitrite registered with four LSG PDAC/ION-rGO electrodes produced in different batches.

4   Conclusion

In this work, sensitive electrodes for the detection of nitrite in water were developed using PDAC/ION-rGO modified laser-scribed reduced graphene oxide electrode. The electrodes' modification was performed by layer-by-layer deposition technique. The sensor has a sensitivity of 0.314 µA/mM, which is better than state of the art sensors [12].

This study combines the use of nanomaterials and the realization of low-cost electrodes, which can be disposable, in the detection of nitrite in water. This can be an alternative for the detection and sensing of many other substances. The realized sensor has a fast response and is economically feasible.

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