



Voltammetric determination of nitrite by using a multiwalled carbon nanotube paste electrode modified with chitosan-functionalized silver nanoparticles

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Abstract

A cyclic voltammetric method is described for the determination of nitrite by using a multiwalled carbon nanotube paste electrode (MWCNT) that was modified with chitosan-functionalized silver nanoparticles (Chit-AgNPs). The AgNPs were prepared by one step procedure using chitosan as stabilizing agent. The resulting modified AgNPs were drop-coated onto the electrode. By combining the advantages of chitosan, AgNPs (in the form of Chit-AgNPs) and MWCNT, the assay exhibits a remarkable improvement in the cyclic voltammetric response towards the oxidation of nitrite at a typical peak potential of 0.81 V (vs. SCE) in buffer of pH 4.0. The accumulation of nitrite on the electrode also was achieved, and this further enhances the analytical sensitivity. Under optimized conditions, the oxidation peak current increases linearly in the 100 nM to 50 μ M nitrite concentration range, and the detection limit is 30 nM. The method has high selectivity for nitrite even in the presence of other potentially interfering ions.

Keywords Chitosan · Functionalized silver nanoparticles · Modified carbon nanotubes paste electrode · Nitrite assay · Cyclic voltammetry · River water

Introduction

Nitrite is an essential plant nutrient [1], an important constituent of the nitrogen cycle [2], widely applicable as an additive for the preservation of large number of foods [3] as well as important in therapeutic applications [4]. Furthermore, salts of

nitrite are mostly used as corrosion inhibitor in steels [5]. However, in spite of all these applications, the discharged of waste water containing nitrite into the environment is a big source of deterioration of lakes, rivers and water sources, which may cause serious health hazards to human. Inside the human body, nitrite reacts with amines and probably causes carcinogenic nitrosamines [6] as well as oxidizes hemoglobin to methemoglobin which diminishes the oxygen carrying capacity [7]. Therefore, due to its toxicity at certain concentration, the most sensitive, selective and reliable methods are required for the determination of nitrite. In this context, numerous analytical methods have been reported by various researchers for the determination of nitrite using different analytical techniques. These include; electrophoresis [8], high-performance liquid chromatography [9], ion chromatography [10], chemiluminescence [11], spectrophotometry [12] and electrochemical methods [13, 14].

Nitrite is electrochemically active towards gold [15], copper [16], platinum [17], and carbon electrodes [18, 19]. However, due to the high oxidation potential, poor sensitivity and reproducibility, these electrodes have limited uses for the determination of nitrite. In comparison, MWCNTs have been considered to be the best electrode materials for the oxidation

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of nitrite owing to their high electrical conductivity (1.85×10^3 S/cm), possess high charge transfer rate, good chemical stability and high mechanical strength [20, 21].

Owing to the prerequisite of high sensitivity and selectivity for the electrochemical determination of nitrite, the bare electrodes substrates have often been modified with different chemical substances.

Chitosan is a natural biopolymer which is nontoxic and has the ability to form film on the electrode surfaces. It possesses reactive positively charged amino and hydroxyl groups (in acidic pH) in its structure that may have the tendency to attract the negatively charged nitrite when present in solution [22]. Due to these properties, make chitosan a highly efficient sensor for nitrite. For this purpose, Jiang et al. [23] have modified GCE with chitosan-MWCNT to investigate the electrochemical behavior of nitrite. This electrode showed a fast response towards the oxidation of nitrite.

To achieve better electrochemical response, metallic nanoparticles and their composite as electrode materials have been used by various researchers for the electrooxidation of nitrite. Because of the large surface to volume ratios, the electrodes fabricated with nanomaterials have exhibited excellent electrocatalytic response and electrochemical conductivity as compared to the bulk metals. For this purpose, various metallic nanoparticles such as Au [24], Cu [25] and Ag nanoparticles [26] have been employed to modify various electrodes. Among them, the electrodes modified with AgNPs have been considered to be cheaper, less prone to surface oxidation and offer good electrocatalytic activities towards nitrite oxidation as compared to the others metallic nanoparticles.

To further improve the electrochemical detection performance; some researchers have used the electrodes modified with both metal nanoparticles and chitosan to exploit the combining properties for the electro oxidation of nitrite. For instance, Yang et al. [27] have employed a glassy carbon electrode fabricated with Cu nanoparticles/carbon nanotube and chitosan film for the electrocatalytic reduction of nitrite. The electrode surface was modified by Cu nanoparticles using electrodeposition method. Similarly, Mo et al. [28] have prepared Au Nanoparticles/graphene-chitosan modified electrode for detection of nitrite. The electrode was constructed by first coating a drop of graphene-chitosan suspension on the GCE and then electrodeposited AuNPs on the electrode surface.

However, in these modified electrodes, the electrodepositions of Cu and Au nanoparticles have been carried out after coating chitosan layer. This may lead to dampen the active sites of chitosan and thus direct interaction of nitrite with chitosan may not be possible. To increase the performance by using the combined benefits of electrode material, the construction of such modified electrode is needed in which chitosan may be available for

the direct interaction of nitrite, while utilizing the characteristic properties of nanoparticles also.

It is known that the functionalization of metal nanoparticles with specific ligands can make such sensors more selective. In this regard, a chitosan functionalized AuNPs have been used by Baishnisha et al. [29] for the selective colorimetric detection of nitrite. The sensitive detection of nitrite was achieved due to the strong binding interaction between positively charged groups present on the surfaces of nanoparticles and negatively charged nitrite.

In the present work, we modified the MWCNT paste electrode with chitosan functionalized AgNPs (Chit-AgNPs) to exploit the combined and direct interaction of chitosan and AgNPs (in the form of Chit-AgNPs) with nitrite. The designed Chit-AgNPs/MWCNTPE was employed for the adsorption cyclic voltammetric determination of nitrite. The Chit-AgNPs were prepared by one step approach using chitosan as stabilizing agent and was drop coated to modify the electrode surface. The combination of nanoparticles and chitosan to modify the electrode in this way increases the sensitivity and may be a simple approach.

Materials and methods

Reagents

The multi-walled carbon nanotubes powder (www.sigmaaldrich.com/materials-science/material-science-products.html?TablePage=104696184), Chitosan (www.sigmaaldrich.com/catalog/substance/chitosan12345901276411?lang=en®ion=PK), silver nitrate (www.sigmaaldrich.com/catalog/product/sigald/209139?lang=en®ion=PK) and sodium nitrite (www.sigmaaldrich.com/catalog/product/sigald/237213?lang=en®ion=PK) were obtained from sigma-Aldrich, Germany. The entire chemicals used in this study were of high purity which needs no further purifications. Deionized water was used throughout the experimental study. The Britton Robinson (BR) buffer was used as supporting electrolyte. The standard buffer solution was prepared by mixing 50 mL of 0.4 M acetic acid (CH_3COOH), 50 mL of 0.4 M phosphoric acid (H_3PO_3), 50 mL of 0.4 M boric acid (H_3BO_3). The stock solution of nitrite (0.01 M) was prepared by dissolving 0.035 g sodium nitrite (NaNO_2) in deionized water.

Instrumentation

DY2113 series Mini Potentiostat (Austin, USA) was used for all the electrochemical measurements. The voltammetric study was performed in an electrochemical cell comprising of three electrode system. In this system, saturated calomel electrode and platinum wire were functioned as reference

and counter electrode, respectively, while multi-walled carbon nanotube paste electrode fabricated with chitosan capped silver nanoparticle was used as a working electrode for the voltammetric detection of nitrite.

Synthesis of chitosan functionalized AgNPs (chit-AgNPs)

Chit-AgNPs were prepared according to the procedure described by Chin et al. [33]. In a typical procedure, 47 mL of 2% chitosan solution was mixed with 2 mL of 0.02 M solution of AgNO_3 . The mixture was subjected to continuous stirring at room temperature for 30 min. After that, 1 mL of 8 mg/mL solution of freshly prepared sodium borohydride (NaBH_4) was added to the above mixture of chitosan and AgNO_3 and the stirring was continued for further 120 min. The as prepared Chit-AgNPs was kept in dark before use.

Preparation of the multiwalled carbon nanotube paste electrode (MWCNTPE)

To prepare the MWCNTPE, first of all the MWCNT powder was pretreated by adding a suitable amount into a mixture of concentrated nitric acid and sulphuric acid (3:1 v/v) to eliminate the residual metal particles that remained from the synthesis process and to promote the generation of functional groups, such as carboxyl, hydroxyl, quinone, nitro and amino groups on the MWCNT surfaces [30]. After that, the mixture was kept under stirring for 12 h at room temperature. Subsequently, the mixture was filtered and washed several times with deionized water. The MWCNT were then finally dried at 120 °C for 5 h. To prepare MWCNT paste electrode, a suitable amount of the dried MWCNT was mixed with paraffin oil (25%) and homogenized in a mortar and pestle for about 30 min. The prepared paste was put into a syringe needle plastic cover and then pressed downward. To make an electrical connection, a copper wire was inserted into the past at the back of the needle cover. Finally, the tip of the cover was cut off with a cutter and then the surface of the paste was smoothed with a paper.

Preparation of Chit-AgNP/MWCNTPE

To construct Chit-AgNP/MWCNTPE, 20 μL Chit-AgNPs solution was drop cast on the surface of the MWCNTPE and dried under IR lamp for 10 min (the construction of Chit-AgNPs/MWCNTPE for nitrite detection is shown in Fig. 1). After drying, a thin film of chitosan capped AgNPs was formed on the surface of MWCNTPE. The modified electrode was used as working electrode for the determination of nitrite and was stable after several continuous CV measurements.

Voltammetric procedure

Before starting voltammetric experiment at each new surface of Chit-AgNP/MWCNTPE, 10 successive cyclic voltammetric scans were recorded in the anodic direction in the potential range from 0.2–1.1 V in the blank solution containing 0.04 M BR. All the cyclic voltammetric measurements were performed in a 10 mL solution containing 0.04 M BR buffer and desired amount of nitrite. In a typical CV procedure for the determination of nitrite, 1 mL of 0.4 M BR was transferred into a voltammetric cell and was diluted up to 10 mL with deionized water. After adjusting the pH of the solution to 4.0, appropriate amount of nitrite (in μL) was added from the stock solution into the cell. Then, after 15 min accumulation time (t_a), cyclic voltammogram was recorded from 0.2 to 1.1 V in the anodic direction using scan rate of $0.05 \text{ V}\cdot\text{sec}^{-1}$. Nitrite was pre-concentrated at the surface of electrode spontaneously. The cyclic voltammetric determination of nitrite in river water sample was carried out by mixing 5 mL river water (without subjecting to filtration process), 1 mL of 0.4 M BR and 4 mL deionized water (total volume 10 mL). The standard addition method was used to determine the concentration of nitrite in river water sample.

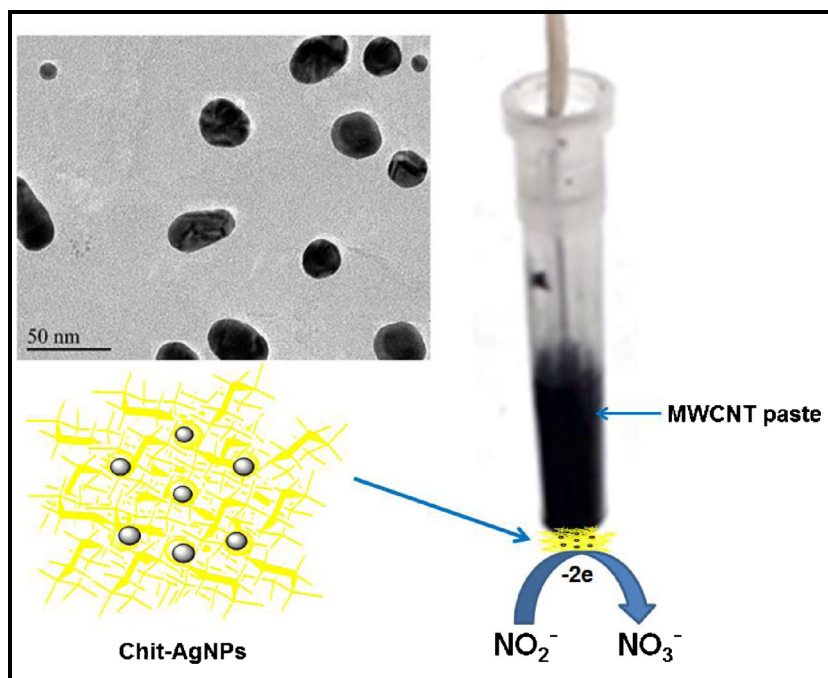
Results and discussion

Voltammetric response of nitrite at the chit-AgNPs/MWCNTPE

The cyclic voltammetric response for the oxidation of nitrite was studied at glassy carbon (GC) electrode, unmodified MWCNTPE, Chitosan-MWCNTPE and Chit-AgNPs/MWCNTPE in BR buffer solution containing $5 \times 10^{-5} \text{ M}$ nitrite at a scan rate of $0.05 \text{ V}\cdot\text{s}^{-1}$. As can be seen from Fig. 2, that among the various electrodes studied, the Chit-AgNPs/MWCNTPE showed the highest and most easily evaluated cyclic voltammetric peak at a typical peak potential of 0.811 V in the anodic scan. There was no cyclic voltammetric peak observed in the reverse scan. The oxidation potential 0.811 V vs. SCE of nitrite at chit-AgNPs paste electrode is lower than the standard potential of 0.813 V and comparable or lower than most of the others modified electrodes (Table 1). According to the previous reports, this result also confirmed the irreversible electrochemical behavior of nitrite. In this process nitrite is oxidized to nitrate.

This study revealed the electrocatalytic oxidation ability of the designed electrochemical assay towards the oxidation of nitrite. The enhanced electrocatalytic response shown by chit-AgNPs/MWCNTPE for nitrite may be ascribed to the increased surface area and greater conductivity of the chit-AgNPs. The positively charged (at lower pH) amino and hydroxyl active groups of the chit-AgNPs on the surface of electrode have promoted the

Fig. 1 Schematic illustration of Chit-AgNPs/ MWCNT paste electrode for the electrochemical sensing of nitrite along with the TEM image of the prepared Chit-AgNPs



electrostatic accumulation of nitrite at the electrode surface, thus, boosting its surface concentration and, consequently, enhancing the oxidation peak currents.

The overall reaction mechanism of nitrite at the chit-AgNPs electrode consists of the charge-transfer step followed by homo-geneous disproportionation step. The overall oxidation process is as follows;

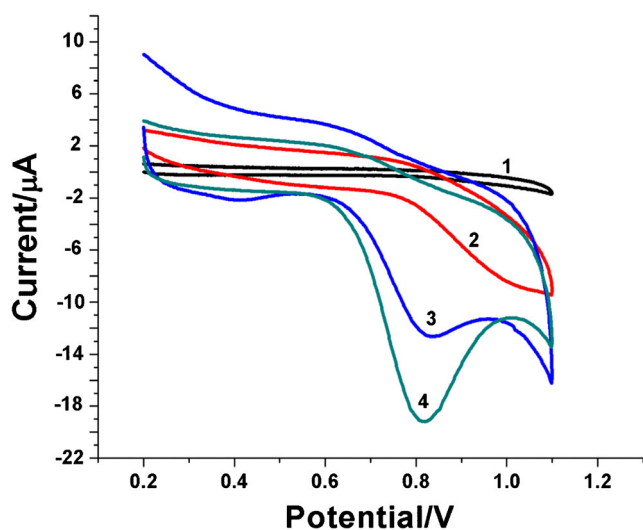


Fig. 2 Cyclic voltammograms of 5×10^{-5} M nitrite solution using, 1) Glassy carbon (GC) electrode, 2) unmodified MWCNTs paste electrode, 3) Chitosan modified MWCNTs (Chit-MWCNTs) paste electrode and 4) Chit-AgNPs/MWCNTs paste electrode in the presence of Britton Robinson buffer (pH: 4.0) as a supporting electrolyte using scan rate of $0.05 \text{ V}\cdot\text{sec}^{-1}$

Thus, the combined benefit of chitosan, AgNPs as Chit-AgNPs and MWCNTPE has established a sensitive electrochemical method for the oxidation of nitrite.

Effect of pH

pH of the medium is an essential factor which greatly influence the electrochemical processes and voltammetric response of the analyte species. In this study Britton Robinson (BR) buffer was used as supporting electrolyte for the determination of nitrite. The pH study was performed in the range from 2.0 5.5. As shown in Fig. 3, the peak current increased remarkably with the increase of pH from 2.0 to 4.0 and attained a maximum value at pH 4.0. The peak current then decreased by further increasing the pH from 4.0 to 5.5. At pH 4.0, the charged amino and hydroxyl groups greatly promoted the electrostatic accumulation of nitrite at the electrode surface, thus enhancing the oxidation peak currents. The decrease observed in the peak currents within the pH range 4.0 5.5 could be explained by the decrease in the density of charged groups occurring as pH increases. The decrease in peak current at lower pH value (pH <4.0) may be attributed to the formation of NO gas from NO_2^- anion or the formation of protonated nitrite [31]. Therefore, pH 4.0 was selected as suitable medium for nitrite determination.

Scan rate study

The effect of scan rate on the cyclic voltammetric peak current of nitrite on the Chit-AgNPs/MWCNTPE was evaluated at different scan rates using different concentrations of nitrite. Figure 4a, shows the cyclic voltammograms at 5 mM nitrite

Table 1 Comparison of the analytical sensitivity of various electrochemical sensors for nitrite

Electrode/Technique	Peak potential (V)	Medium/pH	LR/LOD (μM)	Ref.
PPy-Pt/GCE/CV	-0.124	H ₂ SO ₄ solution/1.0	0.5 1000/0.1	[17]
MC/GCE/CV	+0.808	BR buffer/3.5	0.5 100/0.1	[23]
AgNS/GCE/Amp	+0.86	Phosphate buffer /7.0	0.1 8/0.031	[26]
GO-CS-AuNPs/GCE/CV	+0.89	Phosphate buffer /5.0	0.9 18.9/ 0.3	[28]
GNPs/MWCPE/SWV	-0.60	BR buffer/4.0	0.05 250/0.01	[31]
CuS/MWCNTs-GCE/CV	+0.8	Phosphate buffer /7.0	1 8130/0.33	[33]
AuNPs/CPE/SWV	+0.65	Phosphate buffer /7.0	0.2 15/0.2	[34]
p-NiTAPc/GC/Amp	+0.86	H ₂ SO ₄ + Na ₂ SO ₄ solution/2.0	0.5 800/0.1	[35]
GR/PPy/CS/GCE/DPV	+0.736	Phosphate buffer/4.0	0.5 720/0.6	[36]
G4-NH ₄ /MWNT/GC/CV	+0.78	Phosphate buffer/4.0	5 1500/7	[37]
Au/f-GE/GCE/CV	+0.78	Phosphate buffer /7.0	0.12 2000/0.1	[38]
GNs-GCE/CV	+0.9	BR buffer/3.0	0.5 100/0.2	[39]
AgNP/GCE/CV	+0.82	Phosphate buffer /6.0	10 1000/1.2	[40]
CR-GO/GCE/Amp	+0.8	Phosphate buffer/5.0	8.9 167/1	[41]
Chit-AgNPs/MWCNTPE/CV	+0.83	BR buffer/4.0	0.1 50/0.03	This work

LR Liner range, LOD Limit of detection, NP Nano Plate, GCE Glassy Carbon Electrode, CV Cyclic Voltammetry, CR-GO Chemically Reduced Graphene Oxide, Amp Amperometry, PPy Polypyrrole, MWCNTs Multiwalled Carbon nanotubes, MC Multiwall carbon nanotube, NPs Nanoparticles, CPE Carbon paste electrode, SWV Square Wave Voltammetry, Chit Chitosan, ASV Anodic Stripping Voltammetry, p-NiTAPc Polymeric nickle tetraaminothphalocyanine, GR graphene, CS chitosan, GNs Graphene nanoribbons, G4-NH₄ Amine-terminated poly(amidoamine, generation 4.0)

with various scan rates. With the increase of scan rate in the range from 0.002 to 0.1 V·s⁻¹, the oxidation peak current was found to increase along with a shift of peak potential towards more anodic direction. Similarly, broadening in the peak shape was also observed at higher scan rates. The plot of peak current was lineally proportional to the squire root of the scan rate, as shown in Fig. 4b. This indicated that the electrode process is controlled by diffusion. The scan rate study was carried out at 0.8 mM nitrite (Fig. 4c). At 0.8 mM

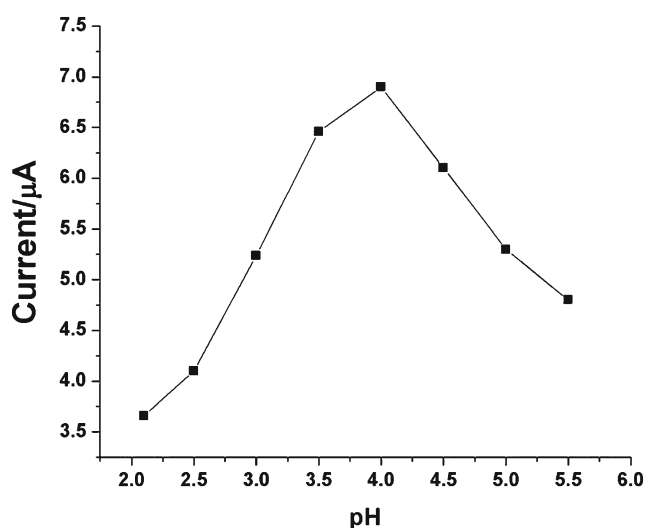


Fig. 3 Effect of pH of electrolyte solution on the voltammetric response of chit-capped AgNPs-MWCNTs paste electrode used for the detection of nitrite at a scan rate of 0.05 V·sec⁻¹

concentration, the corresponding peak current was proportional to the scan rate, as shown in Fig. 4d. This indicated that at low concentration of nitrite, the process at the electrode surface is controlled by adsorption. All these results suggested that the process is partially controlled by diffusion and partially controlled by adsorption i.e. mixed diffusion-adsorption process is taking place at the electrode surface. This is mainly attributed to the surface-active sites and porous nature of the Chit-AgNPs/MWCNTPE.

Among the various scan rates studied, 0.05 V·s⁻¹ scan rate gave a well-defined oxidation peak and was therefore selected for further experiments.

Due to adsorptive nature of the electrode, the adsorption accumulation of nitrite at the Chit-AgNPs/MWCNTPE can be exploited to enhance the voltammetric peak current.

Effect of adsorption accumulation time (t_a) on the peak current of nitrite

To examine the possible adsorption ability of the Chit-AgNPs/MWCNTPE, the effect of accumulation time (t_a) on the oxidation peak current of nitrite was studied without employing the accumulation potential (E_a) i.e. without using electrolysis step. As shown in S1, the peak current increased quickly when ' t_a ' was increased from 0 to 15 min and then remained constant upon further increasing the ' t_a ' from 15 to 50 min, suggesting that the surface has been completely saturated with nitrite. This result obviously revealed that nitrite has been spontaneously

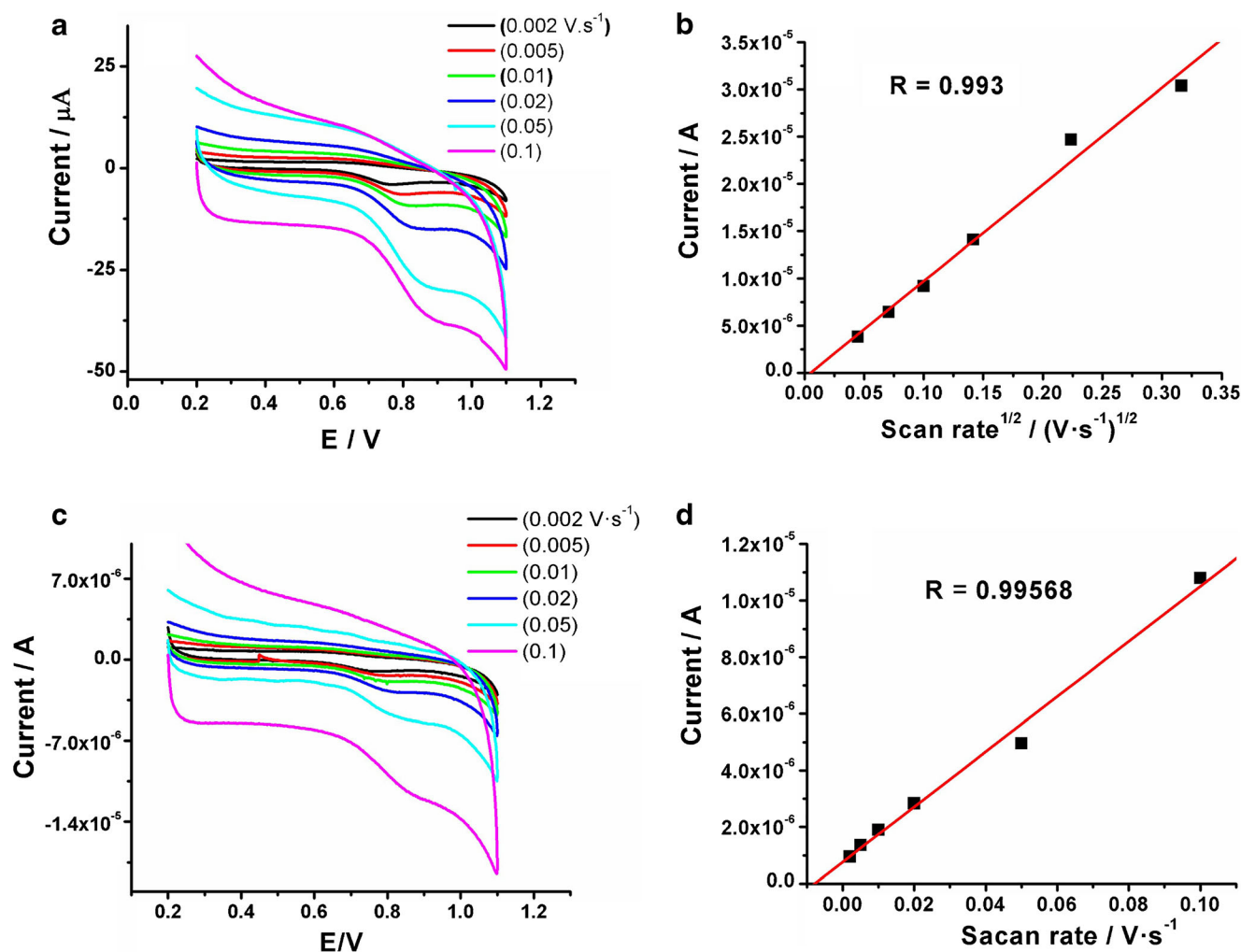


Fig. 4 (a) Cyclic voltammograms of 5 mM nitrite at various scan rates (from; 0.002, 0.005, 0.01, 0.02, 0.05, 0.1 V·s⁻¹). (b) Corresponding plot of peak current vs. square root of scan rate at 5 mM nitrite. (c) Cyclic

voltammograms of 0.8 mM nitrite at various scan rates (from; 0.002, 0.005, 0.01, 0.02, 0.05, 0.1 V·s⁻¹). (d) Corresponding plot of peak current vs. scan rate at 0.8 mM nitrite

adsorbed at the surface of electrode. Similar results have been observed by others researchers using carbon paste electrode [32] and AuNPs/MWCNT/carbon paste electrode [31].

The stability of Chit-AgNPs/MWCNTPE was also evaluated by recording 12 successive voltammetric measurements at the same surface of electrode in the presence of 5×10^{-5} M nitrite in BR buffer, pH 4.0. Each cycle was recorded after 15 min accumulation time. From this study it was observed that the oxidation current of nitrite had the value of RSD of 3.6%. This indicated that the deposited product has effectively been removed from the surface of electrode during cyclic voltammetric scan. Thus, the good stability of Chit-AgNPs/MWCNTPE for the electro-oxidation of nitrite was evident.

Sensitivity of chit-AgNPs/MWCNTPE

The sensitivity of the Chit-AgNPs/MWCNTPE for the electro-oxidation of nitrite was studied at various concentrations using

adsorption cyclic voltammetry in BR buffer, pH 4.0. The cyclic voltammograms with the addition of different concentrations of nitrite ranged from 1×10^{-7} – 1×10^{-5} M are shown in Fig. 5. As, it can be seen that, by increasing the nitrite concentrations, a gradual increased in the voltammetric peak currents was observed. A nice linear correlation between peak current and nitrite concentration was observed in the range of 1×10^{-7} – 1×10^{-5} M with regression coefficient (R^2) of 0.9989, as shown in the inset of Fig. 5. By using the equation '3 s/S' (where 's' is the standard deviation of the blank solution and 'S' is the slope value obtained from the calibration plot), the detection limit (LOD) at this modified electrode was calculated to be 3×10^{-8} M, which was better than those obtained at others modified electrodes using a cyclic voltammetric technique. The analytical sensitivities of the designed modified electrode and others modified electrodes for nitrite determination are listed in Table 1. As shown in the table, the designed modified electrode has wider linear range and lower detection limit than the

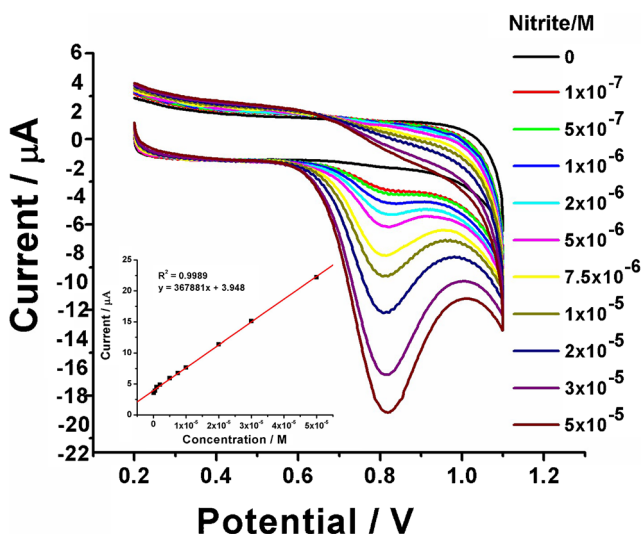


Fig. 5 Cyclic voltammograms obtained with various concentrations of nitrite ranged from 1×10^{-7} – 1×10^{-5} M using chit-AgNPs/MWCNTPE in the presence of Britton Robinson (BR) buffer, pH 4.0. Scan rate was $0.05 \text{ V}\cdot\text{s}^{-1}$ and t_a was 15 min. Nitrite was pre-concentrated (spontaneously adsorbed) without employing electrodeposition potential ' E_p '. Inset is the corresponding linear calibration plot in the range of 1×10^{-7} – 1×10^{-5} M nitrite

others reported modified electrodes (mostly used Amperometry, DPV and square wave techniques) using simple CV technique. Thus, the high sensitivity suggested that the modified electrode can be suitable for the determination of nitrite using adsorption cyclic voltammetric technique.

Selectivity of Chit-AgNPs/MWCNTPE

To examine the possible selectivity of the designed Chit-AgNPs/MWCNTPE for nitrite, cyclic voltammetric study

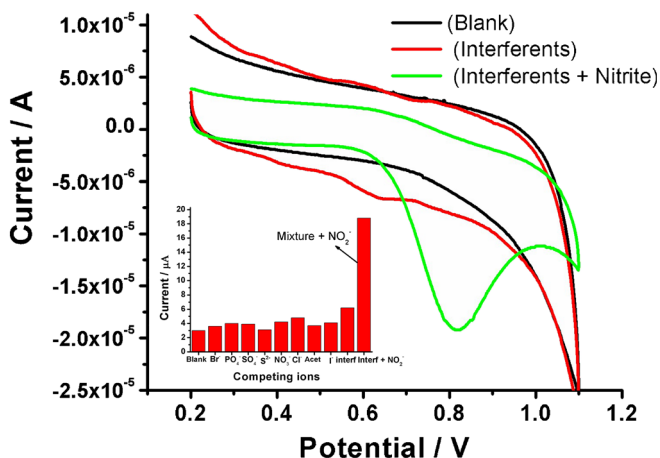


Fig. 6 Cyclic voltammograms of the solution containing 5×10^{-5} M various common interfering anions + 5×10^{-5} M nitrite at Chit-AgNPs/MWCNTPE using adsorption cyclic voltammetry. Inset: is the bar graph showing the peak current response of various tested interferents, mixture of interferents and mixture of interferents + NO_2^- . Each cyclic voltammogram was recorded after 15 min accumulation time. Nitrite was spontaneously adsorbed at the electrode

Table 2 Determination results of nitrite in river water sample using Chit-AgNPs/MWCNTPE

Added (μM)	Found (μM)	Recovery (%)	RSD % ($n = 3$)
0.5	0.53	106.0	5.04
1.0	1.04	104.0	3.10
5.0	4.97	99.40	4.75
10.0	10.51	105.10	6.12
25.0	23.92	95.68	1.80
50.0	47.67	95.34	4.20

was carried out in the presence of other common interfering anions like Br^- , PO_4^{3-} , SO_4^{2-} , S^{2-} , I^- , CH_3COO^- , Cl^- , NO_3^- , NO_2^- in the solution containing BR buffer, pH 4.0. The results showed (Fig. 6), that these anions did not change significantly the voltammetric peak current of nitrite using the Chit-AgNPs/MWCNTPE. Thus, the nanoprobe has the potential to selectively determine nitrite in the presence of common anions.

Determination of nitrite in river water sample

The accuracy of the assay was assessed by applying the Chit-AgNPs/MWCNTPE to river water sample using adsorption stripping voltammetry. Different concentrations of nitrite were spiked to the solution containing river water and BR buffer. The determination was performed by using the standard addition procedure. The determination results for nitrite in river water sample are illustrated in Table 2. These results showed good percent recoveries in the range of 95–106%, thus suggesting that nitrite can be accurately determined in river water samples without any complex medium effect by using Chit-AgNPs/MWCNTPE.

Conclusions

In this work, MWCNTPE was modified with chitosan functionalized AgNPs and was employed for the adsorption cyclic voltammetric determination of nitrite in BR buffer, pH 4.0. The synergistic effect of chitosan, AgNPs and MWCNTs improved the electrochemical response towards the oxidation of nitrite. The capability of chit-AgNPs/MWCNTPE to adsorb spontaneously nitrite at its surface greatly enhanced the sensitivity of nitrite which was found to be lower than the others electrochemically modified electrodes by using cyclic voltammetric technique. The assay presented high selectivity for nitrite over the existence of others common anions. The method exhibited good percent recoveries when applied to river water sample for the determination of nitrite. In addition, due to the easily renewable surface, the MWCNT paste electrode can be a suitable electrode for the electrochemical determination of nitrite.

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Compliance with ethical standards The author(s) declare that they have no competing interests.

References

- Wang G, Han R, Feng X, Li Y, Lin J, Luo X (2017) A glassy carbon electrode modified with poly(3,4-ethylenedioxythiophene) doped with nano-sized hydroxyapatite for amperometric determination of nitrite. *Microchim Acta* 184(6):1721–1727. <https://doi.org/10.1007/s00604-017-2180-9>
- Liu Y, Xue H, Liu J, Wang Q, Wang L (2018) Carbon quantum dot-based fluorometric nitrite assay by exploiting the oxidation of iron(II) to iron(III). *Microchim Acta* 185(2):129. <https://doi.org/10.1007/s00604-018-2668-y>
- Ezhil Vilian AT, Dinesh B, Muruganantham R, Choe SR, Kang S-M, Huh YS, Han Y-K (2017) A screen printed carbon electrode modified with an amino-functionalized metal organic framework of type MIL-101(Cr) and with palladium nanoparticles for voltammetric sensing of nitrite. *Microchim Acta* 184(12):4793–4801. <https://doi.org/10.1007/s00604-017-2513-8>
- Chen L, Liu X, Wang C, Lv S, Chen C (2017) Amperometric nitrite sensor based on a glassy carbon electrode modified with electrodeposited poly(3,4-ethylenedioxythiophene) doped with a polyacenic semiconductor. *Microchim Acta* 184(7):2073–2079. <https://doi.org/10.1007/s00604-017-2189-0>
- Xu G, Liang S, Fan J, Sheng G, Luo X (2016) Amperometric sensing of nitrite using a glassy carbon electrode modified with a multilayer consisting of carboxylated nanocrystalline cellulose and poly(diallyldimethyl ammonium) ions in a PEDOT host. *Microchim Acta* 183(6):2031–2037. <https://doi.org/10.1007/s00604-016-1842-3>
- Wang J, Zhou H, Fan D, Zhao D, Xu C (2015) A glassy carbon electrode modified with nanoporous PdFe alloy for highly sensitive continuous determination of nitrite. *Microchim Acta* 182(5):1055–1061. <https://doi.org/10.1007/s00604-014-1432-1>
- Nasir M, Nawaz MH, Latif U, Yaqub M, Hayat A, Rahim A (2017) An overview on enzyme-mimicking nanomaterials for use in electrochemical and optical assays. *Microchim Acta* 184(2):323–342
- Merusi C, Corradini C, Cavazza A, Borromei C, Salvadeo P (2010) Determination of nitrates, nitrites and oxalates in food products by capillary electrophoresis with pH-dependent electroosmotic flow reversal. *Food Chem* 120(2):615–620
- Wang Q-H, Yu L-J, Liu Y, Lin L, Lu R-g, Zhu J-p, He L, Lu Z-L (2017) Methods for the detection and determination of nitrite and nitrate: a review. *Talanta* 165:709–720
- Von Gunten U, Salhi E (1999) Simultaneous determination of bromide, bromate and nitrite in low $\mu\text{g l}^{-1}$ levels by ion chromatography without sample pretreatment. *Water research* 33 (EPFL-ARTICLE-167332):3239–3244
- Nagababu E, Rifkind JM (2007) Measurement of plasma nitrite by chemiluminescence without interference of S-, N-nitroso and nitrated species. *Free Radic Biol Med* 42(8):1146–1154
- Pourreza N, Fat'hi MR, Hatami A (2012) Indirect cloud point extraction and spectrophotometric determination of nitrite in water and meat products. *Microchem J* 104:22–25
- Jiao M, Li Z, Li Y, Cui M, Luo X (2018) Poly(3,4-ethylenedioxythiophene) doped with engineered carbon quantum dots for enhanced amperometric detection of nitrite. *Microchim Acta* 185(5):249. <https://doi.org/10.1007/s00604-018-2784-8>
- Annalakshmi M, Balasubramanian P, Chen S-M, Chen T-W (2019) Amperometric sensing of nitrite at nanomolar concentrations by using carboxylated multiwalled carbon nanotubes modified with titanium nitride nanoparticles. *Microchim Acta* 186(1):8
- Zhang F, Yuan Y, Zheng Y, Wang H, Liu T, Hou S (2017) A glassy carbon electrode modified with gold nanoparticle-encapsulated graphene oxide hollow microspheres for voltammetric sensing of nitrite. *Microchim Acta* 184(6):1565–1572. <https://doi.org/10.1007/s00604-017-2264-6>
- Wang J, Hui N (2017) A nanocomposite consisting of flower-like cobalt nanostructures, graphene oxide and polypyrrole for amperometric sensing of nitrite. *Microchim Acta* 184(7):2411–2418. <https://doi.org/10.1007/s00604-017-2247-7>
- Li J, Lin X (2007) Electrocatalytic reduction of nitrite at polypyrrole nanowire-platinum nanocluster modified glassy carbon electrode. *Microchem J* 87(1):41–46
- Dai J, Deng D, Yuan Y, Zhang J, Deng F, He S (2016) Amperometric nitrite sensor based on a glassy carbon electrode modified with multi-walled carbon nanotubes and poly(toluidine blue). *Microchim Acta* 183(5):1553–1561. <https://doi.org/10.1007/s00604-016-1773-z>
- Wu W, Li Y, Jin J, Wu H, Wang S, Ding Y, Ou J (2016) Sensing nitrite with a glassy carbon electrode modified with a three-dimensional network consisting of Ni7S6 and multi-walled carbon nanotubes. *Microchim Acta* 183(12):3159–3166. <https://doi.org/10.1007/s00604-016-1961-x>
- Tkachenko O, Rahim A, Baraban A, Sukhov R, Khristenko I, Gushikem Y, Kholin Y (2013) Hybrid silica-organic material with immobilized amino groups: surface probing and use for electrochemical determination of nitrite ions. *J Sol-Gel Sci Technol* 67(1):145–154
- Rahim A, Santos LS, Barros SB, Kubota LT, Landers R, Gushikem Y (2014) Electrochemical detection of nitrite in meat and water samples using a mesoporous carbon ceramic SiO₂/C electrode modified with in situ generated manganese (II) phthalocyanine. *Electroanalysis* 26(3):541–547
- Hu J, Guo F, Wang L (2017) Voltammetric determination of nitrite by using a glassy carbon electrode modified with a self-assembled nanocomposite prepared from CdTe quantum dots, cetyltrimethylammonium bromide, chitosan and multiwalled carbon nanotubes. *Microchim Acta* 184(12):4637–4646. <https://doi.org/10.1007/s00604-017-2500-0>
- Jiang L, Wang R, Li X, Jiang L, Lu G (2005) Electrochemical oxidation behavior of nitrite on a chitosan-carboxylated multiwall carbon nanotube modified electrode. *Electrochem Commun* 7(6):597–601
- Lin P, Chai F, Zhang R, Xu G, Fan X, Luo X (2016) Electrochemical synthesis of poly(3,4-ethylenedioxythiophene) doped with gold nanoparticles, and its application to nitrite sensing. *Microchim Acta* 183(3):1235–1241. <https://doi.org/10.1007/s00604-016-1751-5>
- Wang Q, Yun Y (2012) A nanomaterial composed of cobalt nanoparticles, poly(3,4-ethylenedioxythiophene) and graphene with high electrocatalytic activity for nitrite oxidation. *Microchim Acta* 177(3):411–418. <https://doi.org/10.1007/s00604-012-0794-5>
- Pal M, Ganesan V (2010) Electrochemical determination of nitrite using silver nanoparticles modified electrode. *Analyst* 135(10):2711–2716
- Yang S, Liu X, Zeng X, Xia B, Gu J, Luo S, Mai N, Wei W (2010) Fabrication of nano-copper/carbon nanotubes/chitosan film by one-step electrodeposition and its sensitive determination of nitrite. *Sensors Actuators B Chem* 145(2):762–768
- Mo R, Wang X, Yuan Q, Yan X, Su T, Feng Y, Lv L, Zhou C, Hong P, Sun S (2018) Electrochemical determination of nitrite by Au nanoparticle/graphene-chitosan modified electrode. *Sensors* 18(7):1986

29. Amanulla B, Palanisamy S, Chen S-M, Chiu T-W, Velusamy V, Hall JM, Chen T-W, Ramaraj SK (2017) Selective colorimetric detection of nitrite in water using chitosan stabilized gold nanoparticles decorated reduced graphene oxide. *Sci Rep* 7(1):14182
30. Osorio A, Silveira I, Bueno V, Bergmann C (2008) H₂SO₄/HNO₃/HCl—functionalization and its effect on dispersion of carbon nanotubes in aqueous media. *Appl Surf Sci* 255(5):2485–2489
31. Afkhami A, Soltani-Felehgari F, Madrakian T, Ghaedi H (2014) Surface decoration of multi-walled carbon nanotubes modified carbon paste electrode with gold nanoparticles for electro-oxidation and sensitive determination of nitrite. *Biosens Bioelectron* 51: 379–385
32. Habib IH (2011) Anodic stripping Voltammetric determination of nitrite using carbon paste electrode modified with chitosan. *Am J Anal Chem* 2(02):284–288
33. Zhang S, Li B, Sheng Q, Zheng J (2016) Electrochemical sensor for sensitive determination of nitrite based on the CuS–MWCNT nanocomposites. *J Electroanal Chem* 769:118–123
34. Gobelli D, Mariano Correa N, Fátima Barroso M, Moyano F, Molina PG (2015) “Green electrodes” modified with au nanoparticles synthesized in glycerol, as electrochemical nitrite sensor. *Electroanalysis* 27(8):1883–1891
35. Wen Z-H, Kang T-F (2004) Determination of nitrite using sensors based on nickel phthalocyanine polymer modified electrodes. *Talanta* 62(2):351–355
36. Ye D, Luo L, Ding Y, Chen Q, Liu X (2011) A novel nitrite sensor based on graphene/polypyrrole/chitosan nanocomposite modified glassy carbon electrode. *Analyst* 136(21):4563–4569
37. Zhu N, Xu Q, Li S, Gao H (2009) Electrochemical determination of nitrite based on poly (amidoamine) dendrimer-modified carbon nanotubes for nitrite oxidation. *Electrochem Commun* 11(12): 2308–2311
38. Ce Z, Yang B, Bin D, Wang J, Li S, Yang P, Wang C, Shiraishi Y, Du Y (2017) Electrochemical synthesis of gold nanoparticles decorated flower-like graphene for high sensitivity detection of nitrite. *J Colloid Interface Sci* 488:135–141
39. Mehmeti E, Stanković DM, Hajrizi A, Kalcher K (2016) The use of graphene nanoribbons as efficient electrochemical sensing material for nitrite determination. *Talanta* 159:34–39
40. Wang Z, Liao F, Guo T, Yang S, Zeng C (2012) Synthesis of crystalline silver nanoplates and their application for detection of nitrite in foods. *J Electroanal Chem* 664:135–138
41. Mani V, Periasamy AP, Chen S-M (2012) Highly selective amperometric nitrite sensor based on chemically reduced graphene oxide modified electrode. *Electrochem Commun* 17:75–78

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