

Flow Injection Analysis Nitrite Sensor Based on Reduced Graphene Oxide Modified Electrode

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Abstract. Nitrite is one of the most frequently measured analytes in the environmental analysis due to its detrimental effect on the environment. The development of simple and sensitive analytical method for the detection of nitrite is highly important. In this work, the fabrication and testing of nitrite sensor based on the flow injection analysis by reduced graphene oxide modified electrode were reported. The modified electrode exhibits enhanced electro oxidation behavior towards nitrite oxidation. The proposed method has advantages of high precision, lower sample consumption, lower reagent consumption, less dispersion of the sample as well as higher sensitivity.

Introduction

Nitrite is present ubiquitously in soils, waters, foods and physiological systems and it has been reported as a human threat. Nitrite-containing compound has been used in environmental and food industry as an additive and corrosion inhibitor. Due to the toxicity of nitrite, ingestion of this ion can cause serious implications to animal and human health [1-3]. It has been reported that nitrite can damage the nervous system, spleen and kidneys, and has a strong correlation with high cancer level [4].

Many efforts have been made to develop methods for the detection of nitrite such as spectrometry [5], chromatography [6] and spectrophotometry [7]. However, these methods often require complicated and expensive instruments. In spite of that, great attention has been given to electrochemical methods due to their advantages over the conventional methods. In recent years, electrochemical sensing has attracted great attention due to its high sensitivity, rapid response and simplicity [8-10]. Furthermore, electrochemical sensors are especially suitable for detecting nitrite in real time.

For electrochemical sensors, solid electrode materials play an important role in highly sensitive and effective nitrite detection. At present, a variety of solid electrode materials have been used for the construction of nitrite sensors, such as nanoparticles [11], conducting polymers [12], metal oxides [13], etc. In this work, reduced graphene oxide (rGO) modified electrode has been fabricated on screen printed carbon electrode and the modified electrode shows good electro oxidation activity toward the oxidation of nitrite.

Experimental

Reagents.

Graphite powder, sodium nitrite (NaNO_2), sodium phosphate dibasic (Na_2HPO_4) and monosodium phosphate (NaH_2PO_4) were purchased from Sigma-Aldrich, USA. All other chemicals were of analytical grade and used without further purification. The supporting electrolyte used was 0.1 M phosphate buffer solution (PBS) and it was prepared by mixing different proportions of

Na_2HPO_4 and NaH_2PO_4 . Ultrapure water ($> 18\text{M}\Omega$) from a Milli-Q Plus system (Millipore) was used throughout this experiment.

Instruments.

UV-vis absorption spectra were recorded using a GENESYS 10 UV Spectrophotometer (Thermo Scientific). The morphologies and structural of the samples were characterized by JSM-7800F field-emission scanning electron microscopy (JEOL) and JASCO 480 fourier transform infrared spectrometer (FTIR). The electrochemical measurement was carried out with PGSTAT 30 potentiostat (AUTOLAB). Flow injection analysis (FIA) was carried out with Perimax 12/4 peristaltic pump (SPETEC), coupled with the potentiostat.

Reduced graphene oxide modified screen printed carbon electrode.

Graphene oxide (GO) was synthesized from graphite powder by the Hummers' method [14]. The GO reduction was carried out by adding 1.2 ml hydrazine monohydrate into GO solution (60 mg graphene oxide in 50 ml water), heating at 95°C with stirring overnight. rGO was obtained by vacuum filtration, washed with distilled water and dried at 60°C overnight in vacuum. The rGO suspension was prepared by dispersing rGO in ethanol with the aid of ultrasonication. After preparation, $3\mu\text{L}$ of rGO suspension was drop-casted onto the surface of screen printed carbon electrode (DROPSSENS) and dried at room temperature.

Results and discussion

Characterization of rGO.

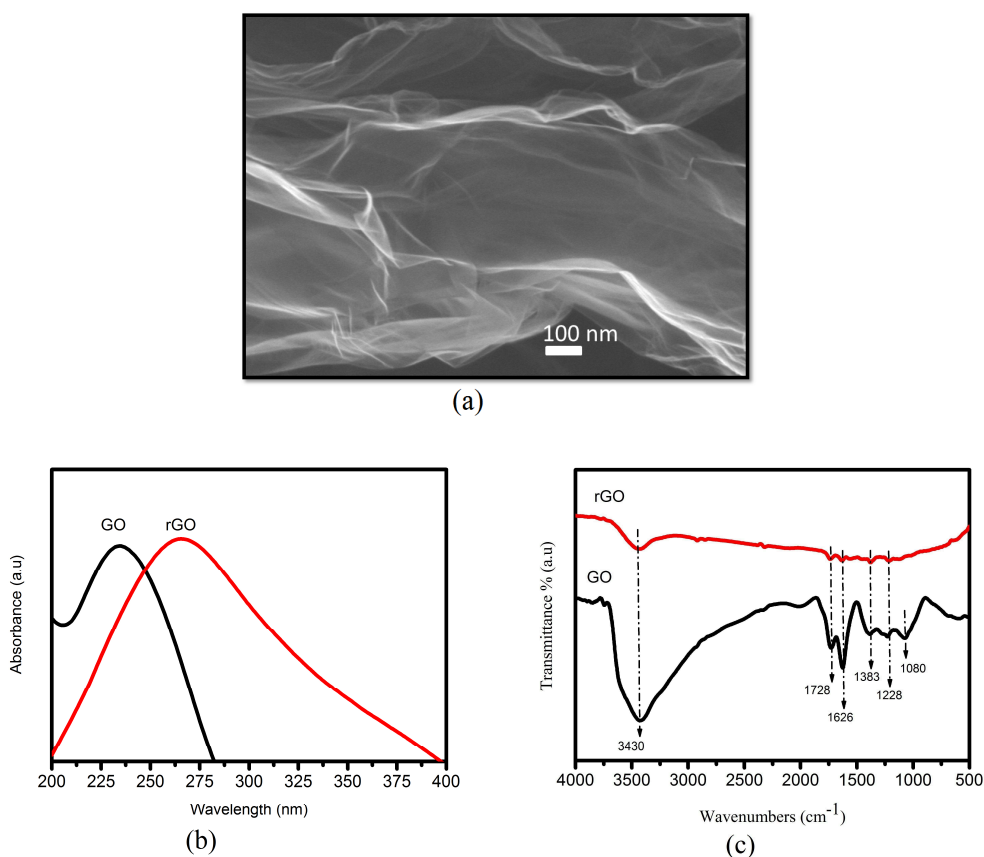


Fig. 1 (a) FESEM image of rGO, (b) UV-vis spectra and (c) FTIR of GO and rGO.

The field emission scanning electron microscope (FESEM) was used to examine the morphology of the rGO. From Fig. 1a, it can be clearly seen the curvy, wrinkled [15] and resemblance of crumpled silk veil waves of rGO structure [16], attributed to the exfoliation treatment during the synthesis process. The UV-vis spectra of GO and rGO are illustrated in Fig. 1b. The strong absorption band observed at 230 nm could be attributed to the π - π transitions of aromatic C=C bonds. After the reduction of GO, the aromatic C=C bonds shifted to 270 nm, indicating the restoration of π -conjugation network. The FTIR spectra of GO and rGO are shown in Fig. 1c. In GO, the peak at 1728 cm^{-1} represents the stretching of C=O of the carboxylic acid group and the stretching vibration peaks of C-O are observed at 1383 , 1228 and 1080 cm^{-1} . Hydroxyl group represents O-H vibration at 3430 cm^{-1} and C=C bonds (C=C stretching) at 1626 cm^{-1} also can be seen. For rGO, the oxygen-related peaks are reduced significantly, indicating the removal of oxygen functional groups on rGO.

Electro oxidation of nitrite

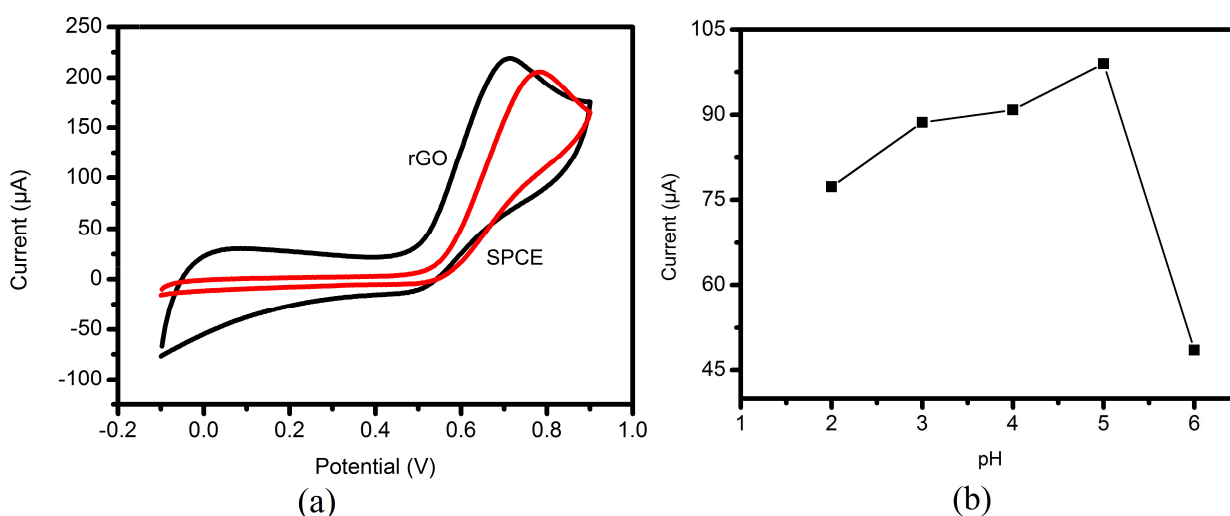


Fig. 2 (a) Cyclic voltammogram recorded at SPCE and rGO modified SPCE in 0.1 M PBS pH 5 containing 1 mM NO_2^- at the scan rate of 100 mV/s. (b) Effect of pH on the oxidation current response of 1mM NO_2^- at rGO modified SPCE.

The electro oxidation response was monitored by cyclic voltammetry in the electrolyte system containing 0.1 M PBS pH 5. Fig. 3a shows the cyclic voltammetry response of bare SPCE and rGO modified SPCE in the presence of 1 mM NO_2^- at scan rate of 100 mV/s. The oxidation peak current increase as compared to bare SPCE and the enhanced nitrite oxidation peak potential is observed at +0.8 V for SPCE and shifted to +0.7 V for rGO. The shifting of 0.1 V on rGO with increase current signal could be attributed to the higher electron mobility on rGO surface that greatly facilitate the oxidation of NO_2^- . pH dependent study was conducted and the results are summarized in Fig. 2b. pH solution in between 2 and 6 were selected as the rate of disproportionation of nitrite is significant as acidic media, according to Eq.1. The peak current densities increase from pH 2 and reach maximum at pH 5 while decrease at pH 6. Hence, pH 5 was selected for the subsequent measurements.



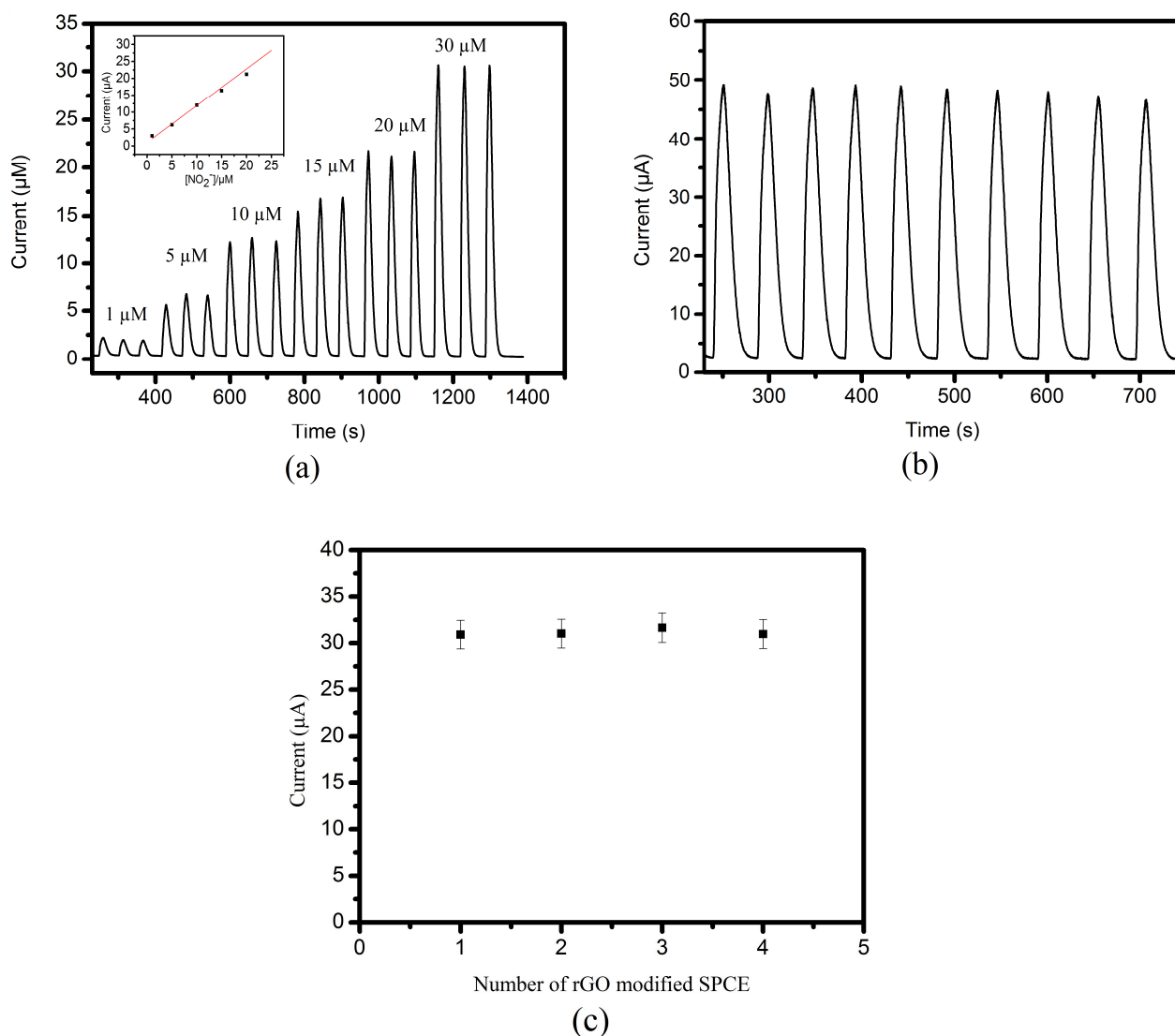
Flow injection analysis determination of NO_2^- 

Fig. 3 (a) Flow injection analysis response of the rGO modified SPCE with increasing NO_2^- concentrations. The inset plots correspond to the calibration graphs. (b) Flow injection analysis response of the ten times for 50.0 μM NO_2^- . (c) Flow injection analysis response of reproducibility of rGO modified SPCE in 30 μM NO_2^- . Supporting electrolyte: 0.1 M PBS pH 5.

Fig. 3a shows the typical flow injection analysis response of the successive injections of different NO_2^- concentrations. The current values obtained at +0.7 V provides a linear relationship with NO_2^- concentrations ranging from 1.0 μM to 30.0 μM (Fig. 3a inset). The limit of detection was calculated as 0.6 μM using the formula $S/N = 3$. The linear regression equation can be expressed as $I (\mu\text{A}) = 1.0873 C (\mu\text{M}) + 1.0237$ and $R^2 = 0.983$.

The repeatability and reproducibility of the rGO modified electrode were evaluated using flow injection analysis for 50.0 μM NO_2^- in PBS pH 5. The relative standard deviation (R. S. D) for 10 repetitive (Fig. 3b) measurements was 1.67 % respectively, validating good repeatability. The reproducibility of the modified electrode was also studied. In Fig. 3c, four newly fabricated electrodes were tested and the relative standard deviation (% RSD) was 1.49%, which reveals the excellent reproducibility.

Summary

In summary, the rGO modified electrode was fabricated and the nitrite oxidation on modified electrode was investigated. The rGO shows promising electrochemical activity toward the oxidation of nitrite. The modified electrode shows the linear response range from 1.0 μM to 30.0 μM with limit of detection is 0.6 μM and also shows good repeatability and reproducibility.

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References

- [1] M. Irandoust, M. Shariati-Rad, M. Haghghi, Nitrite determination in water samples based on a modified Griess reaction and central composite design, *Anal. Methods* 5 (2013) 5977-5982.
- [2] Y. Wang, E. Laborda, R. G. Compton, Electrochemical oxidation of nitrite: Kinetic, mechanistic and analytical study by square wave voltammetry, *J. Electroanal. Chem.* 670 (2012) 56-61.
- [3] C. M. Rushworth, Y. Yogarajah, Y. Zhao, H. Morgan, C. Vallance, Sensitive analysis of trace water analytes using colourimetric cavity ringdown spectroscopy, *Anal. Methods* 5 (2013) 239-247.
- [4] V. L. Souliotis, S. A. Kyrtopoulos, A Novel, Sensitive Assay for O^6 -Methyl- and O^6 -Ethylguanine in DNA, Based on Repair by the Enzyme O^6 -Alkylguanine-DNA-Alkyltransferase in Competition with an Oligonucleotide Containing O^6 -Methylguanine, *Cancer Surv.* 8 (1989) 423-442.
- [5] G.M. Greenway, S.J. Haswell, P.H. Petsul, Characterisation of a micrototal analytical system for the determination of nitrite with spectrophotometric detection, *Anal. Chim. Acta* 387 (1999) 1-10.
- [6] V.D. Matteo, E. Esposito, Methods for the determination of nitrite by high performance liquid chromatography with electrochemical detection, *J. Chromatogr. A* 789 (1997) 213-219.
- [7] K. Horita, G.F. Wang, M. Satake, Column preconcentration analysis spectrophotometric determination of nitrate and nitrite by a diazotization coupling reaction, *Analyst* 122 (1997) 1569-1574.
- [8] N. Zhu, Q. Xu, S. Li, H. Gao, Electrochemical determination of nitrite based on poly(amidoamine) dendrimer-modified carbon nanotubes for nitrite oxidation, *Electrochem. Commun.* 11 (2009) 2308-2311.
- [9] A. Kaushik, R. Khan, P. R. Solanki, P. Pandey, J. Alam, S. Ahmad, B. D. Malhotra, Iron oxide nanoparticles–chitosan composite based glucose biosensor, *Biosens. Bioelectron.* 24 (2008) 676-683.
- [10] P. K. Rastogi, V. Ganesan, S. Krishnamoorthi, A promising electrochemical sensing platform based on a silver nanoparticles decorated copolymer for sensitive nitrite determination, *J. Mater. Chem. A* 2 (2014) 933-943.
- [11] M. Pal, V. Ganesan, Electrochemical determination of nitrite using silver nanoparticles modified electrode, *Analyst* 135 (2010) 2711–2716.
- [12] H. Mao, X. Liu, D. Chao, L. Cui, Y. Li, W. Zhang, C. Wang, Preparation of unique PEDOT nanorods with a couple of cusps tips by reverse interfacial polymerization and their electrocatalytic application to detect nitrite, *J. Mater. Chem.* 20 (2010) 10277–10284.

- [13] Z. Meng, B. Liu, J. Zheng, Electrodeposition of cobalt oxide nanoparticles on carbon nanotubes, and their electrocatalytic properties for nitrite electrooxidation, *Microchim. Act.* 175 (2011) 251–257.
- [14] W. S. Hummers, R. E. Offeman, Preparation of graphite oxide, *J. Am. Chem. Soc.* 80 (1985), 1339-1339.
- [15] H. F. Xu, H. Dai, G. N. Chen, Electrochemistry and electrocatalysis of haemoglobin protein entrapped in graphene and chitosan, *Talanta* 81 (2010) 334-338.
- [16] H. L. Guo, X. F. Wang, Q. Y. Qian, F. B. Wang, X. H. Xia, A green approach to the synthesis of graphene nanosheets, *ACS Nano* 3 (2009) 2653–2659.

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10.4028/www.scientific.net/AMR.1113.411

DOI References

- [1] M. Irandoust, M. Shariati-Rad, M. Haghghi, Nitrite determination in water samples based on a modified Griess reaction and central composite design, *Anal. Methods* 5 (2013) 59775982.
<http://dx.doi.org/10.1039/c3ay40913a>
- [3] C. M. Rushworth, Y. Yogarajah, Y. Zhao, H. Morgan, C. Vallance, Sensitive analysis of trace water analytes using colourimetric cavity ringdown spectroscopy, *Anal. Methods* 5 (2013) 239-247.
<http://dx.doi.org/10.1039/C2AY25889G>
- [5] G.M. Greenway, S.J. Haswell, P.H. Petsul, Characterisation of a micrototal analytical system for the determination of nitrite with spectrophotometric detection, *Anal. Chim. Acta* 387 (1999) 1-10.
[http://dx.doi.org/10.1016/S0003-2670\(99\)00047-1](http://dx.doi.org/10.1016/S0003-2670(99)00047-1)
- [6] V.D. Matteo, E. Esposito, Methods for the determination of nitrite by high performance liquid chromatography with electrochemical detection, *J. Chromatogr. A* 789 (1997) 213219.
[http://dx.doi.org/10.1016/S0021-9673\(97\)00851-0](http://dx.doi.org/10.1016/S0021-9673(97)00851-0)
- [7] K. Horita, G.F. Wang, M. Satake, Column preconcentration analysis spectrophotometric determination of nitrate and nitrite by a diazotization coupling reaction, *Analyst* 122 (1997) 1569-1574.
<http://dx.doi.org/10.1039/a703838k>
- [8] N. Zhu, Q. Xu, S. Li, H. Gao, Electrochemical determination of nitrite based on poly(amidoamine) dendrimer-modified carbon nanotubes for nitrite oxidation, *Electrochem. Commun.* 11 (2009) 2308-2311.
<http://dx.doi.org/10.1016/j.elecom.2009.10.018>
- [9] A. Kaushik, R. Khan, P. R. Solanki, P. Pandey, J. Alam, S. Ahmad, B. D. Malhotra, Iron oxide nanoparticles-chitosan composite based glucose biosensor, *Biosens. Bioelectron.* 24 (2008) 676-683.
<http://dx.doi.org/10.1016/j.bios.2008.06.032>
- [10] P. K. Rastogi, V. Ganesan, S. Krishnamoorthi, A promising electrochemical sensing platform based on a silver nanoparticles decorated copolymer for sensitive nitrite determination, *J. Mater. Chem. A* 2 (2014) 933-943.
<http://dx.doi.org/10.1039/C3TA13794E>
- [11] M. Pal, V. Ganesan, Electrochemical determination of nitrite using silver nanoparticles modified electrode, *Analyst* 135 (2010) 2711-2716.
<http://dx.doi.org/10.1039/c0an00289e>
- [13] Z. Meng, B. Liu, J. Zheng, Electrodeposition of cobalt oxide nanoparticles on carbon nanotubes, and their electrocatalytic properties for nitrite electrooxidation, *Microchim. Acta.* 175 (2011) 251-257.
<http://dx.doi.org/10.1007/s00604-011-0688-y>
- [14] W. S. Hummers, R. E. Offeman, Preparation of graphitix oxide, *J. Am. Chem. Soc.* 80 (1985), 1339-1339.
<http://dx.doi.org/10.1021/ja01539a017>
- [15] H. F. Xu, H. Dai, G. N. Chen, Electrochemistry and electrocatalysis of haemoglobin protein entrapped in graphene and chitosan, *Talanta* 81 (2010) 334-338.
<http://dx.doi.org/10.1016/j.talanta.2009.12.006>
- [16] H. L. Guo, X. F. Wang, Q. Y. Qian, F. B. Wang, X. H. Xia, A green approach to the synthesis of

graphene nanosheets, ACS Nano 3 (2009) 2653–2659.
<http://dx.doi.org/10.1021/nn900227d>