Kütahya Dumlupınar University
Institute of Graduate Studies

Journal of Scientific
Reports-A
E-ISSN: 2687-6167
Number 50, September 2022

RESEARCH ARTICLE

ENGINEERING of a NOVEL SCREEN-PRINTED ELECTRODE MODIFIED by Pt DECORATED SINGLE WALLED CARBON NANOTUBE NANOHYBRID for MONITORING SULFITE in REAL SAMPLES: A NEW APPROACH to a SUSTAINABLE ENVIRONMENT and HEALTH

Ceren KARAMAN[1*]

[1]Akdeniz University, Vocational School of Technical Sciences, Department of Electricity and Energy, Antalya, cerenkaraman@akdeniz.edu.tr, ORCID: 0000-0001-9148-7253

Receive Date:02.08.2022 *Accepted Date: 19.08.2022*

ABSTRACT

Sensitive and selective monitoring of sulfite anions, a food additive, in real-time applications is still a challenging issue to be solved. It is crucial to engineering highly selective and sensitive, facile, and low-cost analytical tools for monitoring trace levels of sulfite anions in real samples. In light of this, the goal of this work was to tailor a Pt-decorated single-walled carbon nanotubes (Pt@SWCNTs) nanohybrid to be utilized in the engineering of an electrochemical sensor to monitor sulfite anions in real samples. The microstructural features of the fabricated nanocatalysts were assessed via transmission electron microscope (TEM), whereas the electrochemical characteristics were enlightened via differential pulse voltammetry (DPV), linear sweep voltammetry (LSV), and electrochemical impedance spectroscopy (EIS) methods. The screen-printed electrode (SPE), as an electrochemical sensor, was modified via Pt@SWCNTs nanocatalysts and the resultant electrochemical sensor (Pt@SWCNTs/SPE) was employed as a powerful electroanalytical tool for monitoring sulfite in the concentration range of 0.1 - 250 µM with a limit of detection value of 10 nM. The optimal catalyst concentration was determined as 9.0mg Pt@SWCNTs, and the pH 5.0 was selected as the optimal pH. At the optimal operating conditions, it was observed that the oxidation current of sulfite was enhanced almost 2.53-fold, and the oxidation potential of it diminished *ca.50* mV at the surface of Pt@SWCNTs/SPE in comparison to bare SPE. The sulfite anions monitoring ability of proposed Pt@SWCNTs/SPE was further confirmed in red wine and tap water samples by the standard addition method, and the recovery range was determined as 98.5 – 102.3%. The enhanced electrochemical performance of the fabricated electrochemical sensor compared to bare SPE was directly ascribed to the coupled effects of co-existing Pt nanoparticles and SWCNTs architecture, which facilitated both the electron transfer and mass transfer. This works paws the way for tailoring of hybrid nanocatalysts to be utilized in electrochemical engineering applications for sustaining the environment and health.

Keywords: *Sulfite, Electrochemical Sensor, Monitoring, Pt@SWCNTs, Screen Printed Electrode*

JSR A
Journal of Scientific Reports

Karaman, C., Journal of Scientific Reports-A, Number 50, 228-244, September 2022.

1. INTRODUCTION

Sulfite anion (SO_3^{2-}) is frequently served as a preserving agent in beverages, foodstuffs, and pharmaceutical products for avoiding spoilage as a result of oxidation and browning reactions and to prevent the reproduction of microorganisms [1, 2]. Despite being used as a food preservative all over the world and having numerous advantages, SO_3^{2-} concentrations above 0.7 $mg.kg^{-1}$ are not permitted in foodstuffs due to potential toxicity [3]. Moreover, SO_3^{2-} is a forerunner to the formation of acid rain caused by the resulted sulfur dioxide, which damages crops, residences, landmarks, aquatic life, and plants by acidifying the soil [4]. The threshold concentration of SO_3^{2-} anion in beverages and food products has been declared as 10 ppm by the United States Food and Drug Administration [5, 6]. Since high concentrations of sulfite anions can lead to health issues including skin irritation, allergic reactions, asthma, nausea, and diarrhea, as well as can deplete the dissolved oxygen in aquatic media, the products that contain more sulfide than the threshold level should be properly labeled [7, 8]. Therefore, it is vital to engineer and design analytical methods that are sensitive, precise, straightforward to use, selective, and reasonably priced to monitor the trace amount of SO_3^{2-} in actual samples.

Among the various available analytical techniques for the monitoring of SO_3^{2-}, spectrofluorometry [9], chemiluminescence [10], spectrophotometry [11], flow injection technique [12], high-performance liquid chromatography [13], and enzymatic methods [14] can be highlighted as the most preferred ones. The effectiveness and mechanism of the substance to be examined in real sample analysis can also be determined using electrochemical analysis methods since they are analogous to biological redox processes and are unaffected by the formulation's interfering chemicals. Electroanalytical methods allow the determination of analytes at very low concentrations and provide information about the degree and speed of adsorption and chemisorption at interfaces, the stoichiometry of charge transfer, mass transfer rate, equilibrium and rate constants of chemical reactions in systems where electrochemical techniques are applied. However, despite the advantages of these techniques, most of these methods still suffer from some obstacles that limit their widespread and real-time employment such as high cost, low sensitivity, time-consuming and complex sample preparation steps, low throughput, and high cost [15]. On the other side, electrochemical techniques have recently garnered exceptional attention due to their benefits such as being easy to apply, superior selectivity and sensitivity, swift analysis times, on-site application possibilities, being customizable portable devices, and comparatively cheapness [16, 17]. For boosting the sensitivity and precision of the electroanalytical techniques, electrode modification has been considered a prosperous approach [18, 19]. Among the various traditional electrode types, screen-printed electrodes (SPEs) have benefits such as small dimensions, lightweight, low cost, and being disposable [20]. Disposable sensors provide some advantages, including the elimination of issues with biofouling or contaminant spillover and the design flexibility provided by the simplicity of chemical modifications through coating with various nanomaterials[21].

Nanomaterials have received a great deal of interest due to their unique characteristics that allow them to be utilized in various areas including environmental application [22-24], pharmaceuticals [25], energy [26-28], catalyst [29, 30], biotechnology [31, 32], etc. Nanomaterials are also used in the design of electrochemical sensors. Nanostructured materials are of a huge specific surface area resulting in more electrochemically active sites, which allows decreasing overpotential of various analytes and facilitates the electron/ion transport between the electrode surface and analyte, thereby boosting the voltammetric responses [33]. So far, numerous metal and metal oxide nanoparticles,

including Pt, Pd, Au, Ag, Zn, Cu, Ni, NiO, Co_3O_4, etc. have been substantially employed in electrochemical sensor fabrication [34-40]. Amongst, Pt nanoparticles have gained great attention thanks to their unique features including high conductivity, and superior electrocatalytic activity [41]. However, its practical application is still restricted due to its high-cost, and limited reserves, as well as the problem of aggregation. Hence, the decoration of Pt nanoparticles onto suitable supporting nanoarchitecture is one of the suitable ways to enhance its potential application in electrochemical sensor fabrication [42]. These drawbacks of Pt-based electrochemical sensors prevent their widespread adoption. Carbon-based nanomaterials can fulfill the limit of detection level, and operating temperature criteria in addition to having higher selectivity and faster response times than other types of nanomaterials-based sensors, showing great promise for use in electrochemical sensors [43]. Among the various carbonaceous nanomaterials, single-walled carbon nanotubes (SWCNTs) are one of the promising ones which have garnered a lot of interest due to their global importance in nanotechnology and their prospective application in designing electrochemical sensors [44, 45]. According to recent studies, hybrid nanoarchitectures can enhance actual electrocatalytic activity, which may be related to the synergistic interaction between the two elements [46]. Regarding the outstanding individual characteristics of Pt nanoparticles and SWCNTs, it can be expected that a hybrid might yield boosted electrochemical performance of the ultimate sensor.

Although there are some valuable works that investigate various electrochemical sensors for sulfide monitoring, as per the best knowledge of the researcher, this is the first effort that has aimed to synthesize a Pt nanoparticle decorated SWCNTs (Pt@SWCNTs) modified SPE for highly sensitive monitoring of sulfite anions in real samples. Superior limit of detection (LOD), ease of application, acceptable recovery data, swift response time, and being available for miniaturization can be listed as the primary benefits of the proposed Pt@SWCNTs/SPE electrochemical sensor for monitoring trace amount of sulfite anions.

2. EXPERIMENTAL

2.1. Materials and Apparatus

NaOH, HNO_3, H_2PtCl_6, SWCNTs, $NaHCO_3$, H_3PO_4, $NaBH_4$, NaCl, SWCNTs (average diameter: 0.78 nm, median length: 1 µm, purity: ≥95% as carbon nanotubes, specific surface area: ≥700 $m^2.g^{-1}$), dimethylformamide (DMF), ethanol, and isopropyl alcohol (IPA) were directly employed in experiments without any extra purification. Deionized (DI) water was utilized to make ready all of the reagent solutions.

The microstructural investigation of fabricated nanostructures was conducted by JEOL 2100 TEM. For pH measurements, a digital pH-meter (METTLER TOLEDO S220-K) was employed.

Electrochemical Workstation Vertex – Ivium linked to a conventional 3-electrode electrochemical cell was employed to implement the electrochemical investigations of the proposed electrochemical sensor. During the electrochemical characterizations, Pt-wire was used as a counter electrode, and Ag/AgCl (3.0 M KCl) as a reference electrode for recording electrochemical signals.

2.2. Synthesis of Pt@SWCNTs Nanostructures

SWCNTs homogenous dispersion (3.0 $mg.mL^{-1}$) was prepared by ultrasonically dispersing a certain amount of SWCNTs in 20 mL IPA over the course of 45 minutes in an ultrasonic bath. Afterward, 100 mg H_2PtCl_6 was ultrasonically dispersed in SWCNTs dispersion for 45 min. Finally, to acquire

Pt@SWCNTs nanostructure, a determined amount of $NaBH_4$ was introduced into as-obtained SWCNTs-H_2PtCl_6/IPA dispersion, following by ultrasonicated for 1 hour. The acquired black precipitates consisting of Pt@SWCNTs nanostructure were vacuum-filtered and thermally annealed at 500 °C in a tubular furnace over 1 h under the high purity Argon atmosphere. Subsequently, the obtained black powder was labeled as Pt@SWCNTs, and placed in a sealed vial to be used later.

2.3. Fabrication of Modified SPE

The Pt@SWCNTs modified screen printed electrode for sulfite monitoring was fabricated by a simple drop-casting technique. In this regard, 9.0 mg of produced Pt@SWCNTs nanohybrid was ultrasonically dispersed in 1.0 mL of ethanol-DI water solution (1:1, by v:v) for one hour. Afterward, *ca*.5 µL of dispersion was drop-casted onto the SPE surface, and the solvent was evaporated at the ambient temperature. Subsequently, the resultant electrode was denoted as Pt@SWCNTs/SPE electrode and stored at 4 °C for forthcoming use.

2.4. Real Sample Preparation

The performance of the fabricated electrochemical sensor to monitor SO_3^{2-} anions in real samples was assessed by using red wine and tap water samples as real samples. In this step, red wine was acquired from a wine cellar in İzmir, Turkey. Just before the real sample analysis, the wine bottle was uncorked. A certain amount of red wine sample was filtered and diluted by phosphate buffer solution (PBS, pH=5.0) whereas tap water was gotten ready to use after centrifuging at 5000 rpm over 15 min, and filtration of the supernatant. The prepared red wine and drinking water samples were separately introduced into the electroctrochemical cell, and sulfide was spiked into the real sample solution and monitored by the standard addition method.

3. RESULTS AND DISCUSSION

3.1. Evaluation of The Electrode Surface

The microstructure of the Pt@SWCNTs nanohybrid was characterized via TEM analysis (Fig.1). The TEM image of the nanohybrid showed the SWCNTs to have a tubular morphology with uniformly distributed Pt nanoparticles on the SWCNT skeleton. Moreover, Fig.1 confirmed the successful decoration of Pt nanoparticles onto SWCNTs supporting material. The uniform dispersion of the Pt nanoparticles without aggregation was also observed in the TEM micrographs of the nanohybrid.

JSR A
Journal of Scientific Reports

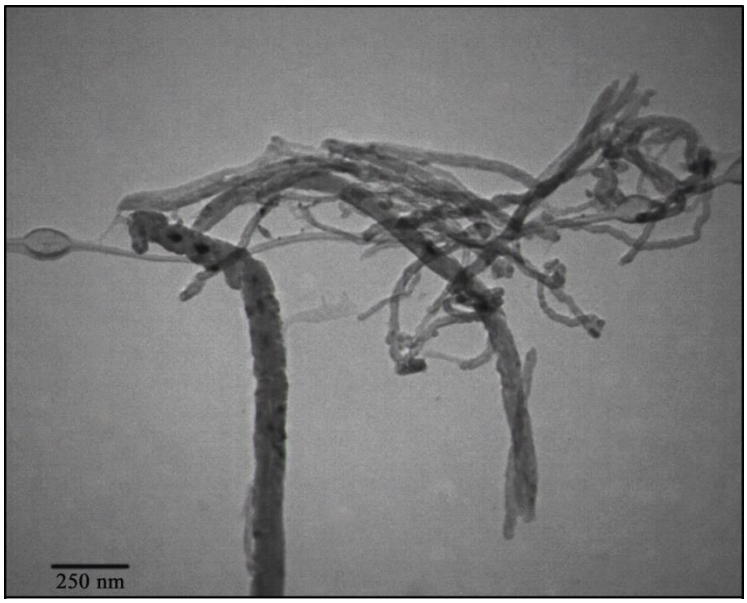

Figure 1. TEM micrograph of Pt@SWCNTs nanohybrid.

The electrochemical impedance spectroscopy technique was implemented in 0.1 M KCl solution containing 5.0 mM $[Fe(CN)_6]^{3-,-4}$ redox probe to evaluate the electrical conductivity of Pt@SWCNTs/SPE. The Nyquist plot of both bare SPE and Pt@SWCNTs/SPE was depicted in Fig.2. The observed smaller semicircle radius of Pt@SWCNTs/SPE compared to bare SPE confirmed the boosting effect of the Pt@SWCNTs modification onto the electrical conductivity. Thanks to the enhanced electrical conductivity, the charge transfer resistance of the resultant modified electrode was decreased, thereby facilitating the detection process of the analyte with high sensitivity.

JSR A
Journal of Scientific Reports

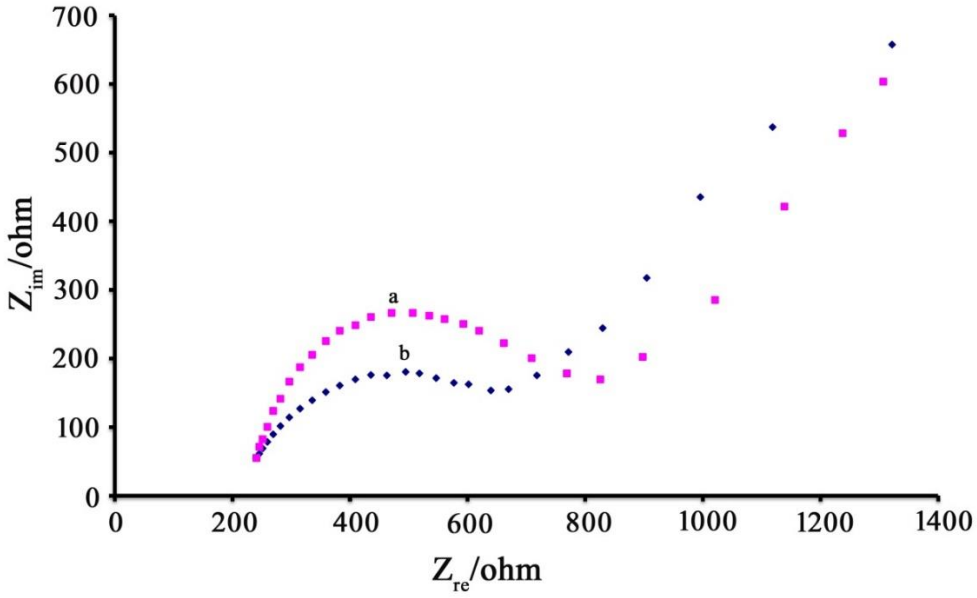

Figure 2. The Nyquist plots of bare SPE (a) and Pt@SWCNTs/SPE (b) in 0.1 M KCl solution containing 5.0 mM $[Fe(CN)_6]^{3-,4-}$.

3.2. Optimization of Catalyst Ratio and pH of the Solution

Firstly, the amount of Pt@SWCNTs catalyst was optimized by investigating various amounts of nanohybrid ranging 2.0 - 8.0 mg dispersed in 1.0 mL DI water-ethanol (1:1, by v:v) solution, and then drop-casted onto SPE to fabricate various Pt@SWCNTs/SPE electrodes. The oxidation signal of 125 µM sulfite was obtained at the surface of the electrode (Fig 3A). The results revealed that the oxidation current of sulfite increased with increasing the concentration of nanohybrid catalyst at the surface of SPE, reaching the maximum value at 9.0 mg Pt@SWCNTs catalyst in 1.0 mL of DI water-ethanol (1:1, by v:v) solution. Hence, this catalyst loading was selected as the optimum catalyst ratio for the fabrication of the modified electrochemical sensor.

The electrochemical features of a fabricated electrochemical sensor can be significantly influenced by the pH of the solution. The adsorbent surface can be affected by the activity of the sulfite anion in real samples due to the pH of the solution in the presence of OH^- and H^+ ions. The pH of the solution was also optimized by evaluating the oxidation signal of the sulfite within the pH range of 3.5-6.0. It was observed that the oxidation signal of sulfite was enhanced by shifting the pH value from acidic to basic (Fig. 3B). The maximum oxidation current was achieved at the alkaline condition of pH 5.0, after this pH value it was observed that the oxidation signal current decreased. Thus, pH 5.0 was shown to be the ideal pH for the electrochemical detection of sulfite anion.

Another parameter that effects the electrochemical performance of the fabricated electrode is type of buffer solution. Thus, three different types of buffer solutions including phosphate buffer, acetate buffer, and Brittion-Robinson buffer solution at the optimal pH value of 5.0 were explored to determine the optimal buffer solution. The recorded oxidation signals (Fig. 3C) revealed that the phosphate buffer solution could be selected as the optimal buffer solution with its superior oxidation

signal value achieved for 125 µM sulfite. As a result, the phosphate buffer solution was selected as the most appropriate buffer solution for the following studies.

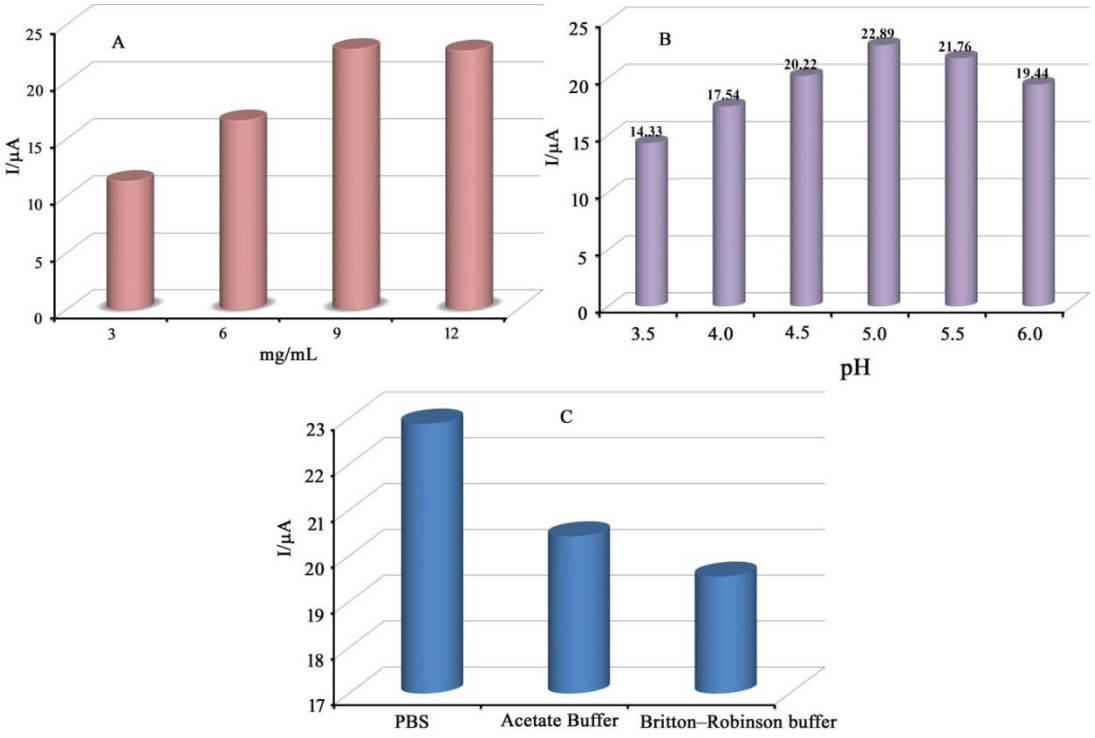

Figure 3. The effect of (A) the Pt@SWCNTs catalyst amount (B) the pH value of the solution ranging between 3.5 to 6.0 (C) type of buffer solution on the voltammetric response of sulfite at a surface of Pt@SWCNTs/SPE.

3.3. Investigation of Catalytic Effect of Pt@SWCNTs Nanohybrid

The electrochemically active surface area (EASE) of bare SPE and Pt@SWCNTs/SPE were evaluated by implementing cyclic voltammetry (CV) measurement in 0.1 M KCl + 1.0 mM $[Fe(CN)_6]^{3-,4-}$ solution at the potential scan rate range of 25-450 $mV.s^{-1}$. The Randles–Sevcik equation was computed to obtain the EASE values of the electrodes. The EASE values were calculated as 0.143 cm^2, and 0.221 cm^2 for bare SPE and Pt@SWCNTs/SPE, respectively. The results confirmed that the modifying SPE by Pt decorated SWCNTs nanohybrid led to an increase in the EASE value, thereby enhancing the electrocatalytic performance of the ultimate electrochemical sensor.

Differential pulse voltammograms of 125 µM sulfite were recorded at the surface of SPE (Fig.4 curve a) and Pt@SWCNTs/SPE (Fig. 4 curve b), respectively. The findings proved that the oxidation current of sulfite increased from 9.055 µA to 22.89 µA, whereas its oxidation potential of it diminished from 970 mV to 920 mV for bare SPE, and Pt@SWCNTs/SPE, respectively. Thereby, it was concluded that the Pt@SWCNTs nanohybrid modification of SPE successfully amplified the oxidation signal of sulfite thanks to the enhanced EASE and electrical conductivity of nanocatalysts.

JSR A
Journal of Scientific Reports

The inset of Fig. 4 reflected the current density diagram for oxidation of sulfite at the surface of SPE, and Pt@SWCNTs/SPE, respectively. The Pt@SWCNTs nanohybrid's exceptional electrical conductivity as a novel electrocatalyst to be used in the creation of modified electrochemical sensors was proven by the current density diagram. The boosted performance of Pt@SWCNTs/SPE was ascribed to the coupled effects of the Pt nanoparticles and high surface area SWCNTs which served as carbonaceous supporting material to enhance the electrocatalytic activity of the resultant hybrid.

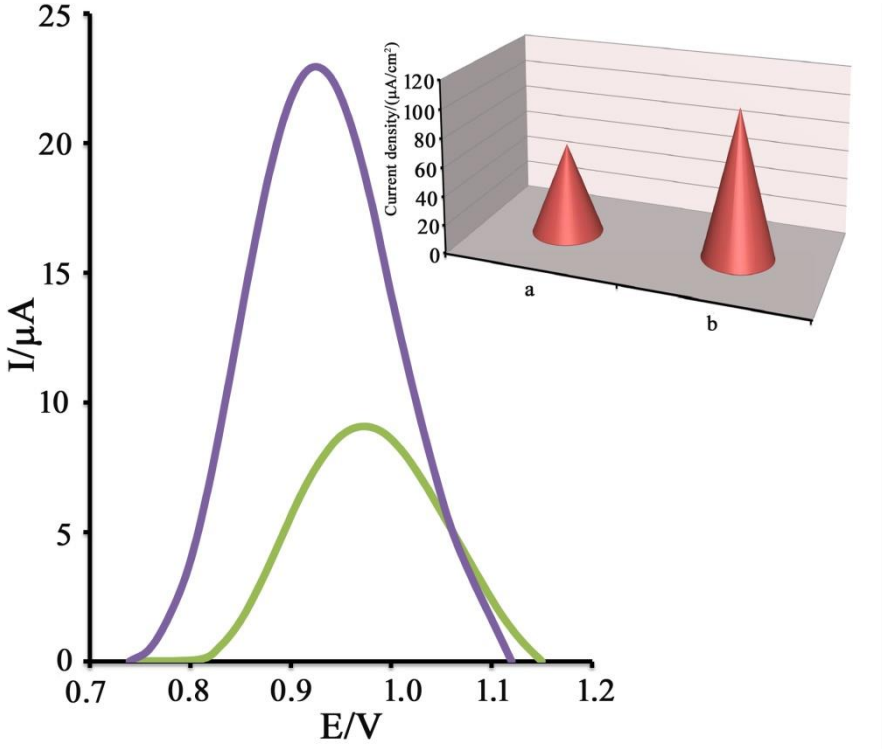

Figure 4. DPV curves recorded at the surface of SPE (curve a) and Pt@SWCNTs/SPE (curve b) (inset; the current density values of sulfite at the surface of SPE and Pt@SWCNTs/SPE electrodes).

3.4. Kinetic Investigations

The kinetic behavior of the fabricated electrochemical sensor towards sulfite monitoring was assessed by linear sweep voltammetry (LSV) measurements. Fig. 5 inset depicted the LSV voltammograms of 700 μM sulfite anions acquired on the surface of Pt@SWCNTs/SPE at a potential scan rate of 10- 150 $mV.s^{-1}$. The linear relation with an equation of $I = 3.2409\ \upsilon^{1/2} + 0.3934$ ($r^2 = 0.9967$)was determined between the oxidation current of sulfite and $\upsilon^{1/2}$, thereby revealing the diffusion process for redox reaction of sulfite on the surface of Pt@SWCNTs/SPE (Fig. 5). The Tafel plot for the oxidation of 700 μM sulfite anions on the of Pt@SWCNTs/SPE surface at the scan rate of 40 $mV.s^{-1}$ was depicted in Fig. 6.

JSR A
Journal of Scientific Reports

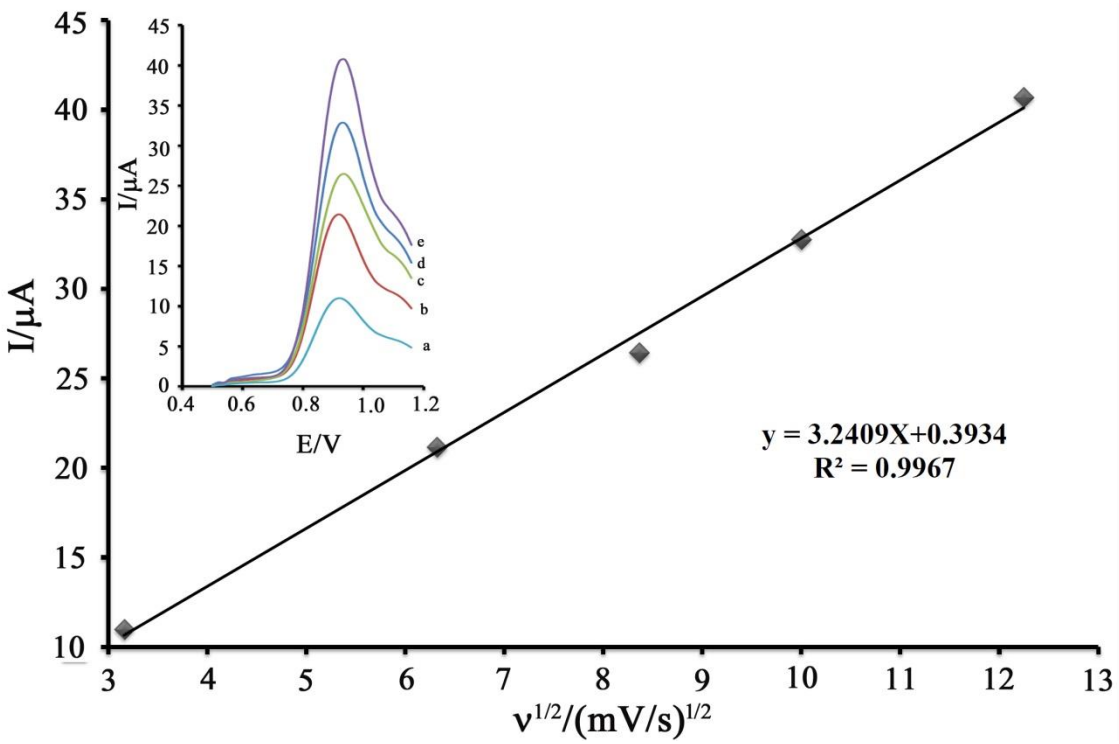

Figure 5. Current- $\upsilon^{1/2}$plot for redox reaction of 700 µM sulfite at surface of Pt@SWCNTs/SPE. Relative LSV voltammograms of 700 µM sulfite at the surface of Pt@SWCNTs/SPE (scan rates; 10; 40; 70; 100 and 150 $mV.s^{-1}$).

JSR A
Journal of Scientific Reports

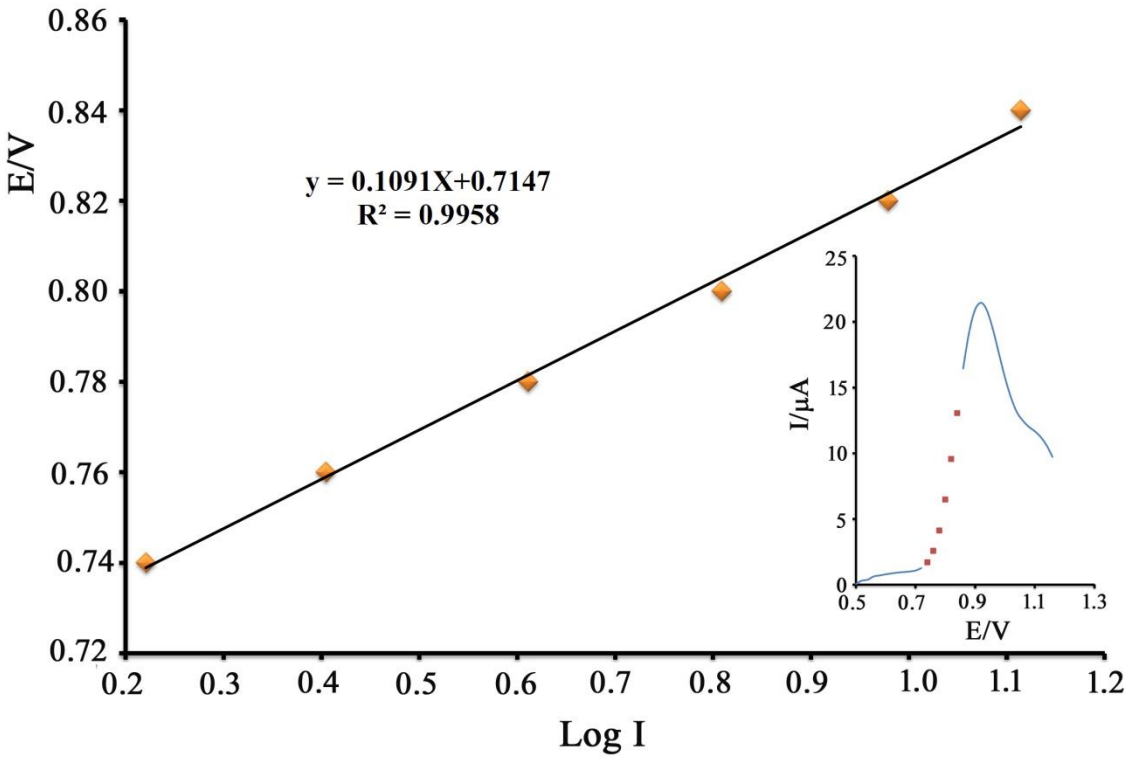

Figure 6. Tafel plot for the oxidation of 700 µM sulfite anions on the of Pt@SWCNTs/SPE surface at the scan rate of 40 $mV.s^{-1}$

3.5. Repeatability and Analytical Parameters

By fabricating five distinct electrodes under the same conditions and recording voltammograms of 125 µM sulfite on the surface of Pt@SWCNTs/SPE, the reproducibility of the fabricated electrode for monitoring sulfite was evaluated. The obtained results showed and RSD value of 4.3% which is acceptable repeatability of Pt@SWCNTs/SPE to detect sulfite.

The differential pulse voltammetry curves of sulfite in the concentration range of 0.1 to 250 µM were obtained at the surface of Pt@SWCNTs/SPE (Fig. 7). The linear relationship was confirmed with the equation of I = 0.1562 C + 2.8897 (r^2 = 0.9932), was obtained between the oxidation current of sulfite and the concentration at the surface of Pt@SWCNTs/SPE with the limit of detection value of 10 nM.

JSR A
Journal of Scientific Reports

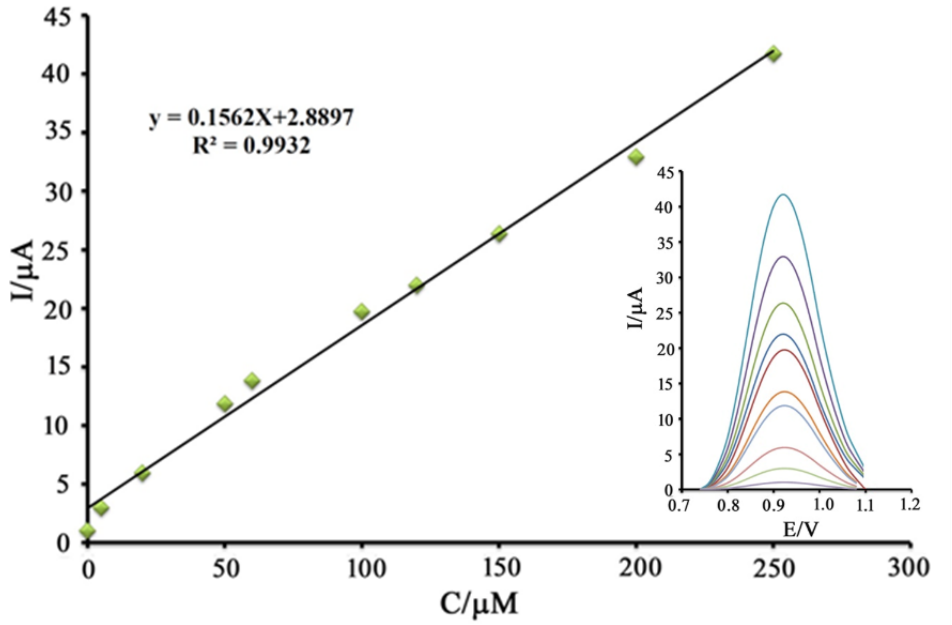

Figure 7. Current-concentration plot for oxidation of sulfite at surface of Pt@SWCNTs/SPE (Inset; Relative DPV curves with the concentrations of 0.01; 5.0; 20.0; 50.0; 60.0; 100; 120; 150; 200 and 250 µM).

3.6. Real sample analysis and interference study

The sulfite monitoring capability of Pt@SWCNTs/SPE was evaluated also in some real samples including red wine and tap water samples. The standard addition method was implemented by using Pt@SWCNTs/SPE to detect sulfite in real samples. The computed results were listed in Table 1. According to acquired data, a recovery range of 98.5-102.3% was determined to monitor sulfite by utilizing Pt@SWCNTs/SPE electrochemical sensor as an analytical tool, proving the outstanding applicability of this novel sensor in real sample analysis with high sensitivity.

Table 1. Real sample analysis data for sensing sulfite using Pt@SWCNTs/SPE.

Sample	Added (µM)	Founded (µM)	Recovery%
Tap water	---	<LOD	---
	10.00	9.85±0.54	98.5
Red wine	---	6.7±0.11	---
	3.3	10.23±0.64	102.3

Moreover, the selectivity metrics of Pt@SWCNTs/SPE towards the detection of 10 µM sulfite were evaluated in the presence of some organic and inorganic pollutants. The results were depicted in Table 2, revealing the excellent selectivity of Pt@SWCNTs/SPE as an electroanalytical sensor for the determination of sulfite thanks to the synergistic features of metal nanoparticles and carbonaceous skeleton as the supporting material.

JSR A
Journal of Scientific Reports

Table 2. Interference study results for sensing 10 µM sulfite.

Species	***Tolerant limits*** ***($W_{Substance}/W_{Analytes}$)***
Li^+, Br^-, Ca^{2+}, F^-	1000
Starch	Saturation
Valine, Glycine, Glucose	500

4. CONCLUSION

Herein, the goal was to engineer a novel electrochemical sensor to be implemented in highly sensitive monitoring of trace amounts of sulfide in real samples. In this regard, to take advantage of the coupled effect of Pt nanoparticles and SWCNTs architecture, Pt nanoparticles were decorated onto SWCNTs via a facile fabrication pathway, and the resultant nanohybrid catalyst was implemented as a mediator for the modification of the screen-printed electrode. The synthesized Pt@SWCNTs nanohybrid offered superior electrical conductivity and enhanced electrochemical oxidation signal of sulfite anion thanks to the synergistic effects of each component of the nanohybrid. The boosted electrochemically active surface area also led to improvement in the electrocatalytic performance of the nanomaterial, thereby increasing the sensitivity of the resultant electrochemical sensor towards sulfite monitoring. The optimal catalyst concentration was determined to be 9.0 mg Pt@SWCNTs, while the optimum operating pH and the buffer solution were specified as 5.0 and phosphate buffer solution, respectively. The results confirmed the oxidation of sulfite anion occurred by a diffusion-controlled process on the surface of Pt@SWCNTs/SPE. The boosted sensing performance of the proposed Pt@SWCNTs/SPE sensor was suggested as the basis of the special catalytic behavior of Pt nanoparticles and the SWCNTs providing more active chemical sites, owing to the co-existence of Pt nanoparticles and SWCNT supporting material. In a nutshell, the proposed Pt@SWCNTs/SPE offered superior and outstanding electrochemical performance metrics for monitoring sulfite anions in real samples without any interference, suggesting its potential implementation as a novel analytical tool for determining sulfite levels in real samples.

ACKNOWLEDGMENT

The author would like to introduce her appreciation to Prof. Hassan Karimi-Maleh (University of Electronic Science and Technology, China) for his substantial scientific support, besides the allowance to use his laboratory for characterizations.

REFERENCES

[1] Maaref, H., Foroughi, M.M., Sheikhhosseini, E., Akhgar, M.R., (2018), Electrocatalytic Oxidation of Sulfite and its Highly Sensitive Determination on Graphite Screen Printed Electrode Modified with New Schiff base Compound, Anal Bioanal Electro, 10, 1080-1092.

[2] Carlos, K.S., Treblin, M., de Jager, L.S., (2019), Comparison and optimization of three commercial methods with an LC-MS/MS method for the determination of sulfites in food and beverages, Food Chem, 286, 537-540.

[3] Venkatachalam, K., Asaithambi, G., Rajasekaran, D., Periasamy, V., (2020), A novel ratiometric fluorescent probe for "naked-eye" detection of sulfite ion: Applications in detection of biological SO32- ions in food and live cells, Spectrochim Acta A, 228, 117788.

[4] Malakootian, M., Hamzeh, S., Mahmoudi-Moghaddam, H., (2022), An efficient electrochemical sensor for determination of sulfite in water and soft drinks based on Ce3+-doped CuO nanocomposite, J Food Compos Anal, 113, 104716.

[5] Zhai, T.T., Li, R., Zhang, N.N., Zhao, L.X., He, M.T., Tan, L., (2022), Simultaneous Detection of Sulfite and Nitrite on Graphene Oxide Nanoribbons-gold Nanoparticles Composite Modified Electrode, Electroanal, 34, 103-110.

[6] Yang, J., Xu, X.Y., Mao, X.Y., Jiang, L., Wang, X.L., (2020), An Electrochemical Sensor for Determination of Sulfite (SO32-) in Water Based on Molybdenum Disulfide Flakes/Nafion Modified Electrode, Int J Electrochem Sc, 15, 10304-10314.

[7] Stohs, S.J., Miller, M.J.S., (2014), A case study involving allergic reactions to sulfur-containing compounds including, sulfite, taurine, acesulfame potassium and sulfonamides, Food Chem Toxicol, 63, 240-243.

[8] Beitollahi, H., Mahmoudi-Moghaddam, H., Tajik, S., Jahani, S., (2019), A modified screen printed electrode based on La3+-doped Co3O4 nanocubes for determination of sulfite in real samples, Microchem J, 147, 590-597.

[9] Yang, X.F., Guo, X.Q., Zhao, Y.B., (2002), Novel spectrofluorimetric method for the determination of sulfite with rhodamine B hydrazide in a micellar medium, Anal Chim Acta, 456, 121-128.

[10] Bonifacio, R.L., Coichev, N., (2004), Chemiluminescent determination of sulfite traces based on the induced oxidation of Ni(II)/tetraglycine complex by oxygen in the presence of luminol: mechanistic considerations, Anal Chim Acta, 517, 125-130.

[11] Segundo, M.A., Rangel, A.O.S.S., Cladera, A., Cerda, V., (2000), Multisyringe flow system: determination of sulfur dioxide in wines, Analyst, 125, 1501-1505.

[12] Su, X.L., Wei, W.Z., Nie, L.H., Yao, S.Z., (1998), 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, 221-224.

[13] Robbins, K.S., Shah, R., MacMahon, S., de Jager, L.S., (2015), Development of a Liquid Chromatography-Tandem Mass Spectrometry Method for the Determination of Sulfite in Food, J Agr Food Chem, 63, 5126-5132.

[14] Situmorang, M., Hibbert, D.B., Gooding, J.J., Barnett, D., (1999), A sulfite biosensor fabricated using electrodeposited polytyramine: application to wine analysis, Analyst, 124, 1775-1779.

[15] Wang, R.R., Mao, Y., Qu, H., Chen, W., Ma, A.J., Zheng, L., (2019), Highly sensitive and selective sulfite sensors based on solution-gated graphene transistors with multi-walled carbon nanotube functionalized gate electrodes, Food Chem, 290, 101-106.

[16] Karimi-Maleh, H., Khataee, A., Karimi, F., Baghayeri, M., Fu, L., Rouhi, J., Karaman, C., Karaman, O., Boukherroub, R., (2022), A green and sensitive guanine-based DNA biosensor for idarubicin anticancer monitoring in biological samples: A simple and fast strategy for control of health quality in chemotherapy procedure confirmed by docking investigation, Chemosphere, 291, 132928.

[17] Karimi-Maleh, H., Darabi, R., Shabani-Nooshabadi, M., Baghayeri, M., Karimi, F., Rouhi, J., Alizadeh, M., Karaman, O., Vasseghian, Y., Karaman, C., (2022), Determination of D&C Red 33 and Patent Blue V Azo dyes using an impressive electrochemical sensor based on carbon paste electrode modified with ZIF-8/g-C3N4/Co and ionic liquid in mouthwash and toothpaste as real samples, Food Chem Toxicol, 162, 112907.

[18] Cheraghi, S., Taher, M.A., Karimi-Maleh, H., Karimi, F., Shabani-Nooshabadi, M., Alizadeh, M., Al-Othman, A., Erk, N., Raman, P.K.Y., Karaman, C., (2022), Novel enzymatic graphene oxide based biosensor for the detection of glutathione in biological body fluids, Chemosphere, 287, 132187.

[19] Karimi-Maleh, H., Karimi, F., Fu, L., Sanati, A.L., Alizadeh, M., Karaman, C., Orooji, Y., (2022), Cyanazine herbicide monitoring as a hazardous substance by a DNA nanostructure biosensor, J Hazard Mater, 423, 127058.

[20] Wang, Y.T., Wang, S., Tao, L., Min, Q., Xiang, J., Wang, Q.M., Xie, J.M., Yue, Y., Wu, S.C., Li, X.F., Ding, H., (2015), A disposable electrochemical sensor for simultaneous determination of norepinephrine and serotonin in rat cerebrospinal fluid based on MWNTs-ZnO/chitosan composites modified screen-printed electrode, Biosens Bioelectron, 65, 31-38.

[21] Carbone, M., Nestico, A., Bellucci, N., Micheli, L., Palleschi, G., (2017), Enhanced performances of sensors based on screen printed electrodes modified with nanosized NiO particles, Electrochim Acta, 246, 580-587.

[22] Mousavi, S.E., Younesi, H., Bahramifar, N., Tamunaidu, P., Karimi-Maleh, H., (2022), A novel route to the synthesis of alpha-Fe2O3@C@SiO2/TiO2 nanocomposite from the metal-organic framework as a photocatalyst for water treatment, Chemosphere, 297, 133992.

[23] Liang, Y.Y., Demir, H., Wu, Y.J., Aygun, A., Tiri, R.N.E., Gur, T., Yuan, Y., Xia, C.L., Demir, C., Sen, F., Vasseghian, Y., (2022), Facile synthesis of biogenic palladium nanoparticles using biomass strategy and application as photocatalyst degradation for textile dye pollutants and their in-vitro antimicrobial activity, Chemosphere, 306, 135518.

[24] Recber, Z.B., Burhan, H., Bayat, R., Nas, M.S., Calimli, M.H., Demirbas, O., Sen, F., Hassan, K.M., (2022), Fabrication of activated carbon supported modified with bimetallic-platin ruthenium nano sorbent for removal of azo dye from aqueous media using enhanced ultrasonic wave, Environ Pollut, 302, 119033.

[25] Kocak, Y., Oto, G., Meydan, I., Seckin, H., Gur, T., Aygun, A., Sen, F., (2022), Assessment of therapeutic potential of silver nanoparticles synthesized by Ferula Pseudalliacea rech. F. plant, Inorg Chem Commun, 140, 109417.

[26] Karaman, O., (2022), Three-dimensional graphene network supported nickel-cobalt bimetallic alloy nanocatalyst for hydrogen production by hydrolysis of sodium borohydride and developing of an artificial neural network modeling to forecast hydrogen production rate, Chem Eng Res Des, 181, 321-330.

[27] Wu, Y., Altuner, E.E., Tiri, R.N.E.H., Bekmezci, M., Gulbagca, F., Aygun, A., ., Xia, C., Van Le, Q., Sen, F., Karimi-Maleh, H., (2022), Hydrogen generation from methanolysis of sodium borohydride using waste coffee oil modified zinc oxide nanoparticles and their photocatalytic activities., International Journal of Hydrogen Energy.

[28] Karimi-Maleh, H., Karaman, C., Karaman, O., Karimi, F., Vasseghian, Y., Fu, L., Baghayeri, M., Rouhi, J., Kumar, P.S., Show, P.L., Rajendran, S., Sanati, A.L., Mirabi, A., (2022), Nanochemistry approach for the fabrication of Fe and N co-decorated biomass-derived activated carbon frameworks: a promising oxygen reduction reaction electrocatalyst in neutral media, J Nanostructure Chem, 12, 429-439.

[29] Akca, A., Karaman, O., (2022), Electrocatalytic Decomposition of Formic Acid Catalyzed by M-Embedded Graphene (M = Ni and Cu): A DFT Study, Top Catal, 65, 643-655.

[30] Karaman, O., (2021), Oxygen Reduction Reaction Performance Boosting Effect of Nitrogen/Sulfur Co-Doped Graphene Supported Cobalt Phosphide Nanoelectrocatalyst: pH-Universal Electrocatalyst, Ecs J Solid State Sc, 10, 061003.

[31] Bostanci, M.T., Bulbul, A.S., Celik, I.S., Kocabas, Y.Z., Burhan, H., Bayat, R., Sen, F., Zakariae, N., Esmaeili, R., Jafari, H., Karimi, F., Karimi-Maleh, H., (2022), Investigation of antibacterial, antifungal, antibiofilm, antioxidant and anticancer properties of methanol extracts of Salvia marashica Ilcim, Celep & Dogan and Salvia caespitosa Montbret & Aucher ex Benth plants with medicinal importance, Chemosphere, 288, 132602.

[32] Khoshkho, S.M., Mahdavian, M., Karimi, F., Karimi-Maleh, H., Razaghi, P., (2022), Production of bioethanol from carrot pulp in the presence of Saccharomyces cerevisiae and beet molasses inoculum; A biomass based investigation, Chemosphere, 286, 131688.

[33] Beitollahi, H., Tajik, S., Maleh, H.K., Hosseinzadeh, R., (2013), Application of a 1-benzyl-4-ferrocenyl-1H-[1,2,3]-triazole/carbon nanotube modified glassy carbon electrode for voltammetric determination of hydrazine in water samples, Appl Organomet Chem, 27, 444-450.

[34] Kianfar, S., Golikand, A.N., ZareNezhad, B., (2021), Bimetallic-metal oxide nanoparticles of Pt-M (M: W, Mo, and V) supported on reduced graphene oxide (rGO): radiolytic synthesis and methanol oxidation electrocatalysis, J Nanostructure Chem, 11, 287-299.

[35] Jahani, P.M., Beitollahi, H., Nejad, F.G., Dourandish, Z., Di Bartolomeo, A., (2022), Screen-printed graphite electrode modified with Co3O4 nanoparticles and 2D graphitic carbon nitride as an effective electrochemical sensor for 4-aminophenol detection, Nanotechnology, 33, 395702.

[36] Qian, T., Yu, C.F., Zhou, X., Wu, S.S., Shen, J., (2014), Au nanoparticles decorated polypyrrole/reduced graphene oxide hybrid sheets for ultrasensitiye dopamine detection, Sensor Actuat B-Chem, 193, 759-763.

[37] Hashemi, P., Bagheri, H., Afkhami, A., Amidi, S., Madrakian, T., (2018), Graphene nanoribbon/FePt bimetallic nanoparticles/uric acid as a novel magnetic sensing layer of screen printed electrode for sensitive determination of ampyra, Talanta, 176, 350-359.

[38] Zuo, Y.X., Xu, J.K., Jiang, F.X., Duan, X.M., Lu, L.M., Xing, H.K., Yang, T.T., Zhang, Y.S., Ye, G., Yu, Y.F., (2017), Voltammetric sensing of Pb(II) using a glassy carbon electrode modified with composites consisting of Co3O4 nanoparticles, reduced graphene oxide and chitosan, J Electroanal Chem, 801, 146-152.

[39] Bagheri, H., Hajian, A., Rezaei, M., Shirzadmehr, A., (2017), Composite of Cu metal nanoparticles-multiwall carbon nanotubes-reduced graphene oxide as a novel and high performance platform of the electrochemical sensor for simultaneous determination of nitrite and nitrate, J Hazard Mater, 324, 762-772.

[40] Ganjali, M.R., Beitollahi, H., Zaimbashi, R., Tajik, S., Rezapour, M., Larijani, B., (2018), Voltammetric Determination of Dopamine Using Glassy Carbon Electrode Modified with ZnO/Al2O3 Nanocomposite, Int J Electrochem Sc, 13, 2519-2529.

[41] Jiang, C.J., Elliott, J.M., Cardin, D.J., Tsang, S.C., (2009), An Electrochemical Study of 4-Aminothiophenol/Pt Nanoparticle Multilayers on Gold Electrodes, Langmuir, 25, 534-541.

[42] Yu, H., Yu, J.B., Li, L.L., Zhang, Y.J., Xin, S.Q., Ni, X.Z., Sun, Y., Song, K., (2021), Recent Progress of the Practical Applications of the Platinum Nanoparticle-Based Electrochemistry Biosensors, Front Chem, 9, 282.

[43] Karimi-Maleh, H., Beitollahi, H., Kumar, P.S., Tajik, S., Jahani, P.M., Karimi, F., Karaman, C., Vasseghian, Y., Baghayeri, M., Rouhi, J., Show, P.L., Rajendran, S., Fu, L., Zare, N., (2022), Recent advances in carbon nanomaterials-based electrochemical sensors for food azo dyes detection, Food Chem Toxicol, 164, 112961.

[44] Barsan, M.M., Ghica, M.E., Brett, C.M.A., (2015), Electrochemical sensors and biosensors based on redox polymer/carbon nanotube modified electrodes: A review, Anal Chim Acta, 881, 1-23.

[45] Wang, J., (2005), Carbon-nanotube based electrochemical biosensors: A review, Electroanal, 17, 7-14.

[46] Neravathu, D., Paloly, A.R., Sajan, P., Satheesh, M., Bushiri, M.J., (2020), Hybrid nanomaterial of ZnFe2O4/alpha-Fe2O3 implanted graphene for electrochemical glucose sensing application, Diam Relat Mater, 106, 107852.