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Simple flow injection for determination of sulfite by amperometric detection using glassy carbon electrode modified with carbon nanotubes–PDDA–gold nanoparticles☆

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ABSTRACT

A new approach is presented for sensitive and selective measurement of sulfite (SO_3^{2-}) in beverages based on a simple flow injection system with amperometric detection. In this work, the sulfite sensor was a glassy carbon electrode modified with multiwall carbon nanotubes–poly(diallyldimethylammonium chloride)–gold nanoparticles composites (CNTs–PDDA–AuNPs/GC). Electrochemical oxidation of sulfite with this electrode was first studied in 0.1 M phosphate buffer (pH 7.0) using cyclic voltammetry. The results indicated that the CNTs–PDDA–AuNPs/GC electrode possesses electrocatalytic activity for the oxidation of sulfite with high sensitivity and selectivity. Sulfite was quantified using amperometric measurement with the new sensor at +0.4 V *vs* Ag/AgCl in conjunction with flow injection. The linear working range for the quantitation of sulfite was 2–200 mg L^{-1} (r^2=0.998) with a detection limit of 0.03 mg L^{-1} (3σ of blank) and an estimated precision of 1.5%.The proposed method was successfully applied to the determination of sulfite in fruit juices and wines with a sample throughput of 23 samples per hour.

1. Introduction

Sulfites in various forms (sulfur dioxide, metabisulfite, bisulfite and sulfite) are commonly used as preservatives and antioxidants in food and beverages to inhibit microbiological growth, to control enzymatic and non-enzymatic browning reactions and to assist in preserving vitamin C [1–4]. Despite these advantages, sulfite should be applied in strictly limited amounts due to its potential toxicity. This level of sulfite in food has been subjected to legislation since it was discovered that at a certain concentration level sulfite causes allergic reactions in some individuals [5]. The United States Food and Drug Administration (FDA) has required labeling of products containing more than 10 μg mL^{-1} of sulfite [6–8]. Therefore, it is essential to have accurate and precise methods available for determination of the sulfite content in these products.

The Association of Analytical Chemist (AOAC) recommended a standard reference method for sulfite measurement that involves a combination of distillation and titration. The method required an acid distillation to extract the sulfur dioxide gas from sample matrices prior to analysis and the conventional titrimetric method suffers from poor precision and long analysis time. Many analytical methods for the sulfite assays such as spectrophotometry [9,10], chemiluminescence [4,11], capillary electrophoresis [12] and electrochemical detections [13–18] have been reported. Among these methods, electrochemical detection is most attractive because of its high sensitivity, simplicity, rapid response and inexpensive equipment.

In previous reports, the determination of sulfite using amperometric detections has been proposed using conventional electrodes, such as platinum [19], glassy carbon [20] and gold electrode [21], as the working electrode. However, all these electrodes have certain drawbacks, such as problems associated with the electrode fouling and high positive potential for oxidation of sulfite (0.8–1.2 V *vs* Ag/AgCl). As a result, many substances can interfere with

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☆This paper is dedicated to Prof. Kate Grudpan on the anniversary of his 60th birthday.

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the measurement. Therefore, modification of electrode is required to achieve high sensitivity and selectivity.

The use of functional hybrid materials composed of carbon nanotubes (CNTs) and conducting polymers for the construction of chemical sensors and biosensors has attracted great attention [22–24]. CNTs are increasingly recognized as a promising material for surface functionalization in electrochemistry and are widely used in research. The lamellar planes of sp^2 carbon in graphite sheets are organized in hexagons with tremendously high degree of delocalization of π-electrons. Thus, CNTs can display metallic, semiconducting and superconducting electron transport properties [25,26] that are able to promote proton or electron transfer reaction. They also have high thermal capacity and are environmental friendly [25]. Recent studies have demonstrated that CNTs can impart high electrocatalytic activity and decrease surface fouling of electrode [27,28]. Poly(diallyldimethylammonium chloride), PDDA, is a conducting polymer used widely in fabrication of chemical [29] or biological sensors [23,24,30] and in various industrial applications [31]. For sensor application, it has been extensively used to immobilize biomolecules and to disperse nanomaterials in the development of electrochemical transducers [23,24,30].

Gold nanoparticles (AuNPs) feature excellent conductivity, high surface area and catalytic properties that make them promising materials for the electrochemical detection of various analytes [32]. AuNPs can be prepared and conjugated with many functionalizing agents such as ligands, surfactants, polymers and CNTs. They have been found to play an important role in augmenting the quality of chemical and biosensors. The synergistic combination of electroactive AuNPs and conducting compounds such as CNTs provides electro-sensitive and selective system for detection of cholesterols [23], hydrogen peroxide [24] and glucose [33]. However, to our knowledge, the use of glassy carbon modified with hybrid nanocomposites of CNTs–PDDA–AuNPs nanocomposite for amperometric detection of sulfite has not yet been reported.

This work describes a simple and effective method for constructing a sulfite sensor using carboxylated functionalized multiwall carbon nanotubes–poly(diallyldimethylammonium chloride)–gold nanoparticles (CNTs–PDDA–AuNPs) composites. The formation of this composite is through electrostatic interaction. The CNTs–PDDA–AuNPs nanocomposite is formed by drop coating on the surface of the glassy carbon (GC) electrode. CNT–PDDA–AuNPs composite film exhibits high activity, sensitivity and selectivity in the detection of sulfite.

2. Experimental

2.1. Chemicals and reagents

All solutions were prepared in deionized-distilled water (Water Pro PS, USA). Sodium sulfite (Na_2SO_3) and poly (diallyldimethylammonium chloride) (PDDA, MW: 100,000–200,000, 20% w/w) were purchased from Sigma-Aldrich (St. Louis, USA). Carboxylated functionalized multiwall carbon nanotubes (CNTs-COOH, diameter: 15 ± 5 nm, length: 1–5 μm, purity: $>95\%$) were purchased from Nanolab Inc. (MA, USA). Hydrogen tetrachloro aurate (III) trihydrate ($HAuCl_4 \cdot 3H_2O$, $Au > 48\%$) was purchased from Acros Organic (Geel, Belgium)

2.2. Apparatus

2.2.1. Cyclic voltammetry

Cyclic voltammetric measurements were carried out using an eDAQ potentiostat (model EA161, Australia) equipped with an e-corder 210 and e-Chem v2.0.13 software. The active surface area of glassy carbon electrode, (diameter 3 mm, CH Instrument, USA) was approximately 0.07 cm^2. An in-house three-electrode cell, comprising a working electrode (CNTs–PDDA–AuNPs/GC electrode), a reference electrode (Ag/AgCl) and a counter electrode (platinum wire) was employed. Measurements were performed using a phosphate buffer (0.1 M, pH 7.0) as supporting-electrolyte solution and pure nitrogen was used for deaeration of the solution.

2.2.2. Simple flow injection system with sulfite sensor

The flow injection (FI) system for amperometric detection of sulfite with the new sulfite sensor consisted of a Shimadzu pump (model LC-10AD, Japan), a Rheodyne injector (model 7725, USA) fitted with 20 μL sample loop and an electrochemical detector. An eDAQ potentiostat (EA161), equipped with an e-corder 210, Chart v5.5.11 software and a thin layer flow cell with three electrodes system (CH Instruments, USA), was used for amperometric measurements. The glassy carbon modified with CNTs–PDDA–AuNPs was used as the working electrode, Ag/AgCl as the reference electrode and a stainless steel tube as the counter electrode. Silicone rubber gasket (flow channel, 0.1×0.6 cm) was used as a spacer in the thin layer flow cell between the base of the cell and the working electrode. The analyte solution was passed through an inlet passage in the base and along a channel in the gasket contacting the electrode, then to the outlet. The area of working electrode was ca.0.06 cm^2.

2.3. Preparation of sulfite sensor

2.3.1. Preparation of AuNPS

Gold nanoparticles (AuNPs) were synthesized according to the method previously described by McFarland et al. [34]. In brief, 20 mL of 1.0 mM $HAuCl_4$ was heated to boiling on a stirring hot plate. Then 2.0 mL of 38.8 mM sodium citrate was added to the solution. The solution was further heated and stirred for about 10 min to obtain a wine-red solution. The solution was then cooled to room temperature while stirring continuously and stored in a dark bottle at 4 °C.

2.3.2. Preparation of CNTs–PDDA

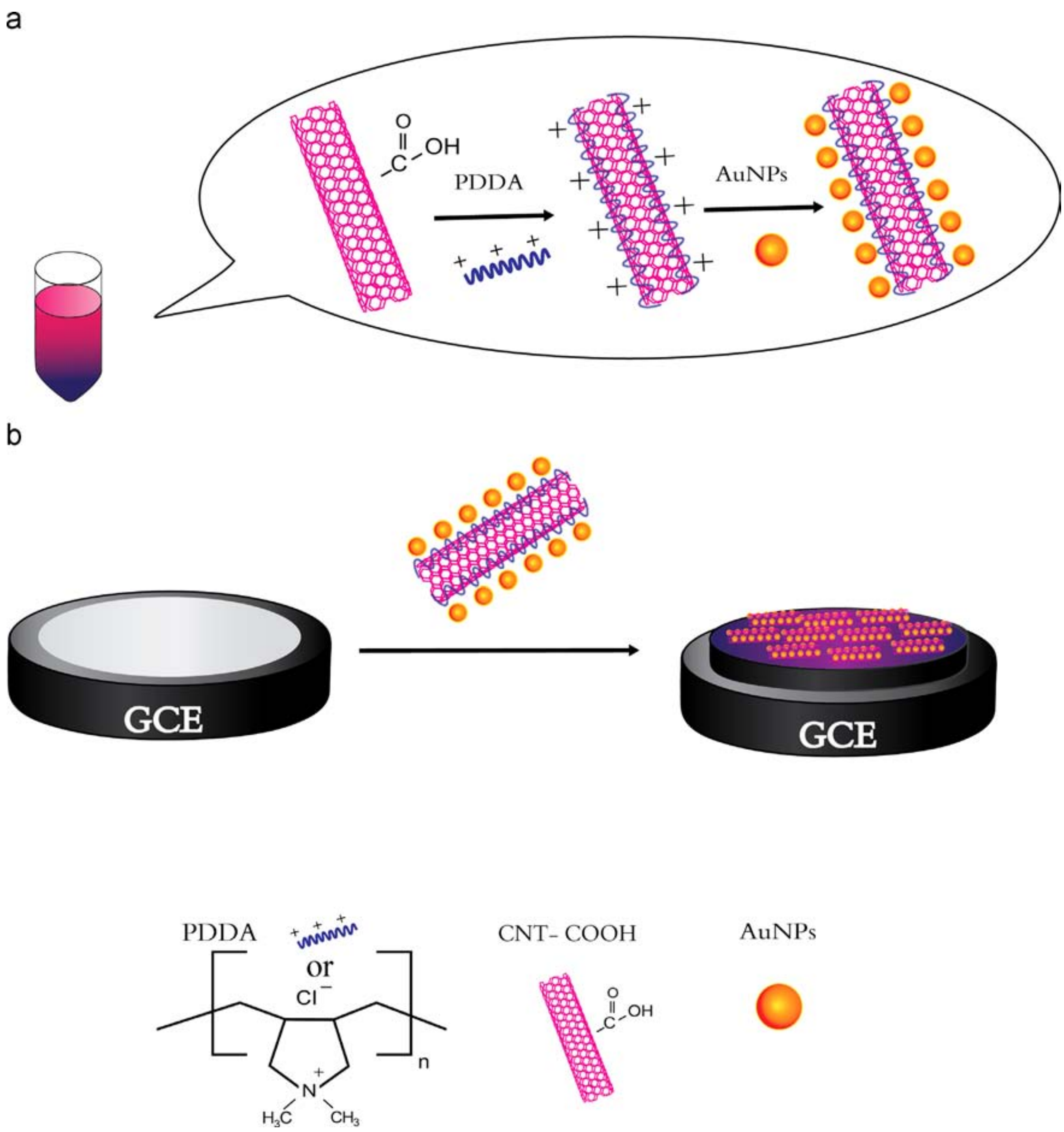
A general method for functionalization of multiwall carbon nanotube with PDDA (CNTs–PDDA) as described by Cui et al. [24] was adopted. Briefly, carboxylated carbon nanotubes (CNTs-COOH) were functionalized with PDDA by dispersing of 10 mg CNTs-COOH into 20 mL of a 0.25% PDDA aqueous solution containing 0.5 M NaCl and ultrasonicated, with stirring, for 30 min. The resulting dispersion was centrifuged and washed with water three times to remove residual PDDA. Finally, 2 mg of the collected product was dispersed in1 mL water and the resulting solution sonicated for 5 min before use.

2.3.3. Preparation of CNTs–PDDA–AuNPs

The preparation of CNTs–PDDA–AuNPs dispersion is schematically shown in Scheme 1a. The CNTs–PDDA was functionalized with AuNPs by the following procedure: 0.5 mL of CNTs–PDDA dispersion (4 mg mL^{-1}) was mixed with an equivalent volume of 0.25% AuNPs solution. The resulting solution was then sonicated for 15 min. The negatively charged AuNPs was adsorbed on the positively charged CNTs–PDDA by electrostatic attraction.

2.3.4. CNTs–PDDA/GC electrode

Prior to the electrochemical experiments, glassy carbon (GC) electrode (diameter 3 mm) was polished using 1.0 and 0.05 μm alumina slurry, successively. The electrode was rinsed with distilled water and then sonicated in de-ionized water for 5 min to remove residual abrasive particles. GC/CNTs–PDDA electrode was prepared by casting 40 μL of the CNTs–PDDA dispersion (2 mg mL^{-1}), mentioned



Scheme 1. Preparation of the sulfite sensor based on the CNTs–PDDA–AuNPs/GC electrode: (a) preparation of CNTs–PDDA–AuNPs dispersion and (b) drop-coating method of CNTs–PDDA–AuNPs dispersion on to glassy carbon (GC) electrode.

above, on the surface of the polished glassy carbon (GC) electrode, and then left to dry at ambient temperature.

2.3.5. CNTs–PDDA–AuNPs/GC electrode

The preparation of sulfite sensor based on the CNTs–PDDA–AuNPs/GC electrode is schematically shown in Scheme 1b. The electrode was prepared by casting 40 μL of the CNTs–PDDA–AuNPs dispersion on the surface of the polished glassy carbon (GC) electrode, and dried at ambient temperature.

2.3.6. Characterization

The TEM image of AuNPs was collected under vacuum at an operating voltage of 200 kV (JEOL 2100 TEM, Japan). A drop of colloidal AuNPs solution was placed on a formvar-coated TEM grid. The hydrodynamic diameter of AuNPs was determined by using dynamic light scattering (DLS, MAL 500261 Particle Size Analyzer) equipped with 35 mW solid-state laser detector at an operating wavelength of 658 nm. Measurements were carried out at 25 °C with 90°detection angle in a PS cuvette. The sample was dispersed in 0.01 M KNO_3 solution.

The SEM images were collected with a field emission scanning electron microscope (FESEM, JEOL JSM 5410 LV, Japan) under vacuum at accelerating voltage of 20 kV. The sample was mounted on a double-sided carbon tape, and then gold sputter coated to minimize charging prior to SEM imaging. Atomic force microscopy (AFM) images were obtained using a scanning microscope probe (Park Systems Corp., Korea.) controlled by the XEI software.

2.4. Standard method for sulfite determination

The iodometric method [35] was employed in order to compare the results obtained using the proposed FI-sulfite sensor method. An accurate sample volume (5.00 mL) was transferred into a 125 mL conical flask and 5 mL of standard iodine solution added. The excess of iodine was titrated with standard sodium thiosulfate solution using starch as indicator. These titrations were carried out as quickly as possible with the end point indicated by the formation of a light blue color.

2.5. Method validation

Various brands of fruit juice and wine were purchased from supermarkets in Ubon Ratchathani Province, Thailand. Five fruit juice samples of (A–E), three white wines (F–H) and four red wines (I–L) were analyzed using the developed amperometric sensor in flow injection system. Dilution of samples (5 or 10 fold) with phosphate buffer was carried out prior to analysis. The amperometric results were compared with those from the iodometric method [35].

3. Results and discussion

3.1. Characterization of nanomaterials

The morphology and size of as-prepared gold nanoparticles were examined by TEM measurement. From the TEM image as shown in Fig. 1(a), the nanoparticles mainly consisted of spherical gold nanostructures having uniform size. In order to investigate the particle size distribution, the as-prepared nanoparticles were characterized by DLS measurement. As shown in Fig. 1(b), the as-prepared nanoparticles exhibit a broad particle size distribution with a mean particle diameter of about 13.23 nm.

Surface morphologies of glassy carbon electrode modified with CNTs–PDDA and CNTs–PDDA–AuNPs were investigated by SEM [Fig. 2(a, b)] and AFM [Fig. 2(c, d)]. As shown in Fig. 2(a), the surface of CNT–PDDA modified electrode displays the characteristic feature of a smooth film. However with the augmented AuNPs, Fig. 2(b) clearly shows that the electrode surface became rougher after modification (CNTs–PDDA–AuNPs), while the feature of CNTs–PDDA is still evident. This indicated that AuNPs play an important role to a modified electrode surface, resulting in a larger surface area. The atomic force microscopy (AFM) is one of the most widely used techniques for topological study. As shown in Fig. 2(c), long and typical tube-like CNTs form a homogeneous hybrid material, with some coexisting from the wrapped structure. Here, PDDA plays the roles of dispersing agent, inhibiting the strong π–π stacking interaction between CNTs [23]. In contrast, the AFM image of CNTs–PDDA–AuNPs displays obviously different surface morphology from CNTs–PDDA. As shown in Fig. 2(d) the CNTs supports are decorated by nanosized AuNPs with some aggregations. These results might be attributed to the interaction between the negatively charged CNTs and the positively charged PDDA-capped AuNPs [33].

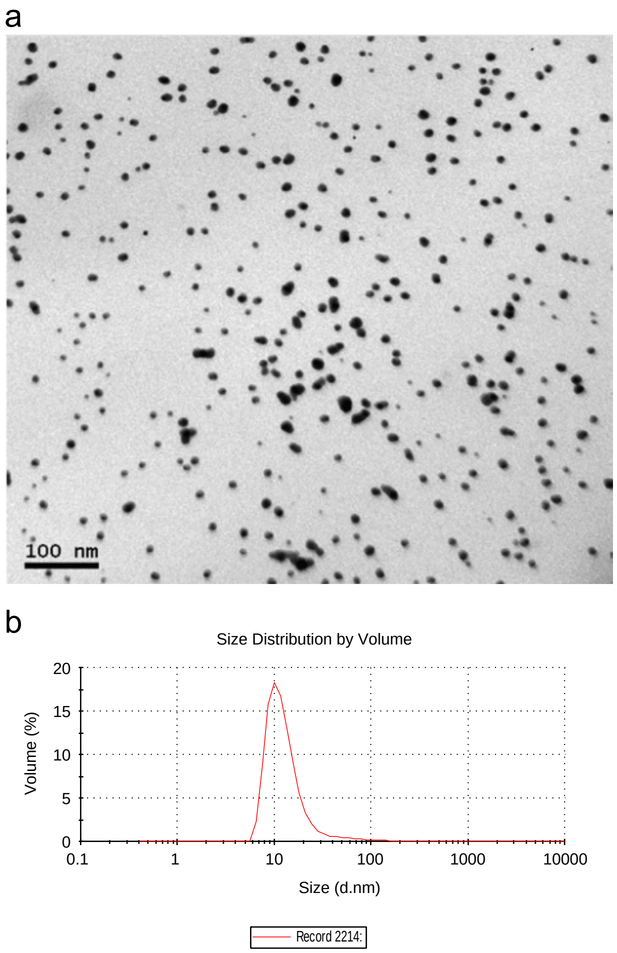


Fig. 1. (a) TEM image and (b) particle size distribution of as-prepared AuNPs.

3.2. Cyclic voltammetry of sulfite

The electrochemical behavior of sulfite at the GC, CNTs/GC, CNTs–PDDA/GC and CNTs–PDDA–AuNPs/GC electrodes were studied using cyclic voltammetry. Fig. 3 shows the comparison of the response of the bare GC, CNTs/GC, CNTs–PDDA/GC and CNTs–PDDA–AuNPs/GC electrodes toward electro-oxidation of sulfite at pH 7.0. Sulfite oxidation is an electrochemically irreversible process. Bare GC electrode (curve a) results in a peak shape signal at about 0.85 V versus Ag/AgCl, whereas the CNTs/GC (curve b), CNTs–PDDA/GC (curve c) and CNTs–PDDA–AuNPs/GC (curve d) shows oxidation peaks at 0.40, 0.33 V and 0.25 V, respectively. A shift of −0.45, −0.52 V and −0.60 V was obtained with the CNTs/GC, CNTs–PDDA/GC and CNTs–PDDA–AuNPs/GC electrodes, respectively, compared to the peak observed at GC electrode. The sulfite signals from CNTs/GC, CNTs–PDDA/GC and CNTs–PDDA–AuNPs/GC are also much larger than that for GC. These results indicate that CNTs can be used to promote electron transfer reactions due to their significant high electrical conductivity, high surface area as well as good chemical stability. These results also show that CNTs–PDDA reduces the overpotential of sulfite oxidation and in fact imparts electrocatalytic activity. There is an enhancement of the anodic peak potential and peak current at CNTs–PDDA–AuNPs/GC relative to that obtained at CNTs–PDDA/GC. This result further shows that the electrocatalytic activity of CNTs–PDDA–AuNPs/GC was higher than the CNTs–PDDA/GC electrode due to the high conductivity and high surface-to-volume ratio of AuNPs, which facilitates electron transfer. This improvement in sensor sensitivity and selectivity using AuNPs is similar to that reported for hydrogen peroxide sensor studied by Xiao et al. [36]. From these results, it can be concluded that the highest electrocatalytic effect for sulfite oxidation is observed at CNTs–PDDA–AuNPs/GC (curve d).

The effect of buffer pH on oxidation peak current and peak potential was investigated for pH 5 to pH 8 using the 0.1 M phosphate buffer as supporting electrolyte (Fig. 4a). It was observed that the values of peak potential shifted slightly towards less positive values (Fig. 4b) when the pH increased. Fig. 4 (c) shows that the maximum peak current was obtained for pH 7.0. Therefore, pH 7.0 was selected as the optimum pH for amperometric detection of sulfite.

Fig. 5(a) shows the cyclic voltammograms of a sulfite solution at the CNTs–PDDA–AuNPs/GC in 0.1 M phosphate buffer (pH7) for various scan rates. As shown in the inset of Fig. 5(a), the oxidation peak current (μA) increased linearly with the square root of scan rate ($V^{1/2}\ s^{-1/2}$) within the scan range of 0.01–0.15 V s^{-1}. Linear regression analysis provided r^2 value of 0.996. These results indicated that the current is limited by diffusion of sulfite to the CNTs–PDDA–AuNPs/GC electrode. It can also be seen in Fig. 5a that with increasing scan rate, the peak potential for the

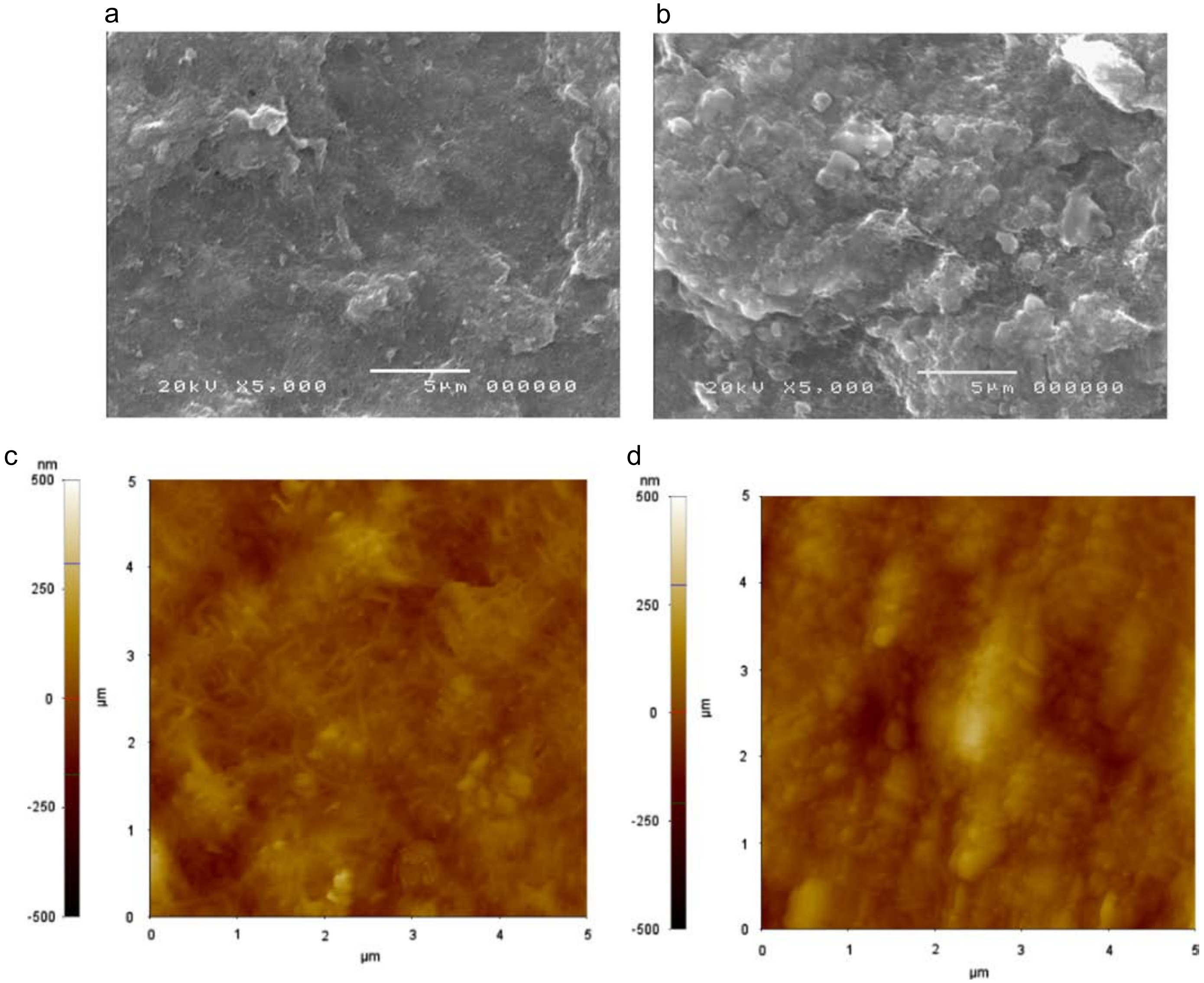


Fig. 2. SEM (a, b) and AFM (c, d) images of CNTs–PDDA (a, c) and CNTs–PDDA–AuNPs (b, d).

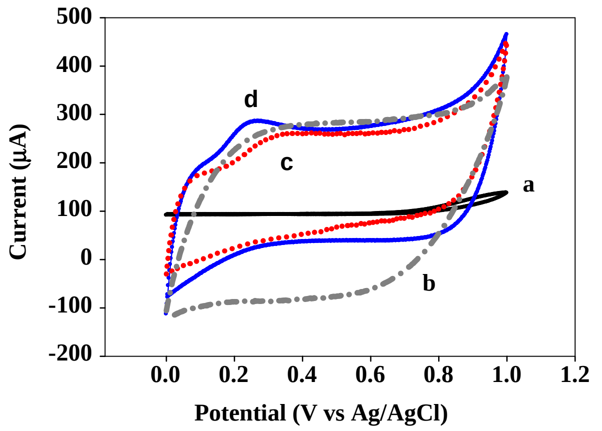


Fig. 3. Cyclic voltammograms of 4 mM sulfite (SO_3^{2-}) in 0.1 M phosphate buffer pH 7.0 on (a) bare glassy carbon (GC), (b) CNTs/GC, (c) CNTs–PDDA/GC and (d) CNTs–PDDA–AuNPs/GC electrodes; scan rate: 0.05 V s^{-1}.

electro-oxidation of sulfite is shifted to more positive values. This result suggests that the reaction between the oxidation sites of CNTs–PDDA–AuNPs/GC with sulfite is rate limiting.

Fig. 5(b) shows the relationship between peak current (µA) and sulfite concentration at 2 to 10 mM. Linear calibration (r^2=0.999) was obtained with a slope of 38.1 µA mM^{-1} (inset of Fig. 5(b)). These data confirm that the CNTs–PDDA–AuNPs/GC electrode is suitable for quantitation of sulfite.

The repeatability of the measurements and the reproducibility between electrodes were also studied. The relative standard deviation (RSD) of the sensor response with 10 mg L^{-1} sulfite was 1.6% for 10 successive measurements. The amperometric responses remained within 90% of the initial response for 4 days without any surface treatment. The sensor exhibited 70% of the initial response on the 7th day of use. Repeat of the set of experiments as described in Section 2.3.4 showed satisfactorily results between electrodes.

3.3. *Amperometric detection in FIA system*

3.3.1. *Optimal potential*

The proposed amperometric method for detection of sulfite is based on the electrochemical monitoring of the oxidation signal from sulfite at the CNTs–PDDA–AuNPs/GC electrode. Detection potential strongly affects the size of the current signal from sulfite. To find the optimal detection potential, hydrodynamic voltammogram was

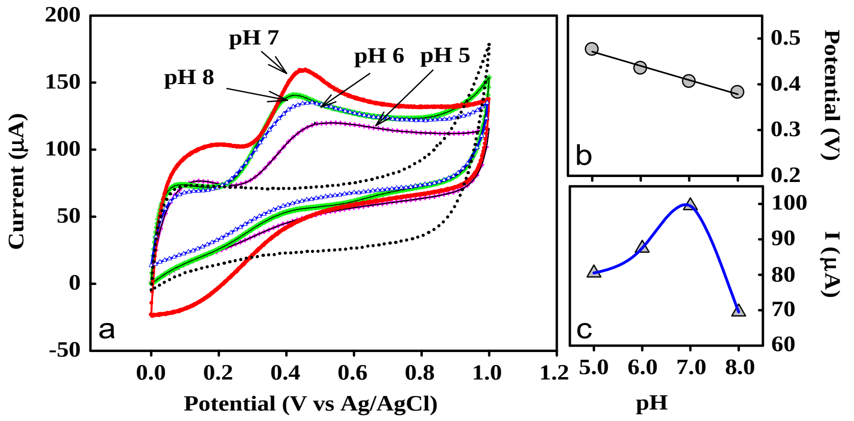


Fig. 4. Results from cyclic voltammetry at various pHs for 2 mM sulfite in 0.1 M phosphate buffer showing (a) CVs on CNTs–PDDA–AuNPs/GC electrode, (b) peak potential and (c) peak current for various pHs.

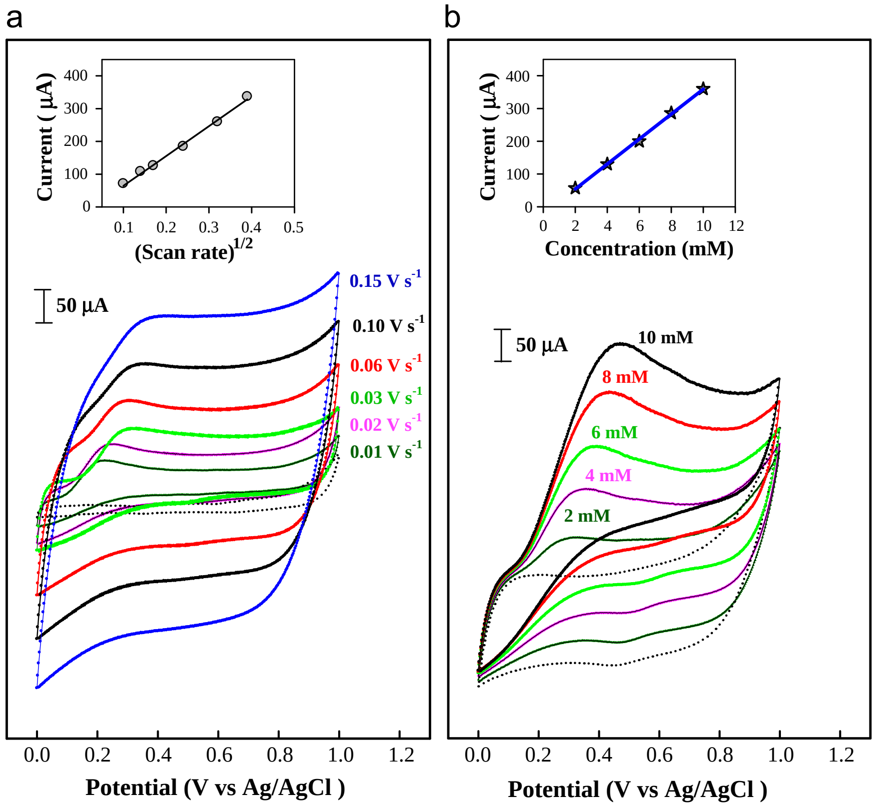


Fig. 5. Cyclic voltammograms for sulfite in 0.1 M phosphate buffer (pH 7.0) at sulfite electrode (a) with variation of the scan rate from 0.01 to 0.15 V s^{-1}; sulfite: 2 mM and (b) variation of the sulfite concentration from 2 to 10 mM; scan rate: 0.05 V s^{-1}. Optimal conditions; modifying solution: 2 mg L^{-1} of CNTs–PDDA containing 0.125% of AuNPs dispersion; modifying volume: 40 μL.

measured. Hydrodynamic voltammetry was obtained from injection of 20 μL of 2 mg L^{-1} standard sulfite solution into the flow injection system with varying detection potential from 0.0 to 1.0 V as shown in Fig. 6. The oxidation current increased with the increase of detection potential between 0 and 0.4 V. Beyond that, a sharp decrease in the peak current response was noted. Therefore, detection potential of 0.4 V was selected for the FIA experiments.

3.3.2. Analytical features

Using the optimum condition, representative signal profiles for multiple injections and calibration plot are depicted in Fig. 7. Calibration curve is linear in the range of 0.1–200 mg L^{-1}. The regression equation is given by $y=10.054x+42.304$ ($r^2=0.998$), where y and x are the height of peak current (nA) and sulfite concentration (mg L^{-1}), respectively, with the slope of the straight line corresponding to linear sensitivity of 10.054 nA mg^{-1} L. The detection limit (3σ) is ~0.03 mg L^{-1}. The system provides good precision (%R.S.D = 1.5) for 20 μL injections ($n=10$) of 2 mg L^{-1} sulfite. Throughput of analysis is 23 samples per hour.

A comparison of the analytical characteristics of the present amperometric sulfite sensor with other modified electrodes for sulfite detection is summarized in Table 1. The applied potential of the proposed method is lower [15,17,18,37] or comparable to those of previous reports [14,16,38]. This has the advantage of reducing the risk of interference from sample matrices. Moreover, the use of

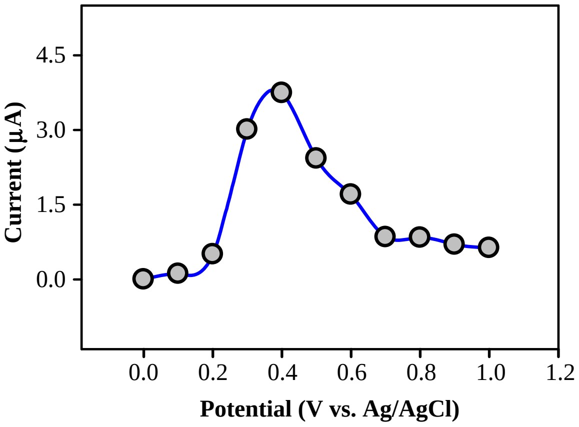


Fig. 6. Influence of the applied potential on the detection of sulfite at CNTs–PDDA–AuNPs/GC. Conditions: sulfite: 2 mg L^{-1}, carrier solution: phosphate buffer pH 7.0, flow rate: 1.0 mL min^{-1}.

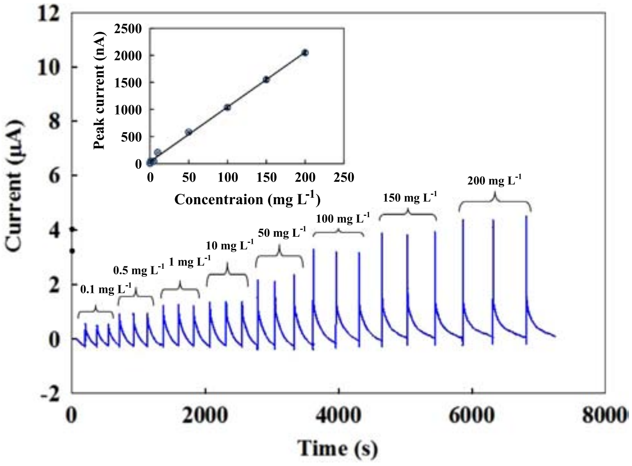


Fig. 7. Typical FIA response obtained for injections of sulfite standards. The inset shows the linear relationship between the signal of sulfite and concentration. Conditions: operating potential: +0.4 V *vs* Ag/AgCl, carrier solution: phosphate buffer pH 7.0, flow rate: 1.0 mL min^{-1}.

CNTs–PDDA–AuNPs/GC electrode gives an improved analytical performance for sulfite determination in terms of lower detection limit and wider linearity range than those of other previously reported modified electrodes. It was observed that our method was easier (*i.e.* more rapid) for modifying the electrode than the previous methods [17,18,37,38]. Although the previous electrodes of NiPCNF [37] and FDA-CNT [38] could provide as high sensitivity as our method, the fabrication or methods for modifying electrodes were relatively more complicated. For example, in Ref. [37], a two-step sol–gel technique was required to construct nickel pentacyanonitrosylferate (NiPCNF) modified composite ceramic carbon electrodes. Whereas, in Ref. [38], grinding for 40 min using mortar and pestle was required to obtain a uniformly-wetted paste to construct the ferrocene dicarboxylic acid modified carbon nanotubes paste (FDA-CNT) electrode. On the other hand, our electrode was easily prepared by drop casting of the CNTs–PDDA–AuNPs dispersion on the surface of glassy carbon electrode. The applicability of electrode surfaces formed with hybrid materials of CNTs–PDDA–AuNPs for simple construction of chemical sensor was demonstrated. This novel way to fabricate amperometric sulfite sensor by CNTs–PDDA–AuNPs composites-covered GC electrode showed obvious synergistic augmentation of the sensor performance. The advantages of this developed method are the ease of preparation and the high stability of the electrode.

Table 1
Comparison of analytical performance of the proposed sulfite sensor towards sulfite determination with previously reported modified electrodes.

Electrode	E_{app} (V)	Linear range (mg L^{-1})	Detection limit (mg L^{-1})	References
Ph[a]	+0.40	0.6–200	0.28	[14]; FIA
FeHCF[b]	+0.85	20–190	6.4	[15], batch
CHIT-Fc/CNT[b]	+0.35	0.4–120	0.22	[16], batch
CuHCF-CNT[c]	+0.55	0.5–50	0.40	[17], FIA
CILE	+0.55	0.48–80	0.32	[18]; batch
NiPCNF[d]	+0.60	0.25–252	0.06	[37], batch
FDA-CNT[c]	+0.35	0.75–12.6	0.04	[38], batch
CNT–PDDA–AuNPs[b]	+0.40	0.1–200	0.03	This work

Ph = phenothiazine, FeHCF = iron hexacyanoferrate, CHIT-Fc = ferrocene-branched chitosan, CNT = carbon nanotube, CuHCF = copper hexacyanoferrate, CILE = carbon ionic liquid electrode, CNT-COOH = carboxylic-functionalized carbon nanotube; PDDA = poly(diallyldimethyl ammoniumchloride), NiPCNF = nickel pentacyanonitrosylferrate, FDA = ferrocenedicarboxylic acid, E_{app} = applied potential,

[a] Screen-printed carbon electrode.
[b] Glassy carbon electrode (GCE).
[c] Carbon paste electrode.
[d] Ceramic carbon electrode.

Table 2
Effect of foreign ions on the alteration of FI signal obtained from replicate injections (n = 3) of sulfite 10 mg L^{-1} standard.

Foreign species/added as	**Results**[a]
Fructose	Do not interfere (studied up to 1000 mg L^{-1})
Glucose	
Sucrose	
Ethanol/C_2H_6O	
NO_3^-/$NaNO_3$	
SO_4^{2-}/Na_2SO_4	
Cl^-/NaCl	
Ascorbic acid/$C_8H_8O_6$	Interfere (at 50 mg L^{-1})

[a] Greater than ± 5% signal alteration is classified as interfering condition.

3.4. Interference study and application to real samples

Interference study was conducted to identify species that may affect the analysis. Compounds were selected for the three types of ingredients which are always found in fruit juices and wines. These include electroactive species (ascorbic acid, nitrate, sulfate and chloride), sugars (fructose, glucose and sucrose) and ethanol. The effect of these substances on the FI signals of a standard 10 mg L^{-1} sulfite using the proposed method was examined. The tolerance limit was defined as the amount which caused signal changes greater than ± 5%. The results are summarized in Table 2. The results show that sugars (fructose, glucose and sucrose), inorganic acids (NO_3^-, SO_4^{2-}, and Cl^-) and ethanol, at 100-fold excess, did not exceed the tolerance limit. However, ascorbic acid produced considerable interference. As it can be seen, ascorbic acid at any five-fold excess caused erratic response. In this method, it is particularly important that ascorbic acid which is a serious interference for sulfite determination in many analytical methods including electrochemical methods [17,18] do not interfere at concentration up to five-fold excess of sulfite. Nevertheless, the determination of sulfite in juices and wines with the CNTs–PDDA–AuNPs/GC electrode includes sample dilution and therefore, at the usual concentration ratios in these samples, the interference from ascorbic acid negligible. Thus, the selectivity of the developed method is satisfied.

The possibility for the use of the developed system in real sample analysis was investigated. Samples of juices and wines were analyzed using our developed system. The results were

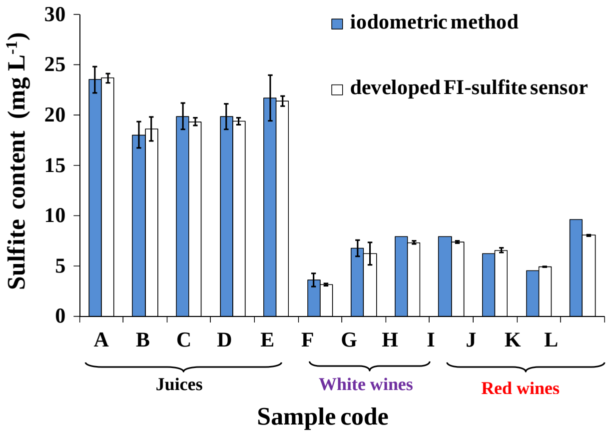


Fig. 8. Comparison of the sulfite content found in fruit juices (A–E), white (F–H) and red (I–L) wines obtained by the developed FI-sulfite sensor (CNTs–PDDA–AuNPs/GC) and the iodometric method [33]. Determination for each method was carried out in triplicate.

compared with the values obtained from the iodometric method and are shown in Fig. 8. It can be seen that the results from our developed system are in good agreement to those obtained from standard iodometric method. The results determined by both methods are considered not significantly different at 95% confidence by paired *t*-test ($t_{\text{observed}}=1.7276$, $t_{\text{critical}}=2.2009$) [39]. The results confirm that the present amperometric sulfite sensor is suitable for the determination of sulfite in juices and wines.

4. Conclusion

In this work, a flow injection system with amperometric detection using a novel sulfite sensor is proposed. The sensor was a CNTs–PDDA–AuNPs composites-modified glassy carbon electrode. The nanocomposite materials were formed by coating negatively charged carboxylated CNTs with positively charged PDDA, followed by capping with negatively charged AuNPs *via* electrostatic interaction. The presence of CNTs–PDDA–AuNPs on the modified GC surface produced an electrocatalytic effect for the detection of sulfite. Enhancement of the anodic peak potential and peak current at CNTs–PDDA–AuNPs/GC with respect to bare glassy carbon electrode was obtained. Sulfite was quantified using amperometric measurement in simple flow injection at the CNTs–PDDA–AuNPs/GC electrode at +0.4 V *vs* Ag/AgCl. The proposed sensor exhibited wide linearity range (0.1–200 mg L^{-1}), low detection limit (0.03 mg L^{-1}), acceptable reproducibility (%R.S.D = 1.5), and rapid sample throughput (23 samples per hour). The application of the developed method to sulfite determination in fruit juices and wines gave results which are in good agreement with those obtained by the standard iodometric method. The method was also applicable for colored sample, including red wines, which is usually a serious interference for sulfite determination in many analytical methods.

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