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PII: S0039-9140(16)30415-5
DOI: <http://dx.doi.org/10.1016/j.talanta.2016.05.079>
Reference: TAL16629

To appear in: *Talanta*

Received date: 14 April 2016
Revised date: 26 May 2016
Accepted date: 31 May 2016

Cite this article as: Eda Mehmeti, Dalibor M. Stanković, Ahmet Hajrizi and Kurt Kalcher, The use of graphene nanoribbons as efficient electrochemical sensing material for nitrite determination, *Talanta*, <http://dx.doi.org/10.1016/j.talanta.2016.05.079>

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The use of graphene nanoribbons as efficient electrochemical sensing material for nitrite determination

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Abstract

In this work new designed, highly sensitive electrochemical method is developed for the determination of nitrites in tap water using glassy carbon electrode modified with graphene nanoribbons (GNs/GCE). Graphene nanoribbons (GNs) have been newly synthesized and aligned to the surface of glassy carbon electrode (GCE) and exhibited excellent electrocatalytic activity for nitrite oxidation with a very high peak currents. Studies about electrochemical behavior and optimization of the most important experimental conditions were done using cyclic voltammetry (CV), while quantitative studies were done with amperometric detection. Nitrite provides a well-defined, oxidation peak at +0.9 V (vs. Ag/AgCl, 3.0 M KCl) in Britton-Robinson buffer solution (BRBS) at pH 3. The influence of most possible interferent ions has been examined and was found to be negligible. Under optimized experimental conditions in BRBS at pH 3 linear calibration curves were obtained in the range from 0.5 to 105 μM with the detection limit of 0.22 μM . Reproducibility of ten replicate measurements of 1 μM of nitrite was estimated to be 1.9 %. Proposed method and constructed sensor is successfully applied for the determination of nitrite present in tap water samples without any pretreatment. This developed method represents inexpensive analytical alternative approach compared to other analytical methods.

Keywords: graphene nanoribbons, nitrite, amperometry, glassy carbon electrode

Introduction

Nitrites are widely used as indicators for information's about environmental pollution and for food control. The presence of high level of nitrite in drinking water can cause several diseases in human health such as methemoglobinemia and stomach cancer by the production of N-nitrosamines [1,2]. The maximum limit value of nitrite present in drinking water is 3 mg /L recommended by the World Health Organization [3].

When this level exceed, it is a signal for contamination of drinking water, agriculture soil and food materials. Due to the importance of its toxicity, several methods have been developed for the analysis and evaluation of nitrites [4] such as spectrophotometry and spectrofluorimetry [5,6] ion-chromatography [7], flow-injection analysis [8], and capillary electrophoresis [9]. Electrochemical methods offer high selectivity and sensitivity, simplicity in sample preparation and low-cost instrumentation [10]. Nowadays, many modified electrodes with carbon materials were developed as electrochemical sensors to determine nitrite ions in solutions [11]. Carbon nanomaterials such as multi-walled carbon nanotubes (MWNTs) [12] and graphene or graphene based nanocomposites are most used due to their large surface area, high conductivity and good catalytic ability [13,14]. Graphene nanoribbons in comparison with carbon nanotubes, they have reactive edges which can increase the adsorption and electrocatalysis of certain molecules which are used as a promising electrode material [15,16]. Glassy carbon electrodes (GCE) are used as analytical tools in electroanalysis, due to their advantages of broad operating potential window, low background current, easy possibility of surface modification, good mechanical and electrical properties and chemical inertness. They are suitable for many different sensing and detection applications [17]. To the best our knowledge, the determination of a nitrite at a glassy carbon electrode modified with graphene nanoribbons has not been reported so far.

The aim of this work was development of an electrochemical method for sensitive and selective determination of nitrite in tap water samples. In this regard, a modified GCE electrode has been prepared using newly synthesized graphene nanoribbons (GNs). The proposed method and constructed sensor (GNs/GCE), has excellent electrochemical activity in a BRBS at pH 3 and enhanced electrocatalytic performance on nitrite oxidation. Nevertheless, the developed sensor has several advantages such as simplicity of electrode preparation, wide linear range, low detection limit, high sensitivity and selectivity, and low cost for the determination of nitrite in water samples.

Experimental

Chemicals

Deionized water was purified with a cartridge purification system (Milli-Q) to a resistivity of 18.2 M Ω cm and was used for all experiments.

Sodium nitrite purchased from Merck (Darmstadt, Germany). Multiwall carbon nanotubes (MWCNT) (o.d. 7-15 nm and tube length 0.5-10 μ m), boric acid, sodium hydroxide, acetic acid and phosphoric acid were purchased from Sigma–Aldrich (Wien, Austria) and used as received without any further purification. Calibration solutions were prepared from the stock solution (1mM) by appropriate dilution with supporting electrolyte. Britton–Robinson buffer solution (BRBS) was prepared by mixing of 40 mM of all necessary components (phosphoric acid, acetic acid and boric acid). The pH of BRBS was adjusted with sodium hydroxide (0.2 M). Working solutions of nitrite were freshly prepared on the day of the experiment by appropriate dilution with the supporting electrolyte. All reagents used in this work were of analytical grade and were used without further purification.

Apparatus

Cyclic voltammetric (CV) measurements and hydrodynamic amperometric measurements were performed using an Autolab PGSTAT 302N (Metrohm Autolab B.V., The Netherlands) potentiostat/galvanostat controlled by corresponding software (Nova 1.10). The electrochemical cell (total volume of 10.0 mL) consisted of a glass vessel (Metrohm) equipped with the Ag/AgCl (3 M KCl, Metrohm 6.0733.100) as a reference electrode, platinum wire as an auxiliary electrode and GNs/GCE as a working electrode. All of the pH values were measured using a pH meter (Orion, model 1230) with a combined electrode (glass-reference electrodes), which was calibrated every day with standard buffer solutions. All potentials given in the text are versus the Ag/AgCl reference electrode at room temperature.

Synthesis of graphene nanoribbons

Graphene nanoribbons (GNs) were prepared according to the procedure described before [18]. First, 100 mg of multi walled carbon nanotubes (MWCNT) was dissolved in 3.4 mL of sulfuric acid (H₂SO₄, 98%) and the resulting suspension was homogenized via ultra-sonication

for 1 h. The suspension solution was then placed in an ice bath with further vigorous stirring and 75 mg of sodium nitrate (NaNO_3) was added. Next, 450 mg of potassium permanganate (KMnO_4) was added into the suspension. After a reaction was completed (2.5-5 h), 20 mL of 5% sulfuric acid solution was transferred and was allowed to cool. When the bubbles were observed 2 mL of hydrogen peroxide (H_2O_2 , 30%) was added dropwise. After 30 min, the resulting suspension was centrifuged and carefully washed with 5% nitric acid three times and deionized water five times, filtered and dried in an oven at 90 °C for 12 h under vacuum. The prepared GNs contained high amounts of oxygen-containing functional groups.

Characterization of synthesized graphene nanoribbons

The morphologies and structure of used MWCNTs and prepared GNs were characterized by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The structure and chemistry of the samples were studied using a 200-kV transmission electron microscope (TEM; JEM-2100, Jeol Inc.) equipped with LaB6 filament and Energy-dispersive X-ray spectrometer (EDS). The micrographs were recorded with high-resolution slow-scan CCD camera (Orius DC1000, Gatan Inc.). Powdered synthesized samples were dispersed in DMF and transferred on commercially available Cu grids (200 mesh Cu holey carbon, SPI Supplies / Structure Probe, Inc.). SEM images were recorder by using SEM Jeol JSM-6610LV.

Preparation of the GCE modified with graphene nanoribbons (GNs/GCE)

The glassy carbon electrode was polished to a mirror-like surface with $\gamma\text{-Al}_2\text{O}_3$ (50 nm particle size), rinsed ultrasonically with nitric acid-water (1:1), twice more with water and dried in room temperature. On to the active area of the GCE surface (inner diameter 3 mm), 5 μL of prepared GNs suspension (0.5mg/mL) were directly applied and waited for about 4 h for drying at 4 °C before measurements.

Procedures

The cell contained a three electrode system. The voltammograms were recorded in a potential range from 0 to 1.4 V at a scan rate of 0.05 V/s for CV (if not stated otherwise), and amperometric measurements were taken at constant potential of 0.9 V.

Interference studies

Electrochemical behavior of some possible interferences such as Na^+ , K^+ , Mg^{2+} , Ca^{2+} , SO_4^{2-} , Fe^{3+} , Pb^{2+} , Cd^{2+} , Cu^{2+} and SO_3^{2-} were tested in concentrations of 10 μM under optimized experimental conditions with proposed sensor. The changes of the peak current obtained for 1 μM of nitrite ion were compared in the absence and in the presence of selected interferences. It was considered that tested compounds strongly interfere with the determination of nitrite ion if gives signal changes more than $\pm 10\%$.

Sample analysis

Samples were taken from two different pipes. First sample was directly measured by adding 1 mL of sample in voltammetric cell. Second sample was artificially spiked with nitrite ion to increase its concentration in cell to the value of 1 μM . All results are repeated three times, estimated from calibration curve and given as mean value of three measurements. In order to evaluate matrix effect recovery experiments were done and results are listed in Table 1.

Results and discussion

3.1. Characterization of synthesized graphene nanoribbons

Transmission electronic microscopy was used for the characterization of used materials, and in Figure 1 images from multi walled carbon nanotubes (Figure 1A) and graphene nanoribbons (Figure 1B) are presented. Carbon nanotubes show typically bundled structures whereas after chemical unzipping structures like shown in the Figure 1B appear showing unfolded and partly folded structures of the ribbons.

>>Figure 1>>

The morphologies of MWCNTs and GNs were studied also by SEM. As it is shown in Figure 2A, the MWCNT are not unzipped and still retain the bamboo-like compartment. In the other hand, the graphene nanoribbons (Figure 2B) have variable thickness and long width, turning to be partially unzipped nanotube.

>>Figure 2>>

3.2. Electrochemical behavior of nitrite on unmodified GCE and GNs/GCE

In order to investigate the effect of modifier, the cyclic voltammograms (CVs) and differential pulse voltammograms (DPV) for unmodified GCE and GNs/GCE in the absence and presence of nitrite at pH 3 were compared in the potential range 0-1.4 V (Fig. 3).

>>Figure 3>>

In the absence of the nitrite ion no presence of peak current was observed for both electrodes (Fig. 3(A), dot-line). The CVs for 100 μM of nitrite using unmodified GCE did show extend anodic peak in the positive scan at around 1 V (Fig. 3(A), red-line). At the surface of the GNs/GCE, the direct oxidation of nitrite produces increased anodic current with a well-defined, sharp peak and decrease in the over potential of the process at around 0.85 V (Fig. 3(A), blue-line). It is well demonstrated that the use of GNs could act as an effective mediator to enhance the kinetics of the electrochemical process. Also, in the reverse scan, no presence of any cathodic peak was observed.

The differential pulse voltammograms (DPVs) for nitrite at the unmodified GCE and GNs/GCE were also established (Fig. 3(B)). The DPVs for nitrite were recorded at scan rate of 0.1 V/s, pulse amplitude of 0.12 V and pulse time of 0.01 s. In the absence of the nitrite ion no presence of peak current was observed also with DPV for both electrodes in the potential range 0-1.4 V (Fig. 3(B), dot-line). The DPV for unmodified GCE showed a small anodic peak in comparison for GNs/GCE obtained anodic response for 100 μM of nitrite was approximately double higher at around 0.8 V. Therefore, it is expected, according to electrochemical properties of GNs, presence of these ribbons in the electrode surface causes enhancement in the electron transfer and hence increasing of the electrochemical response of nitrite.

3.2. Optimization of the experimental parameters for nitrite oxidation

3.2.1. Effect of pH

The effect of the pH value of supporting electrolyte on the peak current of nitrite oxidation was studied using BRBS at different pH values from 3 to 9. Representative voltammograms are shown in Figure 4. The peak current decreased by increasing pH up to 3 and increased again in small extent at higher pH values up to 6 however with a very broad shape of the

peak. At pH 3 the peak current was highest with a well-defined, oval-shape oxidation peak. Therefore BRBS of pH 3 was used for further studies.

>>Figure 4>>

Moreover, this study indicated that the peak potential for nitrite oxidation is not affected by the pH value of the supporting electrolyte. It can be attributed to a kinetically controlled oxidation process of nitrite as it is a proton independent catalytic step [19,20].

3.2.2. Effect of scan rate

The effect of scan rate of potential sweep to the current response of nitrite oxidation was also studied in the range from 0.01 V/s to 0.1 V/s. The obtained results indicate the catalytic effect of mediator at all tested range. With increase of the scan rate, the peak potential for the oxidation of the nitrite slightly shifts to more positive potentials. Peak current is proportional to the square root of scan rate, with the linear regression equation as $I (\mu\text{A}) = 0.25512 v^{1/2} + 2.58828$ ($R^2=0.9846$), which confirms that reaction is diffusion controlled.

3.3. Amperometric studies

3.3.1. Analytical performance

Analytical methods for monitoring, easy and successful quantification of species important for tap water quality, nowadays present compulsory part of human life. For that purpose amperometry was selected due to its advantages compared with other analytical methods. Under the optimum conditions, amperometry (Figure 5) was employed to investigate the electrochemical response of nitrite oxidation in various concentrations from 0.5 to 105 μM at GNs/GCE by setting the working electrode potential at 0.9 V. The currents were proportionally linear to the concentration of nitrite in two ranges: first range 0.5-45 μM with linear regression equation $I (\mu\text{A}) = 0.5074 c (\mu\text{M}) + 2.5658$ ($R^2=0.9998$) and second range 45-105 μM with linear regression equation $I (\mu\text{A}) = 0.3808 c (\mu\text{M}) + 7.9544$ ($R^2=0.9978$). The sensitivity of GNs modified GC electrode was estimated to be $6.3219 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$.

>>Figure 5>>

Limit of detection (LOD) for proposed analytical procedure was calculated as $3\sigma_{\text{intercept}}/\text{slope}$ of first calibration range. It was found LOD value of 0.22 μM . This value is lower or comparable with LOD values proposed by other authors presented in literature offering wide linear range from 0.5 to 105 μM for nitrite ion quantification [21,22]. These facts confirm all benefits of newly synthesized materials for application in electroanalytical chemistry.

3.3.2. Stability of the GNs/GCE

The reproducibility of the proposed sensor GNs/GCE for nitrite determination was examined with intra and inter-assay precision. The intra assay precision was evaluated with the same sensor for the 1 μM nitrite. The relative standard deviation (RSD) for 10 replicate measurements was as 1.9%, indicating an excellent detecting reproducibility. The inter-assay precision was evaluated for the 1 μM nitrite with one sensor during 5 days, and RSD for these measurements was found to be 2.4%. Repeatability of the electrode preparation procedure was estimated by measuring concentration of 1 μM nitrite with 10 different sensors. The obtained RSD value for this study was calculated to be 3.3%. This result indicates that proposed method offers high repeatability of electrode preparation procedure and excellent stability for nitrite determination, even when the sensor was used for more than 5 days there was no significant decrease in current response.

3.3.3. Interference studies

Practical application of one analytical method can be strongly limited with its selectivity. Accordingly, the most possible interferences for the determination of nitrite at the GNs/GCE were studied by addition of interferent ions into the BRBS at pH in the presence of nitrite ion of 1 μM (Figure 6).

>>Figure 6>>

The results indicated that tested interferent ions, Na^+ , K^+ , Mg^{2+} , Ca^{2+} , SO_4^{2-} , Fe^{3+} , Pb^{2+} , Cd^{2+} , Cu^{2+} , Cl^- , OH^- and CO_3^{2-} in concentrations of 10 μM had no interference on nitrite determination with the proposed sensor. However, presence of sulfite ion in high concentration causes current response of GNs/GCE electrode. Nevertheless, in the tap water samples presence of sulfite ion is not expected, due to its easy oxidation with atmospheric oxygen, this interfering compound does not limiting practical applicability of our sensor.

Therefore, this proposed method with developed sensor appears to be highly selective in the presence of tested most common interferent compounds.

3.3.4. Application to the sample

In order to evaluate the practical performance of the proposed method in the determination of nitrite in tap water samples, GNs/GCE was applied to the analysis of nitrite in tap water sample (S1) without any primary preparation (Figure 7). Also, the sample has been spiked with nitrite at the concentration of 1 μM (S2), to causes current increase and makes nitrite ion concentration measurable. Recovery experiments were done by addition three (A1, A2, A3) times 2 μM of nitrite ion. Results from these measurements are listed in Table 1.

>>Figure 7>>

According to the results, the satisfactory recoveries between (99 and 103%) for the investigated samples indicated that the proposed method had great potential in the practical sample analysis. Nevertheless, the proposed method provides a capable alternative for the quick and easy determination of nitrite in tap water samples.

Table 1. Results^a obtained for determination of nitrite in tap water and recovery^b experiments using proposed analytical method.

Sample	Found (μM)	Added/Found (μM)	Recovery (%)	Added/Found (μM)	Recovery (%)	Added/Found (μM)	Recovery (%)
1.	0.00	2.00/2.04	102	2.00/4.01	99	2.00/6.10	101
2.	1.02	2.00/3.04	101	2.00/5.09	102	2.00/7.18	103

^a n=3

^b Recovery = $[\text{nitrite}]_{\text{found}}/[\text{nitrite}]_{\text{added}} \times 100$

4. Conclusions

This work demonstrates the novel and simple electroanalytical method by the modifying glassy carbon electrode with graphene nanoribbons (GNs/GCE) for the determination of nitrite ions in tap water. The modified electrode demonstrated excellent electrocatalytic performance for the oxidation of nitrite. Also, presents a high selectivity toward nitrite ion

oxidation in presence of different ions. The GNs/GCE gives a fast response, low detection limit and excellent stability to be used in long term. The proposed method and sensor provides high selectivity, low limit of detection, wide linear range compared to other reported methods.

Acknowledgments

E.M wishes to acknowledgement Higher KOS Stipendien, financed by ADA and MEST and Austrian Agency for International Cooperation in Education and Research (OeAD-GmbH). D.M.S wishes to acknowledgement Ministry of Education, Science and Technology, Republic of Serbia No. OI 172030.

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Fig. 1. TEM images of MWCNTs (A) and GNs (B)

Fig. 2. SEM images of A) MWCNTs and B) GNs

Fig. 3. (A) Cyclic voltammograms for unmodified GCE (red-line), GNs/GCE (blue-line) in 100 μM of nitrite solution, in absence of nitrite solution (dot-line) in BRBS at pH 3, scan rate of 0.05 V/s. (B) Differential pulse voltammograms for unmodified GCE (red-line), GNs/GCE (blue-line) in 100 μM of nitrite solution, in absence of nitrite solution (dot-line) in BRBS at pH 3, scan rate of 0.1 V/s, pulse amplitude of 0.12 V and pulse time of 0.01 s.

Fig. 4. Representative cyclic voltammograms in absence of nitrite (Blank) and in presence of 100 μM nitrite at GNs/GCE in BRBS at various pH values (3, 5, 7 and 9), scan rate of 0.05 V/s.

Fig. 5. Disposable amperogram in the solutions with different concentrations of nitrite 0.5 to 105 μM for GNs/GCE at potential of 0.9 V.

Fig. 6. Amperometric response of nitrites and tested interferent ions in BRBS at pH 3, with GNs/GCE at potential of 0.9 V.

Fig. 7. Amperogram obtained for nitrite ion quantification with GNs/GCE electrode in tap water under optimized experimental conditions.

Highlights

- Graphene nanoribbons were synthesized and used as a sensing material
- Glassy carbon electrode modified with graphene nanoribbons was fabricated
- Determination of nitrite in tap water samples was studied
- Wide dynamic range from 0.5 to 105 μM with a detection limit of 0.22 μM was achieved

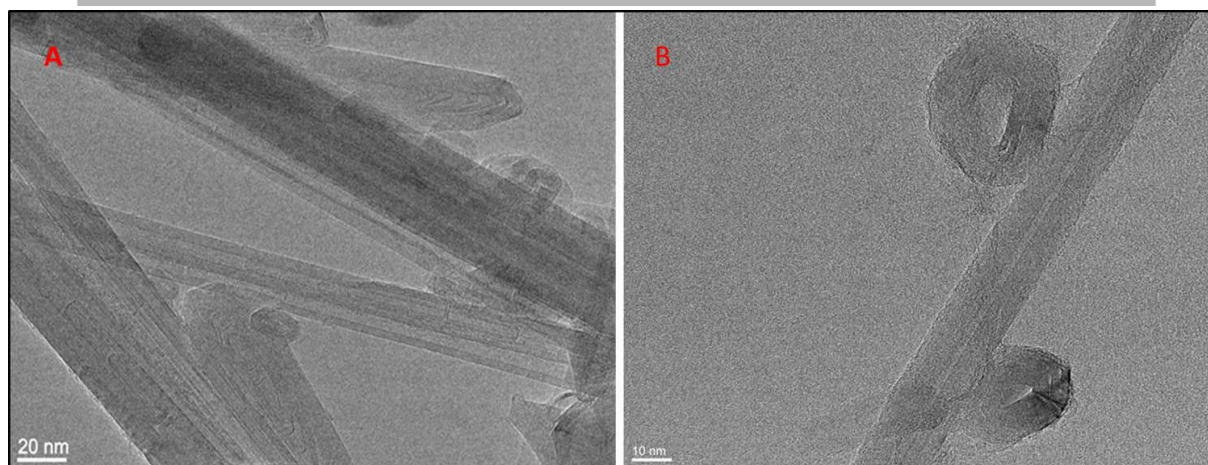


Fig. 1

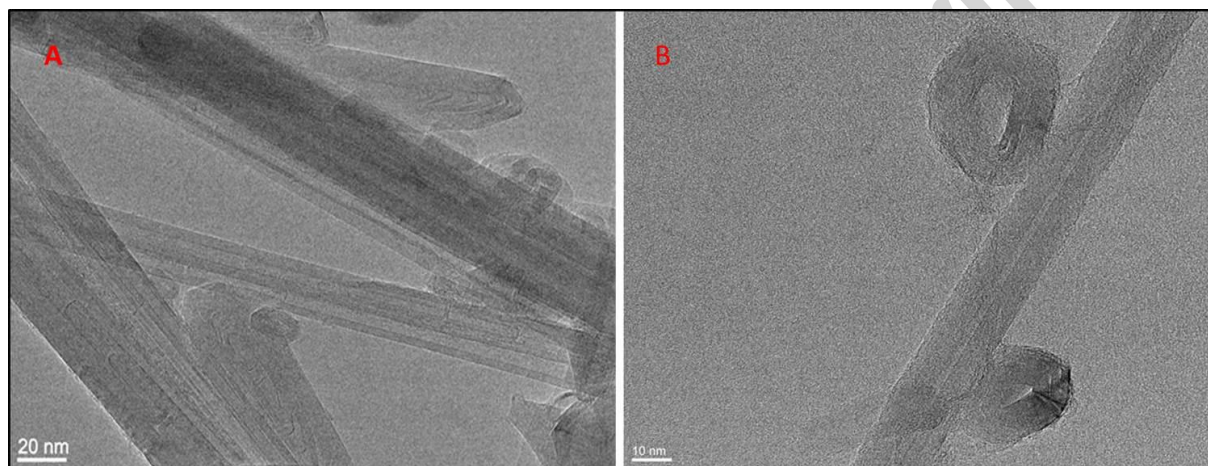


Fig. 2

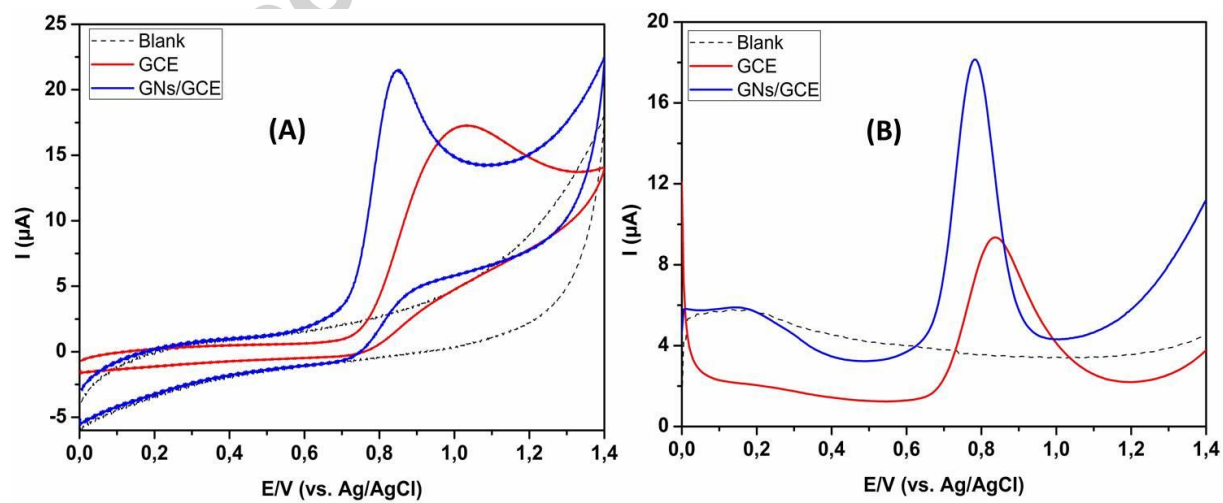


Fig. 3

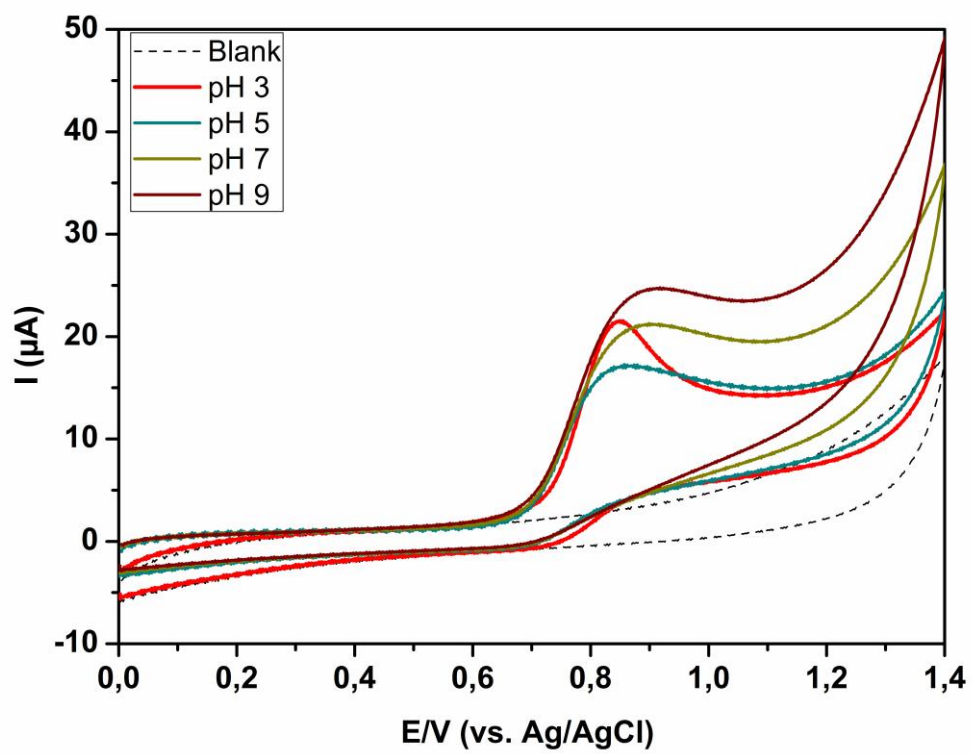


Fig. 4

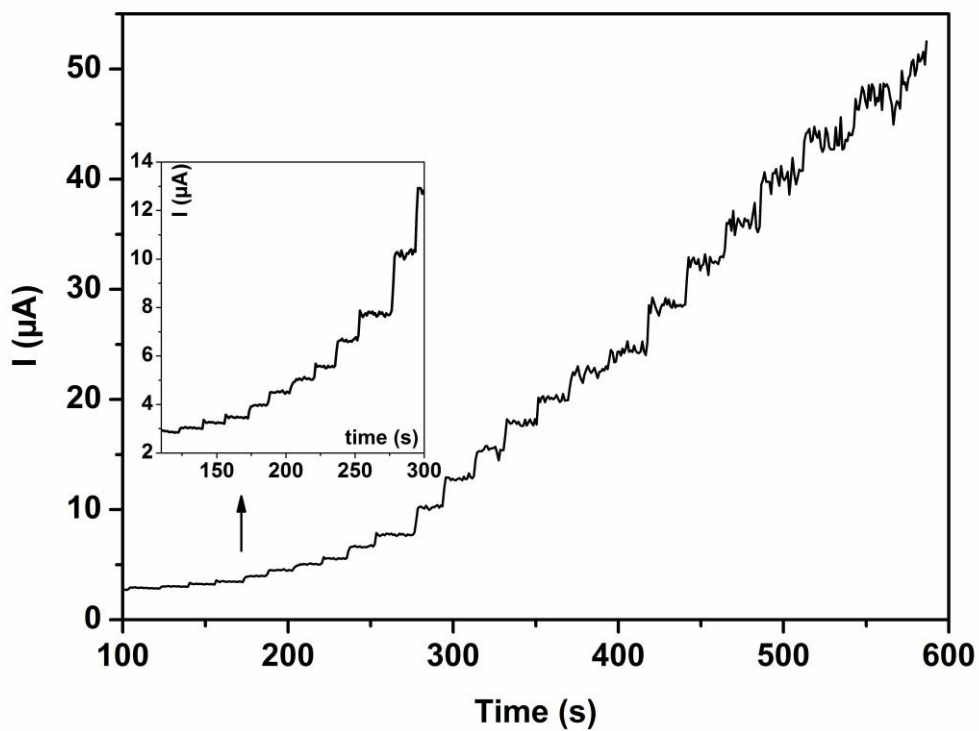


Fig. 5

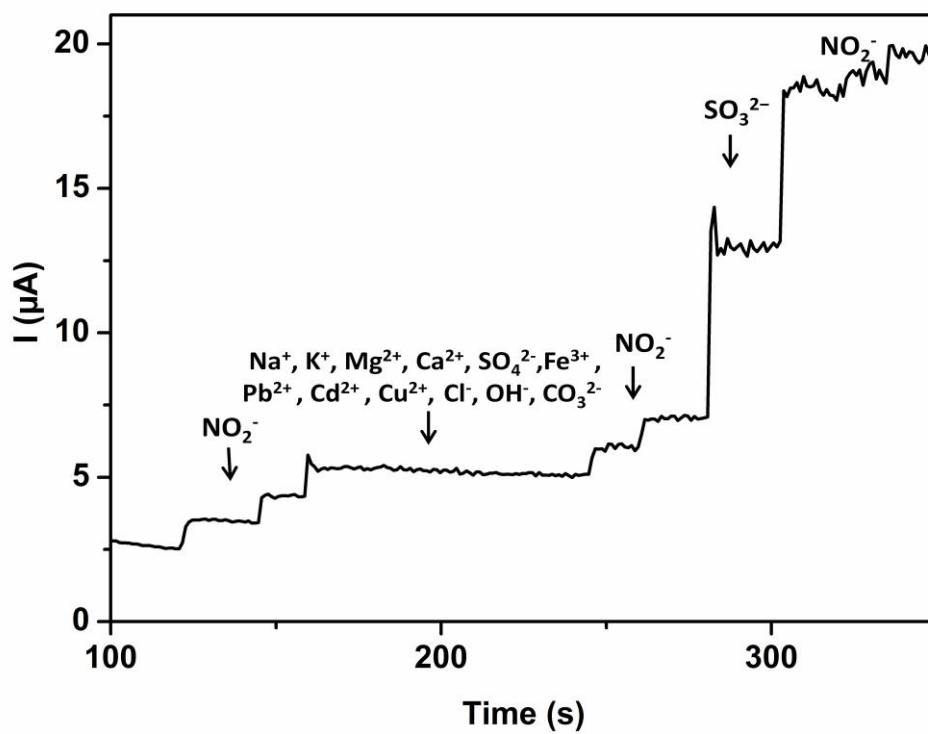


Fig. 6

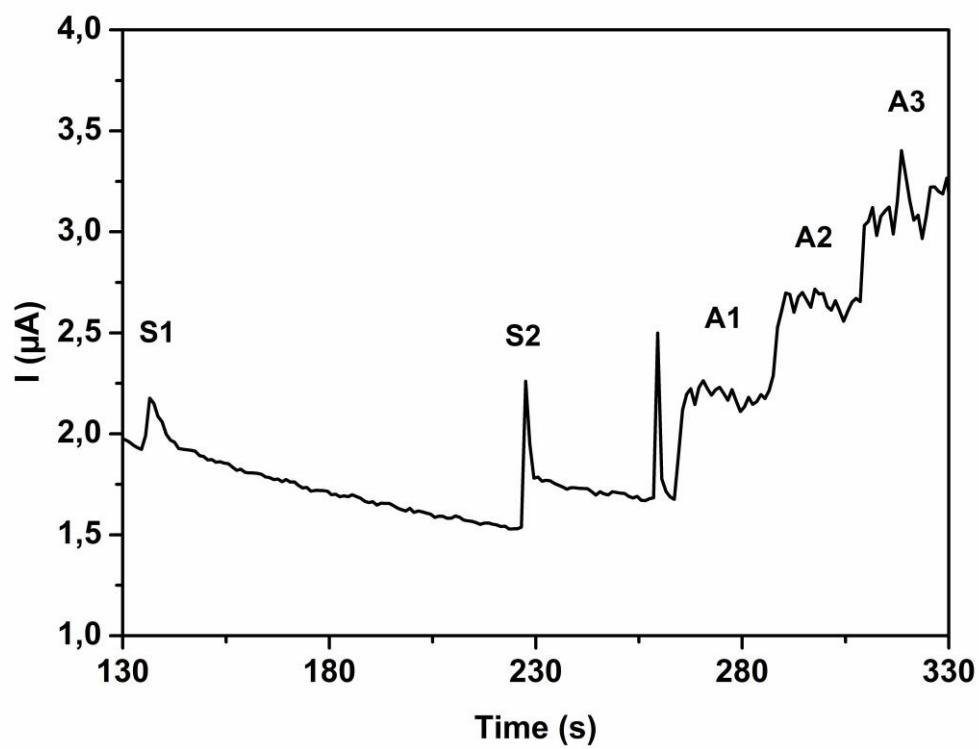
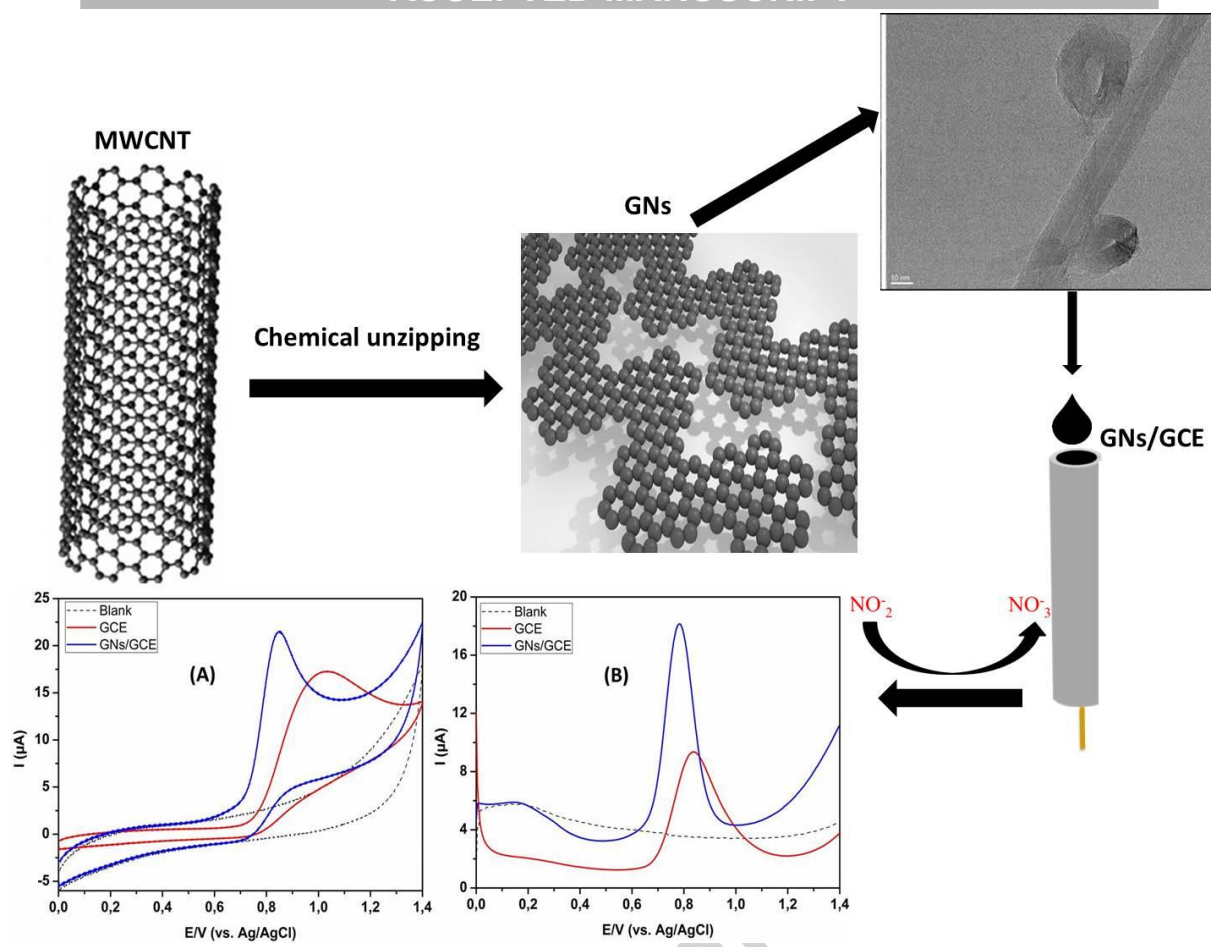


Fig. 7



Graphical Abstract