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Amperometric detection of Nitrite, Iodate and Periodate on Glassy Carbon Electrode modified with Thionin and Multi-wall Carbon Nanotubes

Abdollah Salimi[*] *, Abdollah Noorbakhash, Fatemeh Salehi Karonian*

Deparment of Chemistry, Kurdistan University, P.O.Box 416, Sanandaj, Iran.
[*]E-mail: absalimi@yahoo.com or absalimi@uok.ac.ir

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The multi-wall carbon nanotubes were used as an immobilization matrix to incorporate thionin as electron transfer mediator onto a glassy carbon electrode surface. Due to unique electronic properties of MWCNTs and electrocatalytic activity of thionin, the combination of thionin and MWCNTs results in a remarkable synergistic augmentation on the response. A chemically modified electrode prepared by adsorption of thioinin on CNT shows excellent catalytic activity for reduction iodate, periodate and nitrite in acidic buffer solutions at unusual positive and it can be used as stable and sensitive sensor for these analytes. The results indicated that the modified electrode exhibited efficiently electrocatalytic reduction for iodate, periodate and nitrite in acidic buffer solutions at unusual positive potential. Nitrite, iodate and periodate were determined amperomerically on rotated modified electrode in pH 2. Under optimized condition in amperometry method the concentration calibration range, detection limit and sensitivity were about, 1 μM -10mM, 0.4 μM and 12.44 nA/μM for periodate, 2.0 μM -10 mM, 1 μM and 5.36 nA/μM for iodate and 6 μM-15 mM, 4 μM and 2 nA/μM for nitrite**.** The catalytic rate constants for oxoanions reduction were determined by cyclic voltammetry method based on the Laviron theory, they were about 1.34×10^4 , 1.68×10^4 and 4.93×10^3 M^{-1} s^{-1} , for iodate, periodate and nitrite, respectively. The resultant thionin / MWCNTs modified glassy carbon electrodes exhibit high catalytic activity, fast response time (within 5 s) to above anions reduction, excellent stability, long term life and good reproducibility. This sensor indicate great promise as an amperometry detector for analysis of nitrite, iodate and periodate in chromatographic or flow systems.

Keywords: Thionin, multiwall carbon nanotubes, glassy carbon, nitrite, iodate, periodate, determination.

1. INTRODUCTION

Periodate is an important oxidants which can oxidize many organic and inorganic compounds at trace levels[1-3]. The iodized salt is recognized as the method of choice and the most successful strategy to prevent the iodide deficiency disorders [3-6]. Nitrite, one of the pollutants widely found in atmosphere and natural waters, is an essential precursor in the formation of nitrosamines, many of which have been shown to be potent carcinogens [7-9]. Therefore, the detection of iodate, periodate and nitrite in environmental and food samples are reviving considerable attentions. Numerous chemical and instrumental techniques such as specectrophotometric [10,11], spectrofluorometric [12,13], ion chromatography [14,15], and capillary electrophoresis[16,17], have been examined for determination of above analytes. In contrast to other options, electroanalysis has advantageous of simplicity and high sensitivity. The direct electroreduction of these anions on bare electrodes have numbers of limitations, such as low sensitivity and reproducibility, and high over-potential at which the electron transfer process occurs. The chemical modification of inert substrates of electrodes with redox active thin films offers significant advantageous for design and development of electrochemical sensors. Glassy carbon electrodes modified with tetra iron substituted polyoxotungstate [18], Pd(II) substituted heteropolytungstate [19], iridium(IV)-substituted polyoxotungstate [20], carbon ceramic electrode modified with phosphomolybdic and tungstosilisic acid [21,22], poly-vinyl pyridine modified with silicotungsteic hetropolyanions [23], poly-molybdophosphate modified carbon paste electrode [24], carbon electrode modified with Co(II) porphyrazine [25], edge plane pyrolytic graphite electrode modified with copper complexes [26], and wells-Dawson-derived tetrameric complex [27], have been used successfully for electrocatalytic reduction of nitrite. Glassy carbon electrode modified with molbdenuium oxide [28-30], graphite electrode modified with silicotungstic acid [31], and carbon ceramic electrode modified with 12-polybdophosphoric acid [32], have been used for iodate and periodate detection. Furthermore, iodate was determined with flow injection amperometry method [34] and GC electrode modified with tungsten oxide film has been used for iodate determination [35]. Water soluble dyes, are receiving increasing interest in the field of chemically modified electrodes, electrocatalysis and electroanalysis owing to the excellent stability, low cost and special electrocatalytic processes. Different water soluble dyes redox indicators such as, methylene blue [36], methylen green [37], meldola blue [38], Azure-I and B [39,40], orthophenylendimines [41], neutral red [42], and other azines compounds [43], have been used in electroanalysis. The electron transfer mediator can be immobilized on the electrode surface by adsorption [44], simply mixing into carbon paste[45], direct electropolymerization [39-40], cross-linking methods [46], and sol-gel techniques [37,47]. An adsorbed dye film on the electrode surfaces tends gradually to leach from the solid support and the modified electrode has a decreasing response with time. Due to high catalytic activity of thionin it can be used as an electron transfer mediator for electrocatalytic reduction or oxidation different substances [48-52]. Unfortunately they also suffer from many disadvantages, such as considerable leaching of electron transfer mediator, complex and time consuming preparation procedure, as well as they are not renewable. Then, simple and convenient methods for immobilization of thionin or other electroactive dye compounds still remain a challenge. Due to significant mechanical strength, excellent electrical conductivity and good chemical stability of carbon nanotubes [53], they are promising as supporting substance for immobilization of different electron transfer mediators on the electrode surfaces [54,55]. In continuous our study for preparation sensors and biosensors based on carbon nanotubes [56-60], in this research GC electrode modified with MWCNTs used for immobilization of thionin. The modified electrode will be used to electrocatalytic reduction of iodate, periodate and nitrite. The distinguished electrocatalytic feature of the immobilized material was used in the development of the hydrodynamic amperometry method for determination iodate, periodate and nitrite at reduced over- potential.

2. EXPERIMENTAL

2.1. Chemical and reagents

The Thionin acetate (3,7-diamino-5-phenothiazinium acetate) was from Aldrich and used as received. $NaIO_3$, $NaIO_4$ and $NaNO_2$ were of analytical grade from Merck and used as received. Multiwall carbon nanotubes (MWCNTs)with purity of 95% (10-20 nm diameter) and 1 µm length were obtained from Nanolab (Brighton, MA). Double distillate water was used to prepare all solutions. Buffer solutions (0.1 M) were prepared from sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4) and sodium di- hydrogen phosphate (Na H_2PO_4). Sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) were used for pH adjustment. Solutions were deaerated by bubbling high purity (99.99%) of argon gas through them prior to the experiments. All electrochemical experiments were carried out at $25\pm 0.1^{o}C$.

2.2. Apparatus and procedures

Electrochemical measurements were carried out in a conventional three electrodes cell using an µ-AUTOLAB -2 PGSTAT computer controlled potentiostat (ECO-Chemie, The Netherlands). A three electrode cell, including glassy carbon(2 mm diameter) glassy carbon electrode modified with MWCNTs and glassy carbon electrode modified with MWCNTs and thionin as working electrode, an Ag/AgCl (saturated KCl) and a platinum wire were used as reference and counter electrode, respectively. All of used electrodes were from Metrohm. The electrodes modification procedure is explained in the following section. A Metrohm drive shaft for rotating working electrode was used in amperometric measurements. A personal computer was used for data storage and processing.

2.3. Preparation of thionin - MWCNTs modified glassy carbon electrode

The glassy carbon electrode was carefully polished with alumina on polishing cloth. Then the electrode was placed in ethanol and subjected to vibration to remove adsorbed particles. Finally, the electrode was heated for 5 minutes at 50 ^{0}C in oven. Two mg of purified MWCNTs was placed on a filter paper (Whatman. no 1001 110). The MWCNTs were then abrasively immobilized on to the electrode, immediately after removing preheated GC electrode from oven, by gently rubbing the electrode surfaces on fine qualitative filter paper containing carbon nanotubes for 1 min. The electrode was rinsed with ethanol and distilled water. Then the glasy carbon electrode modified with

MWCNTs was immersed in 1 mM solution of thionin for 1 min. The modified electrode was rinsed with distilled water before use.

3. RESULTS AND DISCUSSIONS

2.1. Electrocatalytic activity of modified MWCNTs / thionin glassy carbon electrode for nitrite, iodate and periodate reduction

The catalytic reduction of iodate, periodate and nitrite on MWCNTs / thionin / GC electrode was studied by cyclic voltammetry. Fig. 1 shows cyclic voltammograms of a MWCNTs/ GC and MWCNTs / thionin modified glassy carbon electrodes in the blank solution of 0.1 M phosphate buffer (pH 2) in the absence and presence of iodate. It can be seen (Fig1 a) that no recognizable response was observed for MWCNTs/ GC electrode in the absence of iodate at potential range 0.45 to -0.15 V. But as shown in Fig. 1b in the presence of iodate a small redox response for iodate reduction was observed. By immersing the electrode in thionin solution at less than 1 min a stable thin layer of thionin adsorbed at the surface of glassy carbon electrode has been modified with MWCNTs. It can be seen (Fig1 a) that no recognizable response was observed for MWCNTs/ GC electrode in the absence of iodate at potential range 0.45 to -0.15 V. But as shown in Fig. 1b in the presence of iodate a small redox response for iodate reduction was observed. By immersing the electrode in thionin solution at less than 1 min a stable thin layer of thionin adsorbed at the surface of glassy carbon electrode has been modified with MWCNTs.

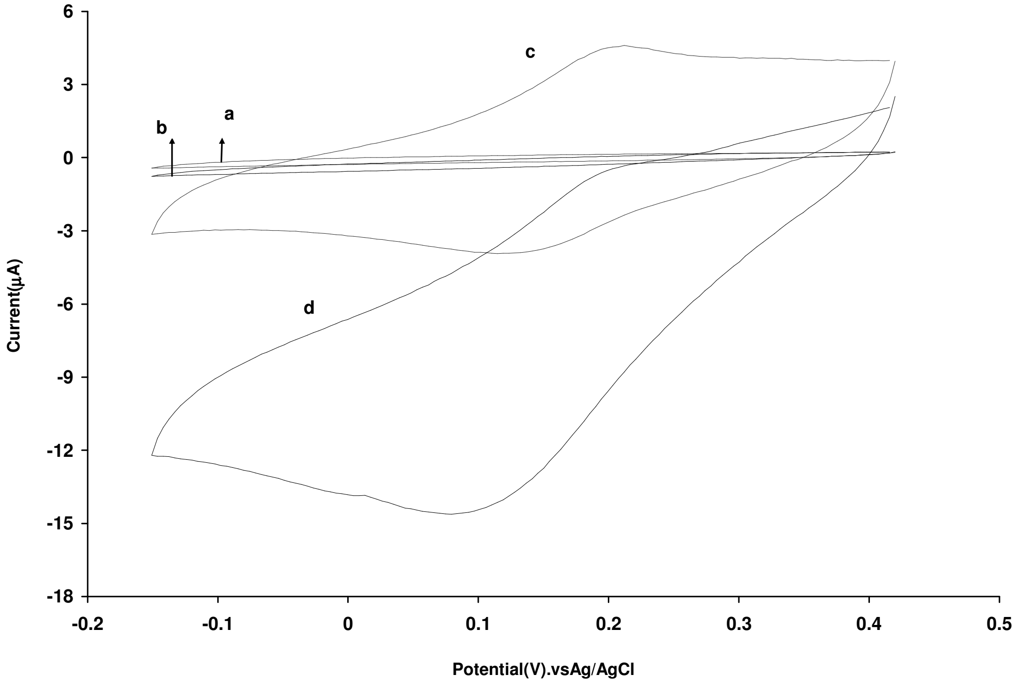

Figure 1. Cyclic voltammograms of thionin -MWCNTs modified GC electrode in buffer solution pH 2 at scan rate 20 mV s^{-1} in the absence (c) and presence 5.0 mM iodate (d). (a and b) as (c and d) for GC electrode modified with MWCNTs.

We found a single and well – defined redox couple with formal potential 0.16 V vs. reference electrode and peak separation $\Delta Ep= 50$ mV in the buffer solution free of iodate (Fig. 1c). The pH dependence, stability and the electrochemical behavior of the modified thionin / MWCNTs / modified GC electrode is reported in our previous study [61]. In order to observe the activity of MWCNTs/ thionin modified glassy carbon electrode, its response to reduction of iodate was studied. Fig. 1d shows cyclic voltammograms of MWCNTs/ thionin modified GC electrode in the presence of 10 mM iodate. The reduction catalytic current of iodate starts at 0.3 V and an obvious catalytic reduction peak appears at the potential of 0.120 V. The same behavior was observed for electrocatalytic reduction of nitrite and periodate. Since, the modified electrode shows catalytic activity for reduction of iodate, periodate and nitrite at the same potential, it can not be used for simultaneous detection these analytes before separation.

In order to optimize the electrocatalytic response of modified electrode towards oxoanions reduction, the effect of pH on the catalytic behavior of modified electrode toward anions was investigated. The cyclic voltammograms of the modified electrode in 1 mM periodate at different pH values were recorded (not shown). At pH range 1-7, the modified electrode shows electrocatalytic activity, but catalytic currents decreased with increasing pH and at pH 9 the catalytic effects of the modified electrode is negligible. Additionally, peak potentials are shifted to negative potentials with increasing pH values. The higher peak currents are observed at pH 2 and this value was chosen as optimized. For nitrite and iodate the catalytic reduction peaks were observed in acidic solutions and peak current decreased at pH> 3. At pH>3.5 , a medium where the nitrite anion predominates according to the acidic equilibrium:

$$HNO_2 \rightarrow H^+ + NO_2^- \quad (pKa = 3.3) \qquad (1)$$

No catalytic effect is observed for reduction process of thionin. This behavior indicates that high acidic pHs are needed to promote for electrocatalysis and the active species must be essentially HNO_2 not NO_2^-. The same behaviors observed for electrocatalytic reduction of iodate and nitrite at different modified electrode surfaces [27,28,32,35,62]. Fig. 2 shows cyclic voltammograms of thionin + MWCNTs modified glassy carbon electrode in solutions containing different concentrations of periodate and the inset shows the plots of catalytic current vs. periodate concentration. The plot of catalytic current vs. periodate concentration was linear in the concentration range 1-12 mM, which fitted the equation Ip (μA) = 1.98 $\mu A.mM^{-1}$ + 1.82 μA and $R^2=0.9908$. The similar cyclic voltammograms were observed for IO_3^-, and NO_2^- and the responses were found to produce a linear behavior over the entire concentration range of 1-10 mM periodate $Ip(\mu A)=1.732[IO_3^-]/mM+ 0.26$ μA, $R^2= 0.9848$) and 0.8-4 mM nitrite ($Ip/\mu A=2.187 [NO_2^-]/mM+ 1.6\mu A$, $R^2= 0.9913$).

The effects of scan rate on the electrochemical signal was studied in order to further verify that the electrochemical reduction of iodate, periodate and nitrite are diffusion controlled. Using a fixed concentration of 1mM analyte in pH 2 buffer we found that the peak current for the reduction of analyte is proportional to the square root of scan rate (not shown).

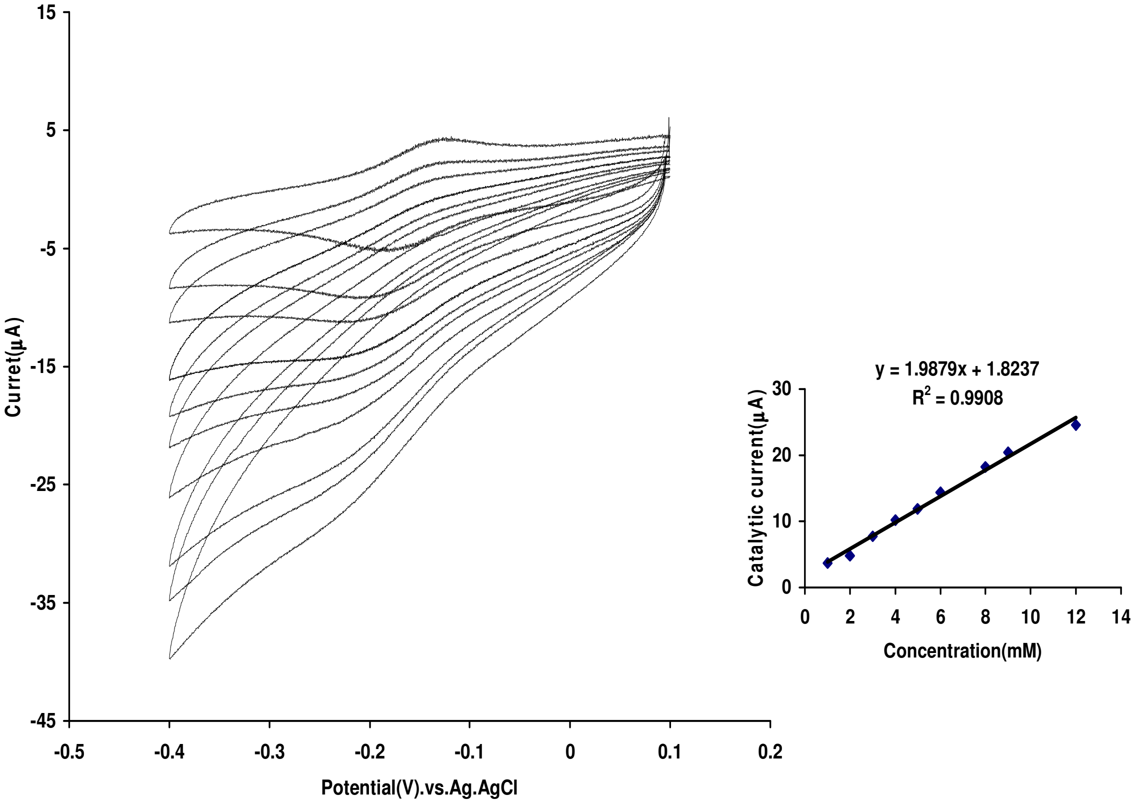

Figure 2. Cyclic voltammograms of thionin-MWCNTs modified GC electrode, at scan rate 20 mVs^{-1} with increasing periodate concentration (from inner to outer) 0.0, 1.0, 2, 3, 4,5,6,8,9 and 12 mM of periodate in pH 7 phosphate buffer solution. Inset, plot of peak current vs. periodate concentrations.

These results indicate that at the sufficient potential the reaction is controlled by diffusion of analyte, which is an ideal case for quantitative applications. It can also be noted that by increasing the sweep rate, the peak potential for the catalytic reduction of analyte shifts to more negative values and a plot of peak current vs. square root of scan rate deviates from linearity; suggesting a kinetic limitation in the reaction between the redox sites of thionin and analyte. These results show that the overall electrochemical reduction of analyte at the GC electrode modified with thionin-MWCNTs might be controlled by the cross exchange process between analyte and the redox site of thionin redox couple. Based on the results, the following catalytic scheme (EC′ catalytic mechanism) describes the reaction sequence in the reduction of iodate by thionin.

$$\text{Thionin} + 2e^- + 2H^+ \rightleftarrows \text{Leucothionin} \qquad (2)$$

$$3\text{Leucothionin} + IO_3^- + 6H^+ \xrightarrow{Kcat} 3\text{Thionin} + I^- + 3H_2O \qquad (3)$$

In order to obtain the information about the rate determining step a Tafel plot was drawn, using the data extracted from the rising part of the current-voltage curve recorded at scan rate 20 mVs^{-1} for solution containing 1 mM iodate. A plot of potential vs. $\log_{10}$(current) produced a value of 175 mV per decade, indicating a one electron process was involved in the rate limiting step, assuming a charge transfer coefficient of $\alpha = 0.39$. The calculated charge transfer coefficient for periodate and nitrate were also 0.4 and 0.31, respectively.

The catalytic rate constant for oxoiodide and nitrite reduction (eq.3) can be calculate based on the Andrieux and Saveant mode [63]. The average calculated value of k_{cat} for periodate reduction was about $1.68(\pm0.15)\times10^{4}$ $M^{-1}s^{-1}$. The values of catalytic rate constants for iodate and nitrite are reported in Table1. Due to high catalytic rate constant of reaction, the reduced form of thionin can be used as an electron transfer mediator for electrocatalytic reduction of iodate, periodate and nitrite at positive potential. The stability of electrocatalytic activity of modified electrode toward reduction of iodate was checked by repetitive scanning at scan rate 20 mVs^{-1}. In the first 5 scans, the electreocatalytic currents decreased with scan number, but the currents then remained at 90-95 % of the initial value after 20 cycles. Same stability for electrocatalytic reduction response was observed for periodate and nitrite. In addition, the reproducibility and working stability of the electrocatalytic effect of the modified electrode was tested by repetitive recording of cyclic voltammograms in iodate solution. It was found that the relative standard deviation (RSD) of the peak currents of 5.0 mM iodate for six replicate determinations was 2.5%. In order to study the reproducibility of the electrode preparation procedure, 5 independently glassy carbon electrode modified with MWCNTs and thionin was prepared. Cyclic voltammograms of prepared modified electrodes in the absence and presence of iodate (5 mM) were recorded. The RSD values were 5 and 8% (from measurement of cathodic peak currents) in the absence and presence of iodate.

2.2. Steady-state amperometric response to iodate, periodate and nitrite

Since the cyclic voltammmetry is not sensitive for low concentrations measurements, the amperometry under stirred conditions or flow injection analysis with amperometric detection is employed instead of cyclic voltammetry. We used amperometry with rotating modified electrode in order to detect lower concentrations of iodate. Fig.3 displays a typical steady-state current time response of the rotating modified electrode (1000 rpm) with successive injection of periodate at an applied potential 0.1 V versus Ag/AgCl reference electrode. As shown in Fig. 3 during the successive addition of 1mM and 10 μM periodate a well-defined response was observed. It demonstrates an stable and efficient catalytic property of the electrocatalyst that immobilized on the CNTs film. Unless, a well response was observed for lower concentration of analytes(2 μM of iodate, 1 μM periodate and 6μM of nitrite, not shown). It can be also seen that only less than 3 sec after addition of periodate current reaches about 90% of its steady–state value. This result shows that the current response of the modified electrode is really rapid. As shown in the inset of Fig. 3 the measured currents increase, by increasing the periodate concentration in the solution. The calibration plot for periodate determination is linear for a wide range1.0μM –10 mM of periodate concentration.

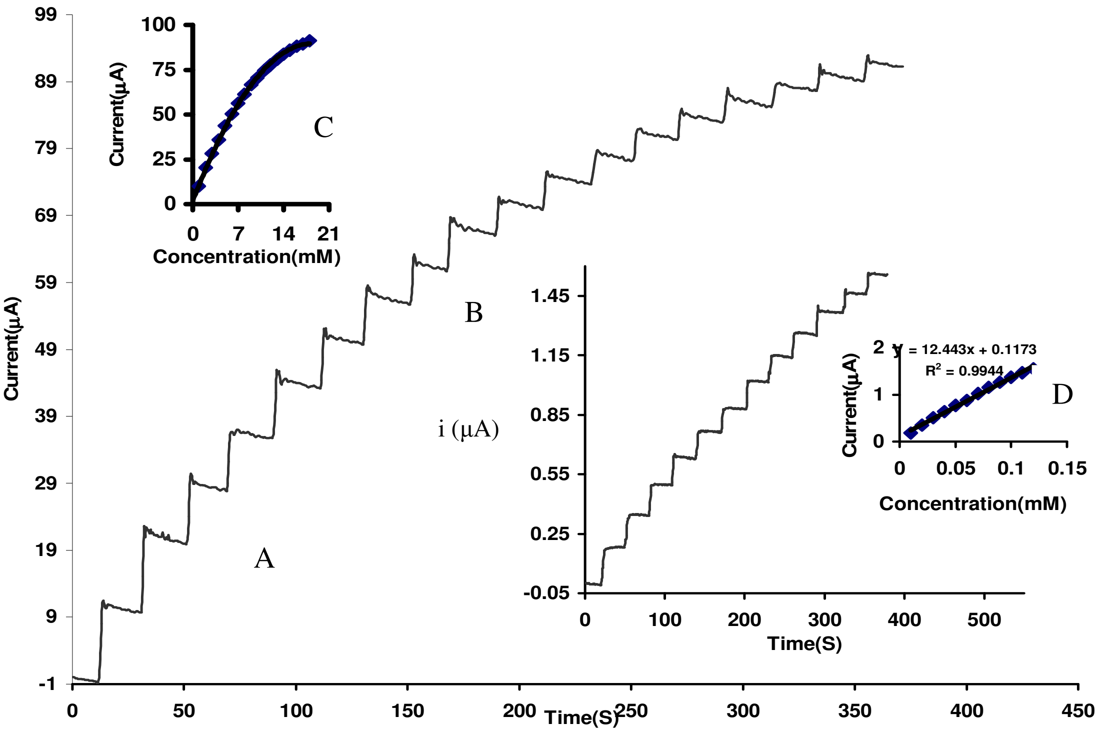

Figure 3. (A) Amperometric response at rotating modified electrode (rotation speed 1000 rpm) held at 0. 25 V in buffer solution (pH 2) for successive addition 1 mM of periodate, (B)as (A) for 10μM addition. (C) Plot of chronoamperometric currents vs. periodate concentrations.(D) as (C) for lower concentration.

Linear least square calibration curves over the range of 10 –120 μM (12 determinations) had a slope of 12.44 nA/ μM (sensitivity) and a correlation coefficient of 0.9944. The detection limit was 0.4 μM for signal to noise ratio of 3. The analytical parameters for iodate and nitrite determination are also reported in Table 1.

Table 1: Analytical parameters for iodate, periodate and nitrite detection at thionin/MWCNTs modified GC electrode

Analyte	K_{cat} /$M^{-1}s^{-1}$	Detection Limit(μM)	Linear concentration range	Sensitivity(nA/μM)
IO_4^-	1.68(±0.15)×10^4	0.4	1.0(μM)-10.0mM	12.44
IO_3^-	1.34(±0.20)×10^4	1	2 (μM)-10. mM	5.36
NO_2^-	4.93(±0.10)×10^3	4	6.0(μM)- 15(mM)	2.0

An extremely attractive feature of the thionin / MWCNts modified glassy carbon electrode is its highly stable amperometric response toward analyte reduction. The amperometric response of 1.0mM iodate is recorded over a continuous 1000 sec period (Fig.4). The response of the modified electrodes remains stable throughout the experiment (only 5 % decrease in current is observed after 1000 sec) remains stable.

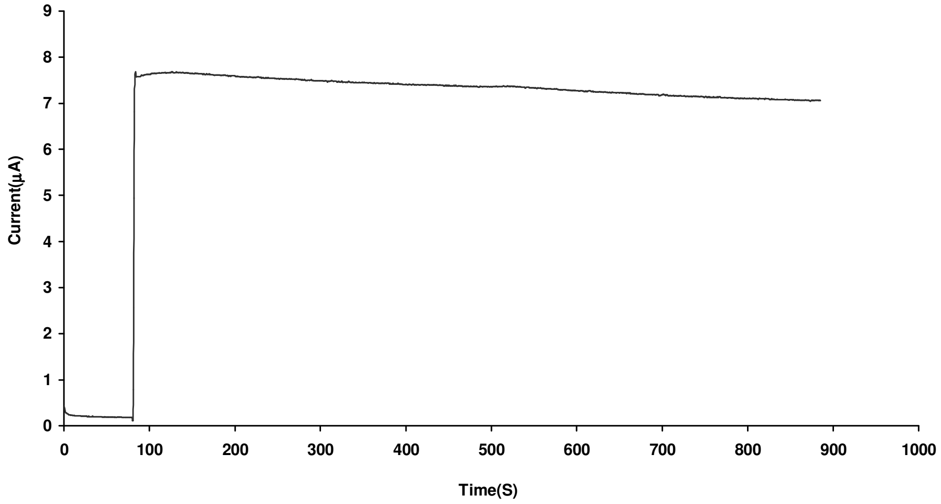

Figure 4. recorded chronoamperogram for 1.0 mM iodate during long period time (15 min), other condition as in Fig.3.

The stable chronoamperograms were obtained for reduction other anions over a continues 900 sec period. Fig.5 shows the steady–state response of modified electrode obtained for the reduction of IO_4^- , IO_3^- and NO_2^-.

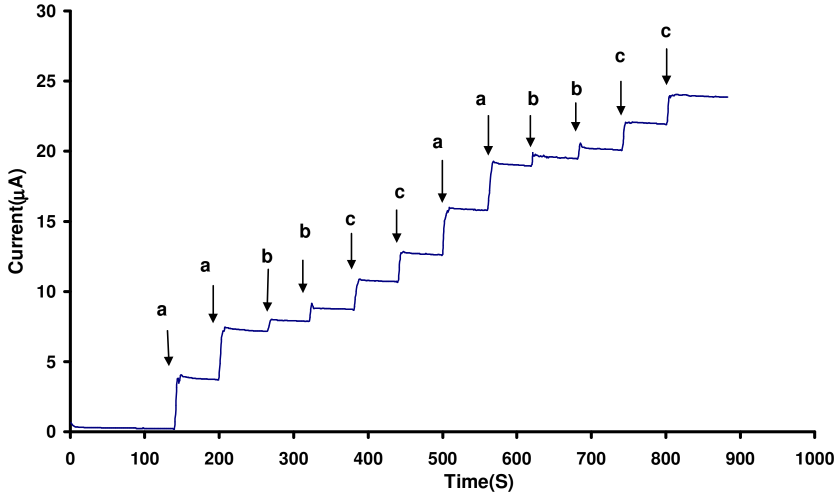

Figure 5. Steady- state current response obtained for reduction of periodate ,iodate and nitrite at thionin-MWCNTs modified GC electrode in pH 2 upon the injection of (a) and(c) 0.5 mM of periodate and iodate,(b) 2mM of nitrite, other conditions as in Fig. 3.

The steady-state current for reduction of these oxoanions was examined at constant potential of electrode at 0.10 V in buffer solution (pH 2) and individually injection of IO_4^- , IO_3^- and NO_2^- into the solution. The nearly equal current response for substrates, at the first and second time injection demonstrates an efficient catalytic property of the electrocatalyst immobilized onto the MWCNTs film and the reproducibility of the measurements. Therefore, this modified electrode can be used as an amperometric detector in flow injection or chromatographic system.

4. CONCLUSION

A simple, fast and reproducible procedure was used for adsorption of thionin as electron transfer mediator on glassy carbon electrode. The results suggest that the thionin-CNT electrode has excellent electrochemical performance for electron transfer reactions. The positive shift of the peak potential and large current response for iodate, periodate and nitrite, demonstrate that the modified electrode possesses good electrochemical activity toward electroreduction of selected analytes. The sensor possesses excellent catalytic activity, good stability, fast response time and high reproducibility. The significant decrease of potential required for reduction of these substrates, combined with good stability of the films suggests that the modified electrode can be used as amperometric sensor for determination of those analytes above at reduced overpotential. The concept of CNT-facilitated redox mediation has a potential to be of general interest for expediting redox processes in electrochemical devices such as sensors and biosensors.

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