J. Electrochem. Sci. Eng. **13(6)** (2023) 937-948; http://dx.doi.org/10.5599/jese.1966

Open Access : : ISSN 1847-9286
https://pub.iapchem.org/ojs/index.php/JESE

Original scientific paper

Electrocatalytic response of nitrogen-doped hollow carbon spheres modified glassy carbon electrode for sulphite detection in water

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Received: July 15, 2023; Accepted: August 26, 2023; Published: October 25, 2023

Abstract

In this work, the glassy carbon electrode (GCE) surface was modified with nitrogen-doped hollow carbon spheres (N-HCSs) to achieve a new electrochemical sulphite sensor (N-HCSs/GCE) in water samples. The N-HCSs were explored for electrocatalytic behavior through voltammetric approaches using a routine three-electrode system. The findings revealed an admirable efficiency for modified electrodes towards sulphite oxidation, highlighting the effectiveness of our as-produced sulphite sensor. The differential pulse voltammetry was utilized under obtained optimal circumstances to study the as-developed sensor, the results of which underlined linear electrochemical current in relation to sulphite concentration, with dynamic range as wide as 1.0-100.0 µM and limit of detection as narrow as 0.35 µM. Moreover, N-HCSs/GCE had commendable practical applicability for sensing sulphite present in real specimens with voltammetric techniques.

Keywords

Electrochemical sensing; electroanalysis; modified electrodes

Introduction

Sulphite, with its multifaceted function as a preservative, antibacterial, bleaching agent and inhibitor of oxidation and enzyme processes, is widely applied as an additive in the pharmaceutical, beverage and food products within production and storage [1,2]. Sulphites added to vegetables and fruits can prevent rotting and browning and cause food starch to whiten [3]. These substances in pharmaceuticals maintain the strength and stability of some drugs [4]. Correspondingly, sulphite content should be determined and maintained within standard limits to prevent toxicity and adverse effects on human health and the environment [5,6]. Sulphite ions (SO_3^{2-}), as the main constituent of aqueous solutions of sulphur dioxide (SO_2), if found in natural waters, can influence the balance of acid and base, and reduce dissolved

oxygen, thus leading to a harmful impact on aquatic organisms. Excessive levels of sulphite in human body may be accompanied by nettle rash, swelling, headache, diarrhea, nausea, stomach irritation, and asthma episodes [7,8]. The sulphite determination has been carried out previously using diverse methods, including high-performance liquid chromatography [9], spectrophotometry [10], flow injection analysis [11], capillary electrophoresis [12] and electrochemical technique [13-16].

In comparison, electrochemical approaches have been of prominent importance in determination of various electroactive compounds due to their admirable advantages such as time-effectiveness, cost-effectiveness, and facile instrumental demands [17-22]. Glassy carbon (GC) is a form of carbon with a smooth, glass-like surface and a high degree of structural disorder. GC has become an interesting and widely applied inert electrode material in electroanalysis because of its low cost, low background current, electrochemical inertness in a wide potential window, chemical stability, good electrical conductivity, impermeability, high hardness, resistance to fouling, and easy surface modification [23-25]. Reports have shown a positive effect of modifying the electrode surface on increasing the performance of the electrochemical methods [26-29]. Today, thanks to nanomaterials and nanoparticles, nanotechnology has led to various technological advances globally, including nanomedicine, water treatment, catalysis, sensors and energy storage, which can be related to their adjustable physical and chemical properties [30-36]. Hence, various nanomaterials were synthesized in the past decades using different approaches to achieve strong properties in various applications in different fields.

Researchers recently reported the production of many electrocatalytic nanomaterials for the fabrication of electrochemical sensors due to their excellent electrochemical properties, such as specific surface area, chemical stability, and admirable electrical conductivity [37-46]. Carbon-based materials, as modified electrode agents, have recently found a special place for themselves due to their unique properties such as green nature, cost-effectiveness, significant conductivity, wide potential range, and portable modification [47]. For example, hollow carbon spheres (HCSs) are appropriate options as effective catalyst materials in electroanalysis and electrochemical determination, owing to their good conductivity, large specific surface area, high surface permeability, chemical stability, and low density [48-50]. One of the surface modification methods is heteroatom doping, which can improve some properties of HCSs, such as increasing catalytic active sites, electrical conductivity, edge plane defect sites, and induction of synergistic impact [51]. Nitrogen-doped HCSs (N-HCSs) have shown recently commendable electroanalysis behaviours [52,53].

According to the merits mentioned for N-HCSs, the present work developed to construct a new electrochemical sulphite sensing system based on N-HCSs/GCE. The electrochemical performance of sulphite was explored on the surface of both bare GCE and modified N-HCSs/GCE. As-developed N-HCSs could significantly enhance the response of sulphite and decrease the potential of oxidation. The differential pulse voltammetry (DPV) findings revealed the admirable performance of N-HCSs/GCE for sulphite determination, with great sensitivity, broad linear dynamic range and narrow limit of detection (LOD). Moreover, our proposed sensor had commendable practical applicability for sensing sulphite present in real specimens with voltammetric techniques.

Experimental

Equipment

The Autolab PGSTAT 302N electrochemical workstation (Eco Chemie, The Netherlands) with a conventional three-electrode cell was used for all electrochemical studies. The Metrohm -713 Model pH meter's combination glass electrode has been employed to measure pH values.

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Chemicals

Each chemical used in this study was of analytical grade and used exactly as supplied. The Millipore Direct-Q® 8 UV (ultra-violet) device (Millipore, Germany) was utilized to create deionized water utilized during all of the tests. This investigation employed phosphate-buffered solutions (PBS, pH 7.0, 0.1 M). The synthesis and characterization of N-HCSs and related nanostructures have been reported in our previous work [54].

Modification of GCE with N-HCSs

GCE was polished using alumina slurries on a polishing cloth before modification, then rinsed thoroughly with deionized water and dried. In the next step, 1 mg of prepared N-HCSs were suspended in deionized water (1 ml) and subjected to ultrasonication for 20 min to disperse completely. Subsequently, N-HCSs dispersion (3 µL) was gently drop-casted on the electrode surface by using a micropipette and allowed to dry at ambient temperature. Finally, a thin layer of N-HCSs was formed on the surface of GCE (N-HCSs/GCE).

To estimate the electrochemically active surface area (EASA) of unmodified GCE and N-HCSs/GCE, cyclic voltammograms were recorded at different scan rates in 0.1 M KCl solution containing 1.0 mM $K_3[Fe(CN)_6]$ as a redox probe. By using Randles–Ševčik equation, the value of ESCA for N-HCSs/GCE (0.128 cm^2) was 4.1 times greater than unmodified GCE.

Results and discussion

Evaluation of electrocatalytic activity of N-HCSs towards sulphite

In order to explore the impact of PBS's pH value (pH 2.0 to 9.0) on the electrochemical detection of sulphite, DPV analysis was performed. When the current response of sulphite in PBS was compared at various pH levels, pH 7.0 produced the highest peak current of 100.0 µM sulphite (Figure 1). As a result, in subsequent investigations, detection of sulphite was done in 0.1 M PBS (pH 7.0). The electrochemical oxidation reaction of sulphite on N-HCSs/GCE can be expressed as Eq. (1):

$$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^- \quad (1)$$

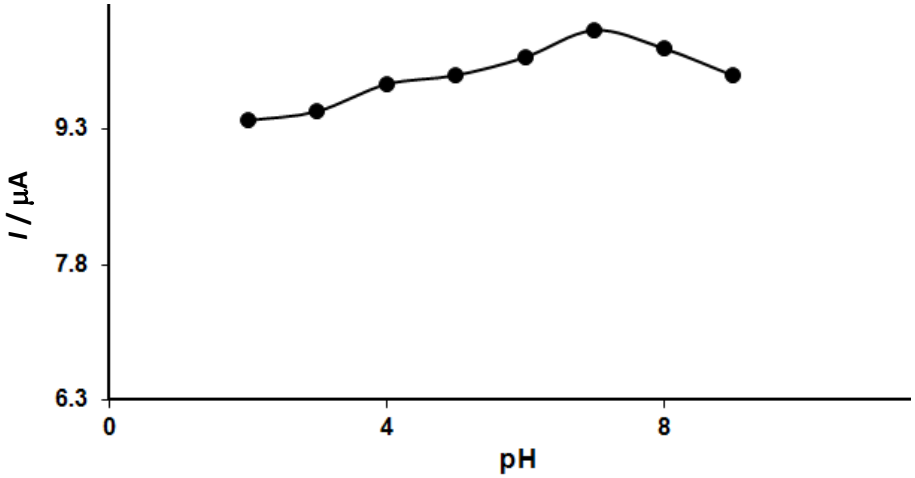

Figure 1. *Plot of* I_p *against pH values of 0.1 M PBS obtained from DPVs in the presence of 100.0 µM sulphite*

The cyclic voltammograms (CVs) recorded for sulphite (100.0 µM) on surfaces of unmodified GCE and N-HCSs/GCE are shown in Figure 2. The oxidation peak current was very low (I_{pa} = 2.25 µA) on unmodified electrode, meaning a weak electrochemical response of unmodified electrode. The I_{pa} increased to 10.4 µA on the N-HCSs/GCE sufface. In addition, sulphite oxidation peak potential (E_{pa})

was decreased from 780 mV (on unmodified GCE surface) to 620 mV (on N-HCSs/GCE surface). These results imply that the catalytic performance of N-HCSs is significant towards sulphite.

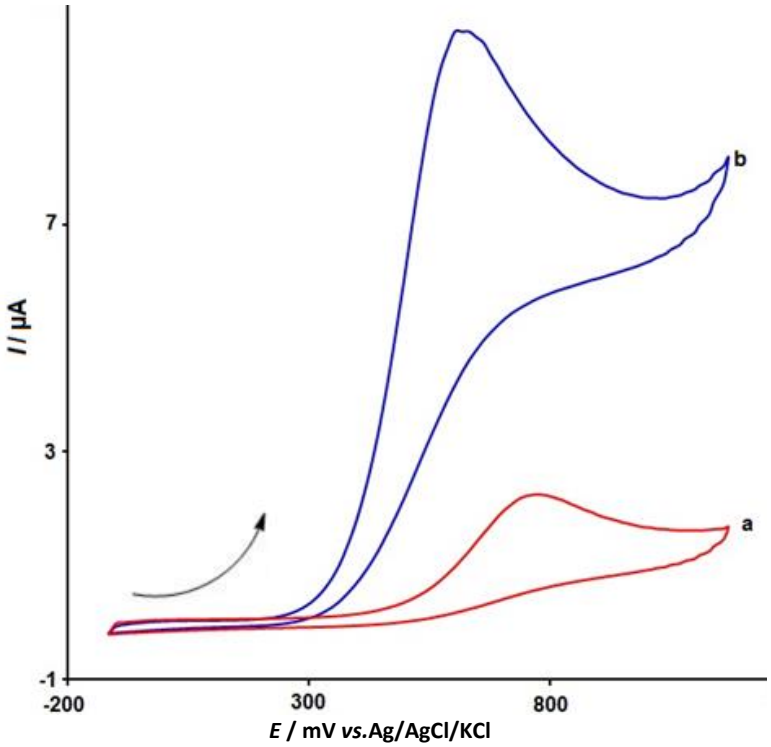

Figure 2. *CVs of unmodified GCE (curve a) and N-HCSs/GCE (curve b) in 0.1 M PBS (pH 7.0) containing 100.0 µM sulphite at scan rate of 50 mV s^{-1}*

Effect of scan rate on oxidation reaction of sulphite

To investigate the effect of scan rate on the oxidation reaction of sulphite, CV responses of 100.0 µM sulphite in 0.1 M PBS (pH 7.0) at different scan rates ranging are recorded (Figure 3).

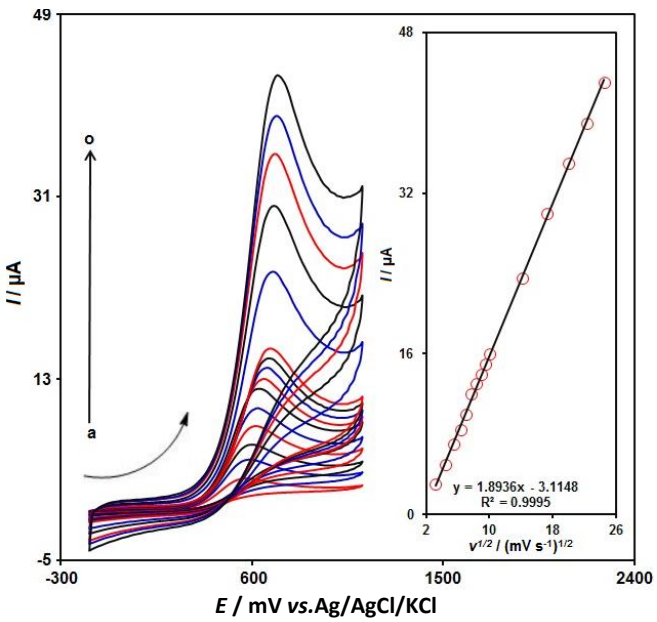

Figure 3. *CV responses of N-HCSs/GCE from a solution of 0.1 M PBS (pH 7.0) and 100.0 µM sulphite at different scan rate (a-o: 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 200, 300, 400, 500 and 600 mV s^{-1}). Inset: Plot of peak currents of sulphite* vs. v$^{1/2}$

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The sulphite's oxidation peak current increases as the scan rate increases. The linearity between oxidation peak currents and the square root of the scan rate ($v^{1/2}$) is depicted in Figure 3 (Inset). With increasing $v^{1/2}$, sulphite oxidation peak currents proportionally increase. This demonstrates that sulphite oxidation reaction on the surface of N-HCSs/GCE is a diffusion-controlled mechanism [55].

Figure 4 (inset) depicts the Tafel plot based on data from the rising section of the current-voltage curve at a scan rate of 10 mV/s for 100.0 µM sulphite to determine the rate-determining step. The role of electrode process kinetics is evident based on the linear relationship of *E* against the log *I* plot, whose slope depends on the number of electrons transferred in the process of rate-determining step. Figure 4 (inset) shows an estimated Tafel slope of 0.1733 V. Therefore, the one-electron transfer process can be seen in the rate-limiting step regarding with the transfer coefficient of α = 0.66 [55].

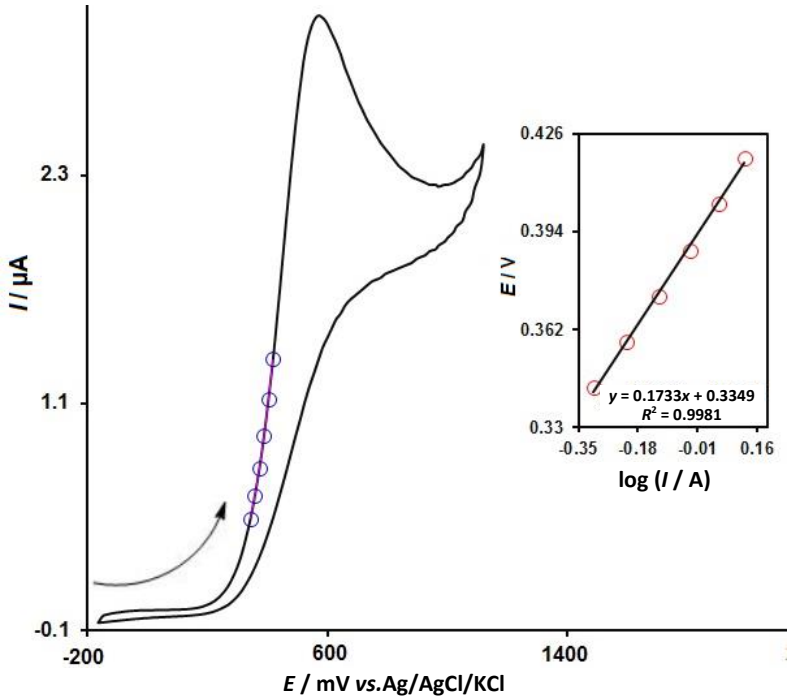

Figure 4. *CV captured from 100.0 µM sulphite at 10 mV s^{-1} scan rate*
Inset: Tafel plot based on rising part of related CV

Chronoamperometric analysis

Using chronoamperometry, the electrochemical reaction of sulphite at N-HCSs/GCE has also been examined. The chronoamperograms of various concentrations of sulphite obtained at a potential step of 660 mV are shown in Figure 5. In chronoamperometric studies, the diffusion coefficient of sulphite was determined. In order to do that, changes in response current were drawn *vs*. $t^{-1/2}$ for different concentrations of sulphite (Figure 5, Inset A). The acquired lines' slopes were plotted against different sulphite concentrations (Figure 5, Inset B). From the slope of the resulting plot and using Cottrell's equation, the diffusion coefficient of sulphite on the surface of N-HCSs/GCE was found to be equal to 4.45×10^{-5} cm^2 s^{-1}. The value of *D* is comparable with values reported in some previous works (1.75×10^{-5} [56], 2.5×10^{-5} [57] and 1.2×10^{-6} cm^2 s^{-1} [58]).

Quantitative determination of sulphite by DPV

Utilizing the DPV method, sulphite oxidation on N-HCSs/GCE was measured. Figure 6 shows DPV results obtained at a modified GCE surface in PBS (pH 7.0, 0.1 M) at sulphite concentrations ranging from 1.0 to 100.0 µM. The constructed sensor's good detection capabilities were demonstrated by increasing oxidation peak currents as sulphite concentration increased. With a coefficient of

determination (R^2) of 0.9996, a plot of sulphite oxidation peak current vs. concentration revealed a perfectly linear response for sulphite ranging from 1.0 to 100.0 µM. The LOD was calculated using this formula: LOD=3S_b/m, S_b represents the standard deviation of response for blank solution (0.1 M PBS) (obtained based on eight measurements) and m denotes slope obtained from linear regression curve. The LOD was calculated to be 0.35 µM. The performance comparison of the developed sensors in this study with previous studies is shown in Table 1. As can be seen, the developed sensor based on N-HCSs/GCE provides the least LOD compared to the other reported sensors (Table 1).

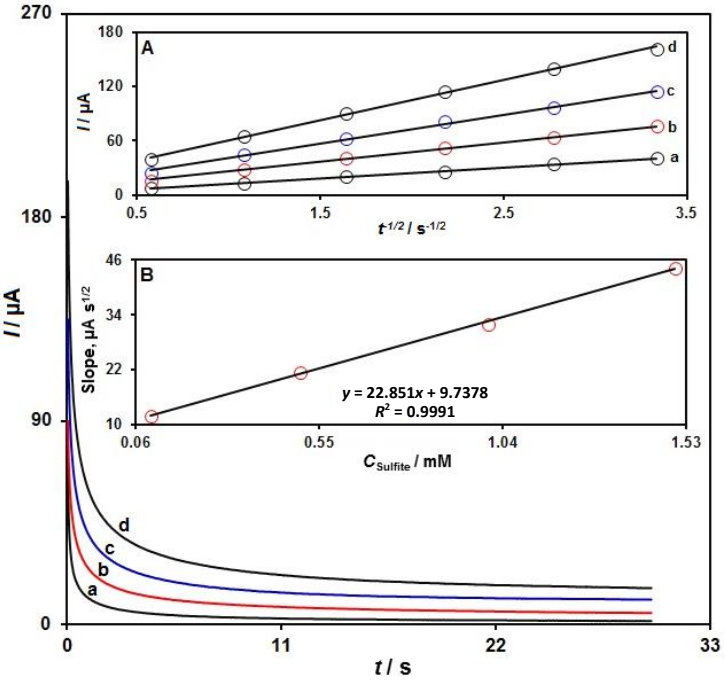

Figure 5. *Single-step chronoamperograms of N-HCSs/GCE sensor in 0.1 M PBS (pH 7.0) with different concentrations of sulphite (a: 0.1, b: 0.5, c: 1.0 and d: 1.5 mM). Insets: Variations of* I vs. $t^{-1/2}$ *taken from chronoamperograms (A) and plot of corresponding slopes against sulphite concentration*

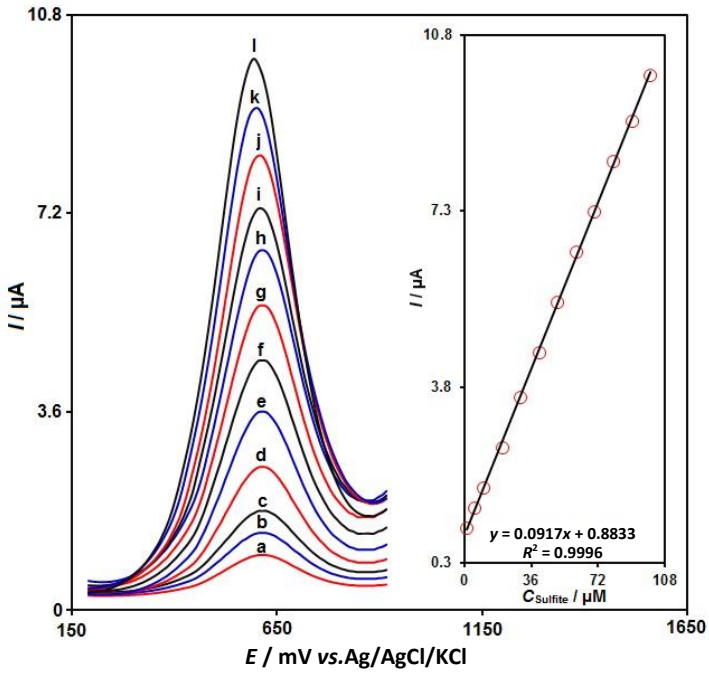

Figure 6. *DPV response at N-HCSs/GCE in 0.1 M PBS (pH 7.0) with different concentrations of sulphite (a-l: 1.0, 5.0, 10.0, 20.0, 30.0, 40.0, 50.0, 60.0, 70.0, 80.0, 90.0 and 100.0 µM)*
Inset: Calibration curve of voltammetric response (I_{pa}) versus sulphite level

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Table 1. *Comparison of N-HCSs/GCE sensor with previously reported sulphite sensors*

Electrochemical sensor	Electrochemical method	Linear range, µM	Limit of detection, µM	Ref.
Multiwalled carbon nano-tubes/carbon paste electrode	Square-wave voltammetry	25-500	16	[2]
MIL-101(Cr) metal-organic framework/CPE	Amperometry	2-70	0.58	[13]
Lutetium (III) hexacyanoferrate microparticles/poly(taurine)/GCE	DPV	-	1.33	[14]
MoS_2 flakes/Nafion/GCE	DPV	5-500	3.3	[15]
CuO nanosheet/GCE	DPV	50-1600	21.10	[16]
N-HCSs/GCE	DPV	1.0-100.0	0.35	This work

Stability, repeatability, and reproducibility studies of N-HCSs/GCE toward determination of sulphite

The stability of the prepared sensor was investigated by examining the current response of N-HCSs/GCE towards sulphite (70.0 µM) every five days over 20 days (stored at ambient temperature). The prepared sensor exhibited only a slight decrease (4.8 %) in the last current response from its original current response after 20 days of storage. To investigate repeatability of N-HCSs/GCE sensor, measurements were repeated in 0.1 M PBS (pH 7.0) containing 70.0 µM sulphite. The acceptable repeatability was obtained with relative standard deviation (RSD) of 3.6 % after using the same sensor for six continuous measurements. The reproducibility of the prepared sensor was also investigated by observing the current response of four electrodes (N-HCSs/GCE) prepared independently under the same conditions. All four prepared electrodes showed a similar response, and RSD was 3.9 % in the determination of sulphite (70.0 µM). These finding verifies that prepared N-HCSs/GCE has good storage stability, reproducibility, and repeatability towards sulphite sensing.

Real sample analysis

To verify the practical application of N-HCSs/GCE for sulphite electrochemical detecting, real water matrices, including tap water and well water, were analysed using the standard addition method. The sulphite oxidation peak currents were determined using the DPV method after adding various known concentrations of sulphite to water samples. The analytical findings are shown in Table 2. According to findings, sulphite recoveries for various water samples ranged from 97.5 to 103.3 %, and RSDs for five consecutive tests were below 3.5 %. These findings show that N-HCSs are a superior material for sulphite sensing in real sample analysis.

Table 2. *Estimation of sulphite in water samples using N-HCSs/GCE (n = 5)*

Sample	Spiked concentration, µM	Found concentration, µM	Recovery, %	RSD, %
Tap water	4.0	3.9	97.5	3.2
	6.0	6.2	103.3	1.7
	8.0	7.9	98.7	3.0
	10.0	10.1	101.0	2.1
Well water	5.0	5.1	102.0	1.9
	7.0	6.9	98.6	2.7
	9.0	8.8	97.8	3.5
	11.0	10.9	99.1	2.2

Conclusion

The current research reported a facile and sensitive electrochemical sulphite sensor using a N-HCSs-modified GCE. Electrochemical investigations by CV showed a considerable increase in current intensity and a decrease in the over-potential for sulphite on N-HCSs/GCE compared with unmodified GCE. The as-developed electrode exhibited a linear response to sulphite with a dynamic

concentration range as wide as 1.0-100.0 µM with a limit of detection as narrow as 0.35 µM. Also, the repeatability, stability, and reproducibility of N-HCSs/GCE sensors were studied and provided good characteristics. Moreover, N-HCSs/GCE had successful applicability for sensing sulphite in real specimens. The good precision (RSD ≤ 3.5 %) and accuracy (recovery for spiked samples ranging from 97.5 to 103.3 %) were obtained.

References

[1] H. Vally, N. L. A. Misso, V. Madan, Clinical effects of sulphite additives, *Clinical & Experimental Allergy* **39** (2009) 1643-1651. https://doi.org/10.1111/j.1365-2222.2009.03362.x

[2] E. M. Silva, R. M. Takeuchi, A. L. Santos, Carbon nanotubes for voltammetric determination of sulphite in some beverages, *Food Chemistry* **173** (2015) 763-769. https://doi.org/10.1016/j.foodchem.2014.10.106

[3] C. S. Pundir, R. Rawal, Determination of sulfite with emphasis on biosensing methods: a review, *Analytical and Bioanalytical Chemistry* **405** (2013) 3049-3062. https://doi.org/10.1007/s00216-013-6753-0

[4] W. A. Adeosun, A. M. Asiri, H. M. Marwani, Fabrication of conductive polypyrrole doped chitosan thin film for sensitive detection of sulfite in real food and biological samples, *Electroanalysis* **32** (2020) 1725-1736. https://doi.org/10.1002/elan.201900765

[5] P. Manusha, S. Senthilkumar, Design and synthesis of phenothiazine based imidazolium ionic liquid for electrochemical nonenzymatic detection of sulfite in food samples, *Journal of Molecular Liquids* **301** (2020) 112412. https://doi.org/10.1016/j.molliq.2019.112412

[6] M. Y. Guo, L. G. Wei, J. W. Shen, X. J. Liu, M. Abbas, Y. S. Yang, H. L. Zhu, A fluorescent probe derived from benzofuranone for turn-on detection of sulfite in living cells and mice, *Dyes and Pigments* **202** (2022) 110261. https://doi.org/10.1016/j.dyepig.2022.110261

[7] M. Zhang, Y. Yang, W. Guo, Electrochemical sensor for sensitive nitrite and sulfite detection in milk based on acid-treated Fe_3O_4@SiO_2 nanoparticles, *Food Chemistry* **403** (2023) 137004. https://doi.org/10.1016/j.foodchem.2023.137004

[8] S. S. Hassan, M. S. Hamza, A. H. Mohamed, A novel spectrophotometric method for batch and flow injection determination of sulfite in beverages, *Analytica Chimica Acta* **570** (2006) 232-239. https://doi.org/10.1016/j.aca.2006.04.030

[9] L. Yang, G. Hu, Y. Huang, C. Wang, X. Liu, C. Lu, G. Ma, Simple and sensitive determination of sulfites in Chinese herbal teas by ultrahigh-performance liquid chromatography tandem mass spectrometry, *Analytical Methods* **14** (2022) 2849-2856. https://doi.org/10.1039/D2AY00759B

[10] P. D. Tzanavaras, E. Thiakouli, D. G. Themelis, Hybrid sequential injection–flow injection manifold for the spectrophotometric determination of total sulfite in wines using o-phthalaldehyde and gas-diffusion, *Talanta* **77** (2009) 1614-1619. https://doi.org/10.1016/j.talanta.2008.09.051

[11] X. Su, W. Wei, Flow injection determination of sulfite in wines and fruit juices by using a bulk acoustic wave impedance sensor coupled to a membrane separation technique, *Analyst* **123** (1998) 221-224. https://doi.org/10.1039/A706727E

[12] G. Jankovskiene, Z. Daunoravicius, A. Padarauskas, Capillary electrophoretic determination of sulfite using the zone-passing technique of in-capillary derivatization, *Journal of Chromatography A* **934** (2001) 67-73. https://doi.org/10.1016/S0021-9673(01)01295-x

[13] R. T. Massah, T. J. M. M. Ntep, E. Njanja, S. L. Z. Jiokeng, J. Liang, C. Janiak, I. K. Tonle, A metal-organic framework-based amperometric sensor for the sensitive determination of sulfite ions in the presence of ascorbic acid, *Microchemical Journal* **169** (2021) 106569. https://doi.org/10.1016/j.microc.2021.106569

(cc) BY

[14] K. Pandi, M. Sivakumar, S. M. Chen, M. Sakthivel, G. Raghavi, T. W. Chen, R. Madhu, Electrochemical synthesis of lutetium (III) hexacyanoferrate/poly (taurine) modified glassy carbon electrode for the sensitive detection of sulfite in tap water, *Journal of The Electrochemical Society* **165** (2018) B469-8474. https://doi.org/10.1149/2.1171810jes

[15] J. Yang, X. Xu, X. Mao, L. Jiang, X. Wang, An electrochemical sensor for determination of sulfite (SO_3^{2-}) in water based on molybdenum disulfide flakes/nafion modified electrode, *International Journal of Electrochemical Science* **15** (2020) 10304-10314. https://doi.org/10.20964/2020.10.48

[16] V. Sudha, K. Krishnamoorthy, S. M. S. Kumar, R. Thangamuthu, Copper oxide nanosheet modified electrodes for simultaneous determination of environmentally hazardous anions, *Journal of Alloys and Compounds* **764** (2018) 959-968. https://doi.org/10.1016/j.jallcom.2018.06.077

[17] S. Tajik, H. Beitollahi, H. W. Jang, M. Shokouhimehr, A screen printed electrode modified with Fe_3O_4@polypyrrole-Pt core-shell nanoparticles for electrochemical detection of 6-mercaptopurine and 6-thioguanine, *Talanta* **232** (2021) 122379. https://doi.org/10.1016/j.talanta.2021.122379

[18] R. S. Kumar, G. K. Jayaprakash, S. Manjappa, M. Kumar, A. P. Kumar, Theoretical and electrochemical analysis of L-serine modified graphite paste electrode for dopamine sensing applications in real samples, *Journal of Electrochemical Science and Engineering* **12** (2022) 1243-1250. https://doi.org/10.5599/jese.1390

[19] G. K. Jayaprakash, B. E. K. Swamy, S. C. Sharma, J. J. Santoyo-Flores, Analyzing electron transfer properties of ferrocene in gasoline by cyclic voltammetry and theoretical methods, *Microchemical Journal* **158** (2020) 105116. https://doi.org/10.1016/j.microc.2020.105116

[20] G. K. Jayaprakash, B. K. Swamy, H. N. G. Ramírez, M. T. Ekanthappa, R. Flores-Moreno, Quantum chemical and electrochemical studies of lysine modified carbon paste electrode surfaces for sensing dopamine, *New Journal of Chemistry* **42** (2018) 4501-4506. https://doi.org/10.1039/C7NJ04998F

[21] J. Mohanraj, D. Durgalakshmi, R. A. Rakkesh, S. Balakumar, S. Rajendran, H. Karimi-Maleh, Facile synthesis of paper based graphene electrodes for point of care devices: A double stranded DNA (dsDNA) biosensor, *Journal of Colloid and Interface Science* **566** (2020) 463-472. https://doi.org/10.1016/j.jcis.2020.01.089

[22] H. Karimi-Maleh, Y. Liu, Z. Li, R. Darabi, Y. Orooji, C. Karaman, F. Karimi, M. Baghayeri, J. Rouhi, L. Fu, Calf thymus ds-DNA intercalation with pendimethalin herbicide at the surface of ZIF-8/Co/rGO/C_3N_4/ds-DNA/SPCE; A bio-sensing approach for pendimethalin quantification confirmed by molecular docking study, *Chemosphere* **332** (2023) 138815. https://doi.org/10.1016/j.chemosphere.2023.138815

[23] A. M. Abdel-Aziz, H. H. Hassan, I. H. Badr, Glassy carbon electrode electromodification in the presence of organic monomers: electropolymerization versus activation, *Analytical Chemistry* **92** (2020) 7947-7954. https://doi.org/10.1021/acs.analchem.0c01337

[24] L. Huang, R. Su, F. Xi, Sensitive detection of noradrenaline in human whole blood based on Au nanoparticles embedded vertically-ordered silica nanochannels modified pre-activated glassy carbon electrodes, *Frontiers in Chemistry* **11** (2023) 1126213. https://doi.org/10.3389/fchem.2023.1126213

[25] B. Shobana, L. Gayathri, P. S. Kumar, P. Prakash, Nonenzymatic interference free nano-molar range detection of L-tyrosine in human serum and urine samples using carbon dots doped cerium titanate modified glassy carbon electrode, *Microchemical Journal* **193** (2023) 109116. https://doi.org/10.1016/j.microc.2023.109116

[26] J. A. Buledi, N. Mahar, A. Mallah, A. R. Solangi, I. M. Palabiyik, N. Qambrani, F. Karimi, Y. Vasseghian, H. Karimi-Maleh, Electrochemical quantification of mancozeb through tungsten

oxide/reduced graphene oxide nanocomposite: a potential method for environmental remediation, *Food and Chemical Toxicology* **161** (2022) 112843. https://doi.org/10.1016/j.fct.2022.112843

[27] A. Hosseini Fakhrabad, R. Sanavi Khoshnood, M.R. Abedi, M. Ebrahimi, Fabrication a composite carbon paste electrodes (CPEs) modified with multi-wall carbon nano-tubes (MWCNTs/N, N-Bis (salicyliden)-1,3-propandiamine) for determination of lanthanum (III), *Eurasian Chemical Communications* **3** (2021) 627-634. https://doi.org/10.22034/ecc.2021.288271.1182

[28] H. Peyman, H. Roshanfekr, A. Babakhanian, H. Jafari, PVC membrane electrode modified by lawson as synthetic derivative ionophore for determination of cadmium in alloy and wastewater, *Chemical Methodologies* **5** (2021) 446-453. https://doi.org/10.22034/chemm.2021.135266

[29] S. Tajik, Y. Orooji, F. Karimi, Z. Ghazanfari, H. Beitollahi, M. Shokouhimehr, H. W. Jang, High performance of screen-printed graphite electrode modified with Ni–Mo-MOF for voltammetric determination of amaranth, *Journal of Food Measurement and Characterization* **15** (2021) 4617-4622. https://doi.org/10.1007/s11694-021-01027-0

[30] V. Tallapaneni, L. Mude, D. Pamu, V. V. S. R. Karri, Formulation, characterization and in vitro evaluation of dual-drug loaded biomimetic chitosan-collagen hybrid nanocomposite scaffolds, *Journal of Medicinal and Chemical Sciences* **5** (2022) 1059-1074. https://doi.org/10.26655/JMCHEMSCI.2022.6.19

[31] S. Karimi, H. Namazi, Fe_3O_4@PEG-coated dendrimer modified graphene oxide nanocomposite as a pH-sensitive drug carrier for targeted delivery of doxorubicin, *Journal of Alloys and Compounds* **879** (2021) 160426. https://doi.org/10.1016/j.jallcom.2021.160426

[32] C. Karaman, O. Karaman, P. L. Show, Y. Orooji, H. Karimi-Maleh, Utilization of a double-cross-linked amino-functionalized three-dimensional graphene networks as a monolithic adsorbent for methyl orange removal: equilibrium, kinetics, thermodynamics and artificial neural network modeling, *Environmental Research* **207** (2021) 112156. https://doi.org/10.1016/j.envres.2021.112156

[33] R. Han, L. Guan, S. Zhang, Y. Lin, J. Tao, Boosted cycling stability of CoP nano-needles based hybrid supercapacitor with high energy density upon surface phosphorization, *Electrochimica Acta* **368** (2021) 137690. https://doi.org/10.1016/j.electacta.2020.137690

[34] S. Janitabar Darzi, H. Bastami, Au decorated mesoporous TiO_2 as a high performance photocatalyst towards crystal violet dye, *Advanced Journal of Chemistry-Section A* **5** (2022) 22-30. https://doi.org/10.22034/ajca.2022.305643.1281

[35] H. Zu, D. Gao, Non-viral vectors in gene therapy: Recent development, challenges, and prospects. *The AAPS Journal* **23** (2021) 78. https://doi.org/10.1208/s12248-021-00608-7

[36] F. M. Nareetsile, T. P. Matshwele, S. Odisitse, Metallo-drugs as promising antibacterial agents and their modes of action, *Journal of Medicinal and Chemical Sciences* **5** (2022) 1109-1131. https://doi.org/10.26655/JMCHEMSCI.2022.6.24

[37] H. Beitollahi, F. Garkani-Nejad, Z. Dourandish, S. Tajik, A novel voltammetric amaranth sensor based on screen printed electrode modified with polypyrrole nanotubes, *Environmental Research* **214** (2022) 113725. https://doi.org/10.1016/j.envres.2022.113725

[38] G. Jeevanandham, K. Vediappan, Z. A. ALOthman, T. Altalhi, A. K. Sundramoorthy, Fabrication of 2D-$MoSe_2$ incorporated NiO Nanorods modified electrode for selective detection of glucose in serum samples, *Scientific Reports* **11** (2021) 13266. https://doi.org/10.1038/s41598-021-92620-2

[39] H. Karimi-Maleh, C. T. Fakude, N. Mabuba, G. M. Peleyeju, O. A. Arotiba, The determination of 2-phenylphenol in the presence of 4-chlorophenol using nano-Fe_3O_4/ionic liquid paste

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electrode as an electrochemical sensor, *Journal of Colloid and Interface Science* **554** (2019) 603-610. https://doi.org/10.1016/j.jcis.2019.07.047

[40] H. Beitollahi, H. Mahmoudi-Moghaddam, S. Tajik, Voltammetric determination of bisphenol A in water and juice using a lanthanum (III)-doped cobalt (II, III) nanocube modified carbon screen-printed electrode, *Analytical Letters* **52** (2019) 1432-1444. https://doi.org/10.1080/00032719.2018.1545132

[41] S. Saghiri, M. Ebrahimi, M. R. Bozorgmehr, Electrochemical amplified sensor with MgO nanoparticle and ionic liquid: a powerful strategy for methyldopa analysis, *Chemical Methodologies* **5** (2021) 234-239. https://doi.org/10.22034/chemm.2021.128530

[42] H. Roshanfekr, A simple specific dopamine aptasensor based on partially reduced graphene oxide–AuNPs composite, *Progress in Chemical and Biochemical Research* **6** (2023) 61-70. https://doi.org/10.22034/pcbr.2023.381280.1245

[43] A. M. Attaran, S. Abdol-Manafi, M. Javanbakht, M. Enhessari, Voltammetric sensor based on Co_3O_4/SnO_2 nanopowders for determination of diltiazem in tablets and biological fluids, *Journal of Nanostructure in Chemistry* **6** (2016) 121–128. https://doi.org/10.1007/s40097-015-0186-6

[44] M. Bijad, H. Karimi-Maleh, M. Farsi, S. A. Shahidi, An electrochemical-amplified-platform based on the nanostructure voltammetric sensor for the determination of carmoisine in the presence of tartrazine in dried fruit and soft drink samples, *Journal of Food Measurement and Characterization* **12** (2018) 634-640. https://doi.org/10.1007/s11694-017-9676-1

[45] S. Tajik, M. R. Aflatoonian, H. Beitollahi, I. Sheikhshoaie, Z. Dourandish, F. Garkani-Nejad, M. Bamorovat, Electrocatalytic oxidation and selective voltammetric detection of methyldopa in the presence of hydrochlorothiazide in real samples, *Microchemical Journal* **158** (2020) 105182. https://doi.org/10.1016/j.microc.2020.105182

[46] H. Karimi-Maleh, R. Darabi, F. Karimi, C. Karaman, S. A. Shahidi, N. Zare, M. Baghayeri, L. Fu, S. Rostamnia, J. Rouhi, State-of-art advances on removal, degradation and electrochemical monitoring of 4-aminophenol pollutants in real samples: A review, *Environmental Research* **222** (2023) 115338. https://doi.org/10.1016/j.envres.2023.115338

[47] A. C. Power, B. Gorey, S. Chandra, J. Chapman, Carbon nanomaterials and their application to electrochemical sensors: a review, *Nanotechnology Reviews* **7** (2018) 19-41. https://doi.org/10.1515/ntrev-2017-0160

[48] M. Liu, Q. Guan, S. Liu, Nitrogen-doped hollow carbon spheres for electrochemical detection of heavy metal ions, *Ionics* **24** (2018) 2783-2793. https://doi.org/10.1007/s11581-017-2390-5

[49] Y. Wang, Q. Dai, L. Yang, Y. Liu, C. Yu, C. Yao, X. Xu, One-pot and surfactant-free synthesis of N-doped mesoporous carbon spheres for the sensitive and selective screening of small biomolecules, *Journal of Electroanalytical Chemistry* **873** (2020) 114462. https://doi.org/10.1016/j.jelechem.2020.114462

[50] M. Liu, T. Zhang, H. Ren, L. Wang, T. Meng, J. Zhao, Y. Zhang, Nitrogen-doped hollow carbon nanospheres for highly sensitive electrochemical sensing of nitrobenzene, *Materials Research Bulletin* **104** (2018) 15-19. https://doi.org/10.1016/j.materresbull.2018.04.005

[51] H. Yang, S. Li, H. Yu, F. Zheng, L. Lin, J. Chen, Y. Lin, In situ construction of hollow carbon spheres with N, Co, and Fe co-doping as electrochemical sensors for simultaneous determination of dihydroxybenzene isomers, *Nanoscale* **11** (2019) 8950-8958. https://doi.org/10.1039/C9NR01146C

[52] C. Peng, S. Zhou, X. Zhang, T. Zeng, W. Zhang, H. Li, P. Zhao, One pot synthesis of nitrogen-doped hollow carbon spheres with improved electrocatalytic properties for sensitive H_2O_2

sensing in human serum. *Sensors and Actuators B* **270** (2018) 530-537. https://doi.org/10.1016/j.snb.2018.05.036

[53] W. Long, Y. Xie, H. Shi, J. Ying, J. Yang, Y. Huang, L. Fu, Preparation of nitrogen-doped hollow carbon spheres for sensitive catechol electrochemical sensing, *Fullerenes, Nanotubes and Carbon Nanostructures* **26** (2018) 856-862. https://doi.org/10.1080/1536383X.2018.1512973

[54] S. Tajik, F. Sharifi, H. Beitollahi, Differential pulse voltammetric analysis of hydrazine in water samples by using screen-printed graphite electrode modified with nitrogen-doped hollow carbon spheres, *Industrial & Engineering Chemistry Research* **62** (2023) 4694-4703. https://doi.org/10.1021/acs.iecr.2c03107

[55] A. J. Bard, L. R. Faulkner, Electrochemical Methods Fundamentals and Applications, Wiley, New York (2001). ISBN: 978-1-118-31280-3

[56] H. Karimi-Maleh, A. A. Ensafi, H. Beitollahi, V. Nasiri, M. A. Khalilzadeh, P. Biparva, Electrocatalytic determination of sulfite using a modified carbon nanotubes paste electrode: application for determination of sulfite in real samples, *Ionics* **18** (2012) 687-694. https://doi.org/10.1007/s11581-011-0654-z

[57] A. Siroueinejad, A. Abbaspour, M. Shamsipur, Electrocatalytic oxidation and determination of sulfite with a novel copper-cobalt hexacyanoferrate modified carbon paste electrode, *Electroanalysis* **21** (2009) 1387-1393. https://doi.org/10.1002/elan.200804535

[58] T. Kondori, S. Tajik, N. Akbarzadeh-T, H. Beitollahi, R. Hosseinzadeh, F. Mousazadeh, C. Graiff, A novel carbon paste electrode-modified electrocatalytic CO–Ce–NPs for sulfite detection: a sonochemical synthesis, *Iranian Journal of Science and Technology, Transactions A* **46** (2022) 1387-1398. https://doi.org/10.1007/s40995-022-01345-y

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