

A promising electrochemical sensing platform based on a graphene nanomaterials for sensitive sulfite determination

Nurulasma Zainudin
Faculty of Industrial Sciences &
Technology
Universiti Malaysia Pahang
Kuantan, Pahang
nurulasma.zainudin@yahoo.com

Mashitah Mohd Yusoff
Faculty of Industrial Sciences &
Technology
Universiti Malaysia Pahang
Kuantan, Pahang
mashitah@ump.edu.my

Kwok Feng Chong
Faculty of Industrial Sciences &
Technology
Universiti Malaysia Pahang
Kuantan, Pahang
ckfeng@ump.edu.my

Abstract—In this work, graphene, as a new electrode material, was used to modify carbon electrode for the simultaneous determination of sulfite (SO_3^{2-}) under neutral conditions. The nanomaterial graphene was characterized by field-emission scanning electron microscopy and fourier transform infrared spectroscopy. Cyclic voltammetry and flow injection analysis were used to study the electrochemical properties of the proposed sensor. Under optimum conditions, the sensor exhibited good reproducibility and repeatability for sulfite determination. Linear response was obtained in the range of 5.0 – 160 μM with a detection limit of 1.0 μM for sulfite determination.

Index Terms—Graphene, sensor, sulfite, flow injection analysis.

I. INTRODUCTION

Recently, graphene, the 2D carbon material has attracted tremendous attention because of its extraordinary electronic and electrocatalytic properties [1]. The important advantages of graphene based materials such as low cost, mass production, high conductivity, large surface area, wide potential window have promoted their further applications [2]. Nanoelectronic biosensors based on graphene have been used for detecting gas molecules [3], metal ions [4] and various biomolecules including DNA [5], glucose [6] and proteins [7].

Researches have been focused on the detection of sulfite due to its potential toxicity but widely used as a preservative in the food and beverage industries. The US Food and Drug Administration regulations have indicated that the sulfite ions contained in food and beverage should not exceed 10 ppm [8]. Besides, sulfite is also used in boilers and boiler-feed waters for dissolved oxygen control. Therefore a simple and effective method for the analysis of sulfite in these products is required. Many analytical methods for the sulfite assay have been reported, such as high performance liquid chromatography [9], capillary electrophoresis [10], chemiluminescence [11] and spectrophotometry [12]. Compared to electrochemical detections, these techniques are not convenient. Therefore, there is still an increasing demand in electrochemical

detections, as these generally have the advantages of simplicity, short analysis time, low cost, high reproducibility, and sensitivity.

In this work, a simple electrochemical approach using a graphene modified carbon electrode by using cyclic voltammetry and flow injection analysis of sulfite were reported. The proposed system is useful for the simultaneous determination of sulfite. Hence, the modified electrode exhibits the following characteristics: cost-effective, simple preparation, high sensitivity, stability and reproducibility.

II. EXPERIMENTAL

A. Reagents.

Graphite powder, sodium sulphite (Na_2SO_3), 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.

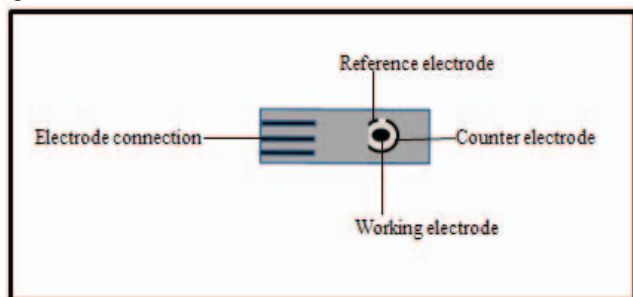
B. Instruments.

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.

C. Graphene modified carbon electrode.

Graphene oxide (GO) was synthesized from graphite powder by the Hummers' method [13]. 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. Graphene was obtained by vacuum filtration, washed with distilled water and dried at 60 °C overnight in vacuum. The graphene suspension was prepared by dispersing graphene in ethanol with the aid of ultrasonication. After preparation, 3 μL of graphene suspension was drop-casted onto the surface of carbon electrode (4 mm diameter) as shown in Scheme 1, and dried at room temperature.



Scheme 1. Schematic illustration of three-electrode carbon electrode system.

III. RESULTS AND DISCUSSION

A. Characterization of graphene

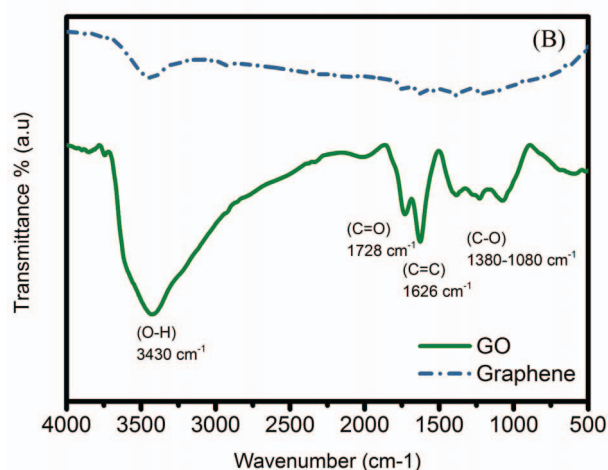
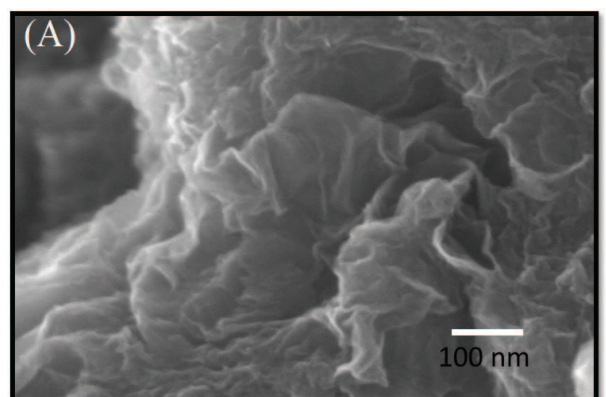


Fig. 1. (A) FESEM image of graphene and (B) FTIR of GO and graphene.

The field emission scanning electron microscope (FESEM) was used to examine the morphology of the graphene. From Fig. 1a, it can be clearly seen the curvy, wrinkled [14] and resemblance of crumpled silk veil waves of graphene structure [15], attributed to the exfoliation treatment during the synthesis process. This expanded morphology is essential in the oxidation process of sulfite as it maximizes the surface area [16]. The FTIR spectra of GO and graphene are shown in Fig. 1b. 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 graphene, the oxygen-related peaks are reduced significantly, indicating the removal of oxygen functional groups on graphene.

B. Electro oxidation of sulfite

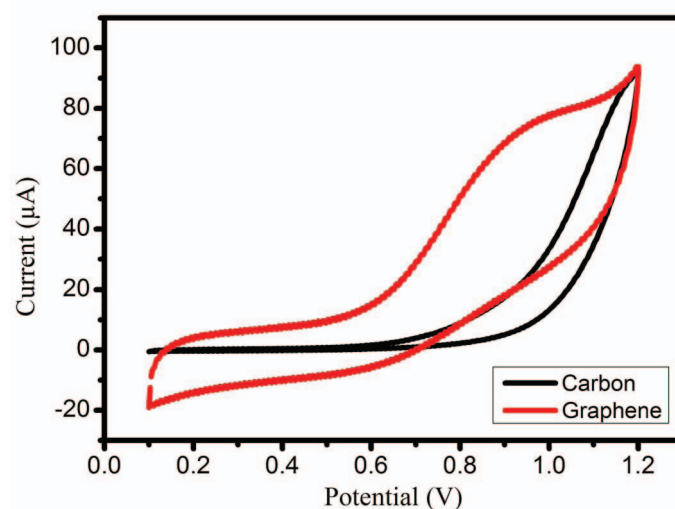


Fig. 2. Cyclic voltammogram recorded at carbon electrode and graphene modified carbon electrode in 0.1 M PBS pH 4 containing 1 mM sulfite at the scan rate of 100 mV/s.

Electrochemical behaviour of graphene modified carbon electrode was studied using cyclic voltammetry. Fig. 2 shows the cyclic voltammograms obtained at (a) carbon electrode and (b) graphene modified carbon electrode in presence of 1 mM sulfite. As shown in Fig. 1(a), no significant oxidation peak was detected at a carbon electrode. In contrast, as shown in Fig. 3(b), a much improved and sharp electrochemical peak at +0.9 V of sulfite oxidation was observed at the graphene modified carbon electrode, which is corresponding to the conversion of SO_3^{2-} to SO_4^{2-} .

C. Flow injection analysis determination of sulfite

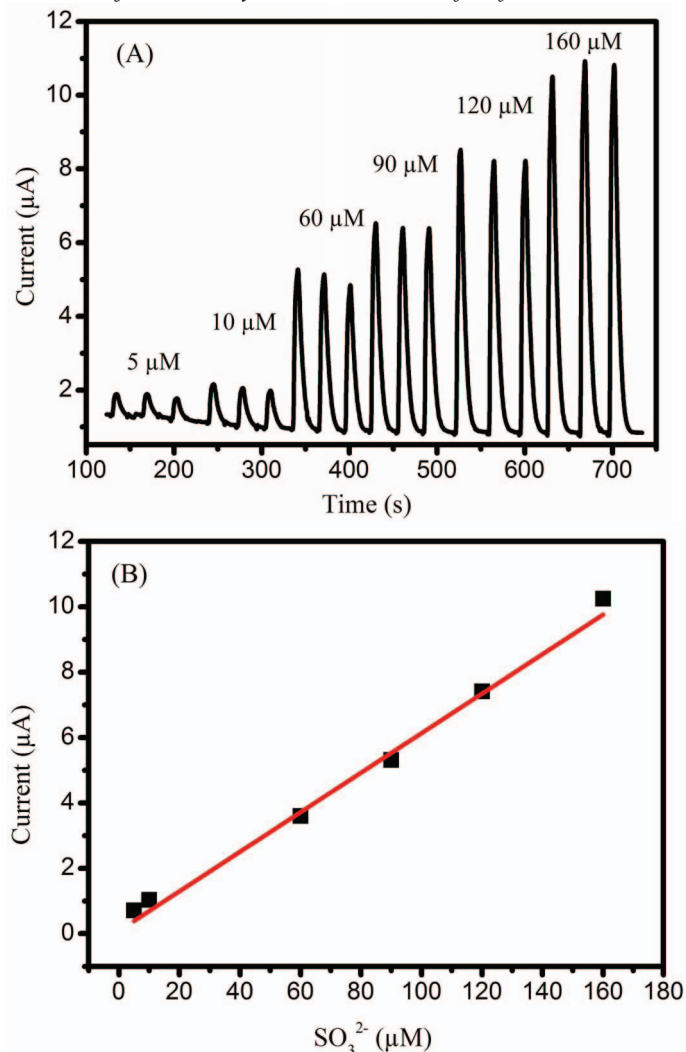


Fig. 3. (A) Flow injection analysis response of the graphene modified carbon electrode with increasing sulfite concentrations and (B) The plots correspond to the calibration graphs.

Fig. 3A shows the typical flow injection analysis response of the successive injections of different sulfite concentrations from 5.0 μM to 160.0 μM. The current values obtained at +0.9 V provides a linear relationship which shows in Fig. 3(B). The limit of detection was calculated as 1.0 μM using the formula $S/N = 3$. The linear regression equation can be expressed as $I (\mu A) = 8.72 C (\mu M) + 6.04$ and $R^2 = 0.987$.

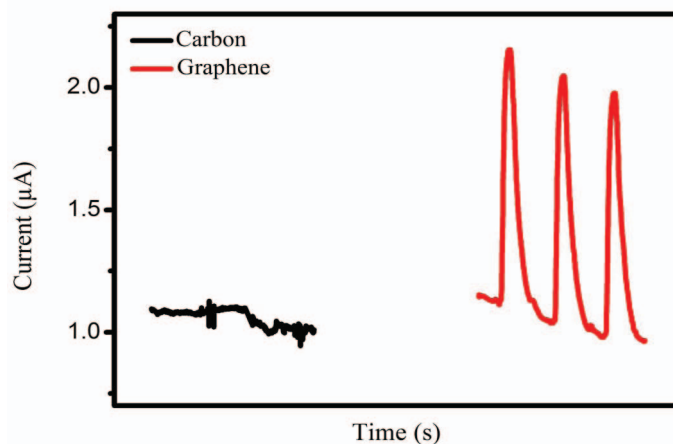


Fig. 4. Flow injection analysis responses of the carbon and graphene modified carbon electrode which perform in 5 μM concentrations of sulfite.

As a comparison, 5 μM aliquots of sulfite were injected into supporting electrolyte solution, 0.1 M PBS (pH 4) and the flow injection analysis responses for carbon and graphene modified carbon electrode were recorded as shown in Fig. 4. There was an obvious signal of current that can be seen for the sulfite aliquots injection on graphene modified, but none on carbon electrode. It indicates that graphene modified carbon electrode really have excellent detection towards sulfite oxidation.

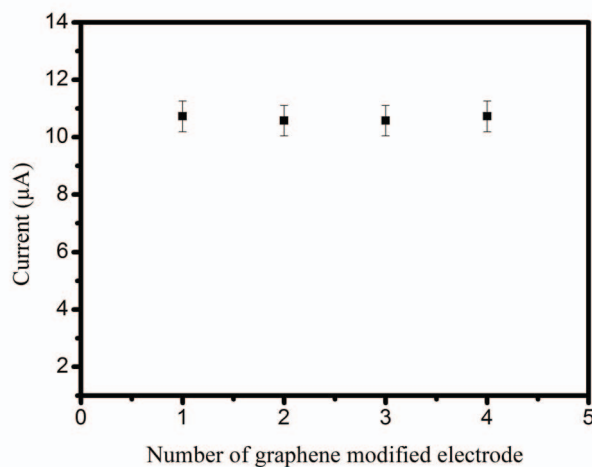


Fig. 5. Flow injection analysis responses of reproducibility of graphene modified carbon electrode in 160.0 μM sulfite.

The fabrication reproducibility of four electrodes, made independently, in Fig. 5, shows an acceptable reproducibility with the % relative standard deviation (R.S.D) was 1.87% for the current determination of 160.0 μM. Thus, the sensors have excellent reproducibility.

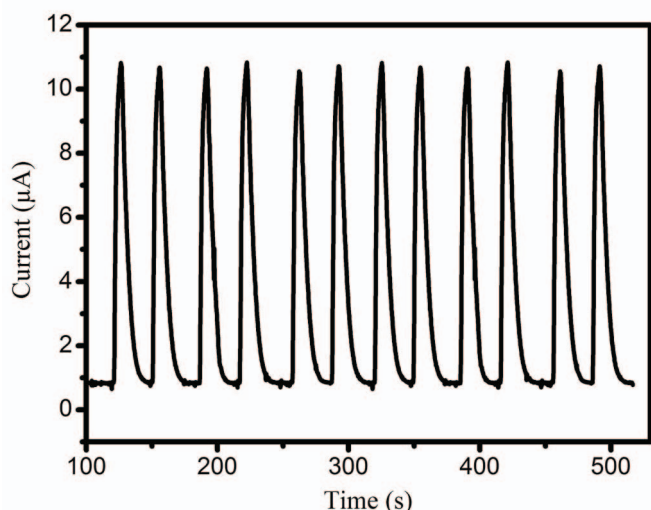


Fig.6. Flow injection analysis response for the twelve times repetitively measurements in 160.0 μM sulfite.

The repeatability of the proposed graphene modified based sensor for the sulfite determination has been evaluated in Fig. 6. The % relative standard deviation (R.S.D) for 12 repetitive measurements (performed in 160 μM nitrite additions) is 1.17%, respectively. This result validates the good repeatability of the proposed nitrite sensor toward determination of nitrite.

IV. CONCLUSIONS

In conclusion, we have demonstrated the feasibility of the graphene electrode for the simultaneous determination of sulfite. By comparison of the responses of sulfite on carbon and graphene electrode, the graphene nanomaterials were found to have favorable activity toward oxidation of sulfite. The oxidation current response at the modified electrode was found to be linearly proportional to the sulfite concentration in the range of 5.0 μM to 160.0 μM with a low detection limit of 1.0 μM . The graphene modified electrode showed excellent sensitivity, reproducibility and repeatability.

ACKNOWLEDGMENT

KF Chong and co-workers would like to acknowledge the funding from Ministry of Education Malaysia (RDU120604 & RDU141309).

REFERENCES

[1] A. K. Geim and K. S. Novoselov, "The Rise of Graphene," *Nat Mater*, vol. 6, pp. 183-191, 2007.
 [2] Y. Shao, J. Wang, H. Wu, J. Liu, I. A. Aksay and Y. Lin, "Graphene Based Electrochemical Sensors and Biosensors," *Electroanal*, vol. 22, pp. 1027-1036, 2010.

[3] G. H. Lu, L. E. Ocola and J. H. Chen, "Reduced graphene oxide for room-temperature gas sensors," *Nanotechnology*, vol. 20, pp. 445502, 2009.
 [4] H. G. Sudibya, Q. Y. He, H. Zhang and P. Chen, "Electrical Detection of Metal Ions Using Field-Effect Transistors Based on Micropatterned Reduced Graphene Oxide Films," *ACS Nano*, vol. 5, pp. 1990-1994, 2011.
 [5] X. C. Dong, Y. M. Shi, W. Huang, P. Chen and L. J. Li, "Electrical Detection of DNA Hybridization with Single-Base Specificity Using Transistors Based on CVD-Grown Graphene Sheets," *Adv. Mater.*, vol. 22, pp. 1649-1653, 2010.
 [6] Y. X. Huang, X. C. Dong, Y. M. Shi, C. M. Li, L. J. Li and P. Chen, "Graphene-based Biosensors for Detection of Bacteria and their Metabolic Activities," *Nanoscale*, vol. 2, pp. 1485-1488, 2010.
 [7] S. Mao, G. H. Lu, K. H. Yu, Z. Bo and J. H. Chen, "Specific Protein Detection Using Thermally Reduced Graphene Oxide Sheet Decorated with Gold Nanoparticle-Antibody Conjugates," *Adv. Mater.*, vol. 22, pp. 3521-3526, 2010.
 [8] F. Register, "Food Label," *Declarat. Sulf. Agents*, vol. 51, pp. 25012-25020, 1986.
 [9] M. Koch, R. Köppen, D. Siegel, A. Witt and I. Nehls, "Determination of total sulfite in wine by ion chromatography after in-sample oxidation," *J. Agric. Food Chem.*, vol. 58, pp. 9463-9467, 2010.
 [10] M. Masár, M. Danková, E. Olvecká, A. Stachurová, D. Kaniánsky and B. Stanislawski, "Determination of Total Sulfite in Wine: Zone Electrophoresis-isotachopheresis Quantitation of Sulfate on a Chip after an In-sample Oxidation of Total Sulfite," *J. Chromatogr. A*, vol. 1084, pp. 101-107, 2005.
 [11] R. L. Bonifácio and N. Coichev, "Chemiluminescent Reaction of Sulphite Auto-oxidation in the Presence of Ni (II)/tetraglycine and Ruthenium (II)/bipy complexes: Mechanistic Considerations," *Luminescence*, vol. 20, pp. 428-434, 2005.
 [12] S. S. M. Hassan, M. S. A. Hamza and A. H. K. A. Mohamed, "A Novel Spectrophotometric Method for Batch and Flow Injection Determination of Sulfite in Beverages," *Anal. Chim. Acta*, vol. 570, pp. 232-239, 2006.
 [13] W. S. Hummers and R. E. Offeman, "Preparation of Graphitic Oxide," *J. Am. Chem. Soc.*, vol. 80, pp. 1339-1339, 1985.
 [14] H. F. Xu, H. Dai, G. N. Chen, "Electrochemistry and Electrocatalysis of Haemoglobin Protein Entrapped in Graphene and Chitosan," *Talanta*, vol. 81, pp. 334-338, 2010.
 [15] 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*, vol. 3, pp. 2653-2659, 2009.
 [16] N. Zainudin, A. R. M. Hairul, M. M. Yusoff, L. L. Tan and K. F. Chong, "Impedimetric Graphene-based Biosensor for the Detection of *Escherichia coli* DNA," *Anal. Methods*, vol. 6, pp. 7935-7941, 2014.