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Catalytic oxidation of thiols at preheated glassy carbon electrode modified with abrasive immobilization of multiwall carbon nanotubes: applications to amperometric detection of thiocytosine, L-cysteine and glutathione

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Abstract

The performance of preheated glassy carbon electrode modified with carbon nanotubes is described. First glassy carbon electrode is heated for 5 min at 50 °C, then abrasive immobilization of multiwall carbon nanotubes on a preheated glassy carbon electrode was achieved by gentle rubbing of electrode surface on a filter paper supporting carbon nanotubes. Carbon nanotubes (CNTs)-modified glassy carbon electrodes exhibit strong and stable electrocatalytic response toward thiols oxidation in wide pH range. These properties permit an important decrease in over voltage for the oxidation of thiocytosine, glutathione and L-cysteine, as well as a dramatic increase in the peak currents in comparison with bare glassy carbon electrode. Furthermore, the thiols amperometric response of the coated electrodes is extremely stable, with more than 95% of the initial activity after 30 min stirring of 0.1 mM thiols. The electrocatalytic behavior is further exploited as a sensitive detection scheme for thiols detection by hydrodynamic amperometry. The substantial decrease in the overvoltage of the thiols oxidation associated with a stable amperometric response and antifouling properties of nanotubes films allow the development of highly sensitive thiols sensor without using any redox mediator. Such ability of carbon nanotubes to promote the thiols electron transfer reaction, short response time (5 s) and long-term stability, low detection limit, extended linear concentration range, high sensitivity suggest great promise for thiols amperometric sensors and detector for chromatographic analysis of thiol derivatives.

Keywords: Carbon nanotubes; Modified electrode; Preheated glassy carbon; Thiol detection; Amperometry

1. Introduction

Since the discovery of carbon nanotubes, they have been the target of numerous investigations because of remarkable nanostructures combining high electrical conductivity, high surface area, significant mechanical strength and good chemical stability [1,2]. Carbon nanotubes (CNTs) behave electrically either as metals or as semiconductors [3,4], and their electronic properties suggest that they have the ability to promote electron transfer reactions when used as an electrode material in electrochemical reactions. Recent studies demonstrated the excellent electrocatalytic ability and antifouling properties of carbon nanotubes on the electrochemical devices. Both multiwall and single-wall carbon nanotubes were used to fabricate carbon nanotube electrodes. Several authors have reported the excellent electrocatalytic properties of nanotubes in the redox behavior of different molecules and biomolecules. Wang and co-workers have reported the advantages of using glassy carbon modified with single and multiwall carbon nanotubes on the voltammertric behavior of NADH [5], insulin [6], carbohydrates [7], hydrogen peroxide [8] and 2,4,6-trinitrotoluene [9]. Pedano and Rivas have described the catalytic properties of car-

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bon nanotubes paste electrodes towards the oxidation of nucleic acids [10], ascorbic acid, uric acid, dopamine and 3-4-dihydroxyphenyl acetic acid [11]. Other authors have used electrodes modified with single and multiwall carbon nanotubes for electrocatalytic oxidation of 3-4-dihydroxyphenyl acetic acid [12], norepinephrine [13], 4-aminophenol [14], 6-mercaptopurine [15], nitric oxide [16], ascorbic acid [17], cytochrome *c* [18], myoglobine [19], thymine [20], glucose [21], indole-3-acetic acid [22], and dopamine [23]. These carbon nanotube-modified electrodes have shown interesting catalytic properties toward electrochemical processes, but the method of modification is difficult and irreversible, requiring a substantial preparation to be improved. Hence it is pertinent to explore and develop a single and reliable method to fabricate electrode surfaces modified with carbon nanotubes and their applications in electroanalytical detection of important compounds. Given the wide spread involvement of thiols and the corresponding disulfides in many essential biological functions, much effort has been made to develop sensitive and selective methods for their detection. Investigations of the redox behavior of biologically occurring thiols by means of electrochemical techniques have the potential for providing valuable insights into biological redox reaction of such biomolcules. Numerous chemical and instrumental techniques for the determination of thiols have been reported. However, most of them suffer from difficulty with sample preparation, the need for derivatization or the lack of sufficient sensitivity, all of which limit their utility [24]. Compared to other options, electroanalysis has the advantages of simplicity and high sensitivity. Since the direct oxidation of thiols at solid electrodes is slow and requires a potential of at least 1.0 V [25,26], the study of electrocatalytic reactions of thiols are important in the electroanalysis of thiols. Several electron transfer mediator have been used for shuttle electrons between thiols and electrode surfaces and also for decreasing surface fouling and oxide formation in compared to inert substrate electrodes. Electrodes modified with cobalt phthalocyanine [27], prussian blue [28], ruthenium cyanide [29], aquocobalamine [30], copper hexacyanoferrate [31], lead ruthenate pyrochlore [32], phenothiazine derivatives [33], coenzyme pyrroloquinone quinine [34], and octacyanomolybdate(V) [35] and other alternative electroanalytical methods [36], have been used for voltammetry and amperometric detection of thiols. Recently, we used several modified electrodes for determination sulfur derivatives [37–40]. Unfortunately, most modified electrodes have certain disadvantages such as considerable leaching of electron transfer mediator and poor long-term stability, furthermore the methods of preparation are expensive and difficult and some of them are not sensitive enough for real sample analysis. Hence it is pertinent to explore and develop a simple and reliable method to fabricate modified electrodes with other electron transfer mediators for electrocatalytic oxidation of thiols. Carbon nanotube-modified glassy carbon electrodes has been used for electrochemical detection of insulin [6]. Electrochemical oxidation of L-cysteine at the surface of fullerene-C60 modified glassy carbon electrode and carbon nanotube powder microelectrode have been reported [41,42]. A functionalized multiwall carbon nanotube-modified glassy carbon electrode has been used as an amperometric detector in determination of 6-mercaptopurine and thiols after separation with liquid chromatography [43]. These carbon nanotube-modified electrodes have shown interesting catalytic properties, but the method of modification is difficult and irreproducible, requiring a substantial preparation time and there is clearly scope for the method of electrode preparation to be improved. We have recently prepared a basal plane pyrolytic graphite electrode modified with abrasive immobilization of CNTs [44]. Glassy carbon electrode is one of the best materials for modifying, but it is usually polished. Unlike a basal plane pyrolytic graphite electrode, direct adhesion of carbon nanotubes is difficult and its surface should be pretreatment for allowing adhesion of carbon nanotube particles. In this report, multiwall carbon nanotubes were abrasively attached to the surface of preheated glassy carbon electrode. The activity of the modified electrode toward the electrocatalytic oxidation of thiols was investigated. Finally, the electrocatalytic performance of CNTs modified glassy carbon electrodes are described.

2. Experimental

2.1. Reagents and instruments

Multiwall carbon nanotubes with a 95% purity (10–20 nm) and 1 μm length were obtained from Nanolab (Brighton, MA). Thiocytosine (4-amino-2-mercapto pyrimidine), L-cysteine (*R*-2-amino-3-mercapto propionic acid) and glutathion (γ-L-glutamyl-L-cysteine-glycine) were obtained from Aldrich and used without further purification. Buffer solutions (0.1 M) were prepared from H_2SO_4, HCl, CH_3COOH, K_2HPO_4 and KOH for the pH range 1–10. All solutions were prepared with double distilled water. Solutions were deaerated by bubbling high purity (99.99%) argon gas through them prior to the experiments and the electrochemical cell was kept under argon atmosphere throughout the experiments. A computer controlled Auto Lab modular electrochemical systems (ECO Chemie Ultrecht, The Netherlands) equipped with a PSTA 20 module and driven GPES software (ECO Chemie) was used for amperometric and voltammetric measurements. The working electrode was a GC electrode with a diameter of 2 mm, a platinum wire and an Ag/AgCl (std.) 3 M KCl were used as auxiliary and reference electrode, respectively. All applied electrodes were from Metrohm Company. The glassy carbon electrodes modified with carbon nanotubes layers were characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM), using a Cambridge stereoscan electron microscope and a digital instruments multimode SPM scanning probe microscope.

2.2. Preparation of MWCNT glassy carbon-coated electrodes

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 min at 50 °C in on oven. Two milligrams of purified MWCNT was placed on a filter paper (Whatman no. 1001110). The MWCNTs were then abrasively immobilized on to the electrode, immediately after removing preheated GC electrode from the oven, by gently rubbing the electrode surfaces on the fine qualitative filter paper containing carbon nanotubes for 1 min. The modified electrode was rinsed with ethanol and distilled water before use.

3. Results and discussion

3.1. Electrocatalytic oxidation of thiols at MWCNT-modified glassy carbon electrode

Characterization of the MWCNT film on a GC electrode was investigated with SEM and AFM microscopes. As is shown in SEM image (Fig. 1), many MWCNT bundles with a general diameter in the range 10–20 nm can be observed. Fig. 2 shows AFM images of a MWCNT forest on GC electrode and bare glassy carbon electrode. As shown in Fig. 2B, a significant amount of MWCNT was adsorbed on the surface of GC electrode.

The electrocatalytic activity of MWCNT-modified GC electrode was examined by cyclic voltammetry. The cyclic voltammograms of thiols derivatives recorded at preheated GC electrode and preheated GC electrode modified with abrasive immobilization MWCNTs are presented in Fig. 3. The CNT-coated electrode exhibits significant oxidation currents starting around 0–0.2 V versus reference electrode and no reduction signal is observed in the reversed scan. In contrast, no redox activity is observed at the unmodified GC electrode over most of the potential range (0–1.2 V versus Ag/AgCl, 3 M KCl). A substantial large negative shift of the anodic peak potential for thiols and dramatic increase of current indicate significant catalytic ability of MWCNT to thiols oxidation. The anodic response decreased slightly (<15%) during five scans and remained highly stable and the peak potentials were unchanged to positive values there after for up to 30 repetitive scans. Then glassy carbon electrode modified with carbon nanotubes not only shows catalytic activity but also they have

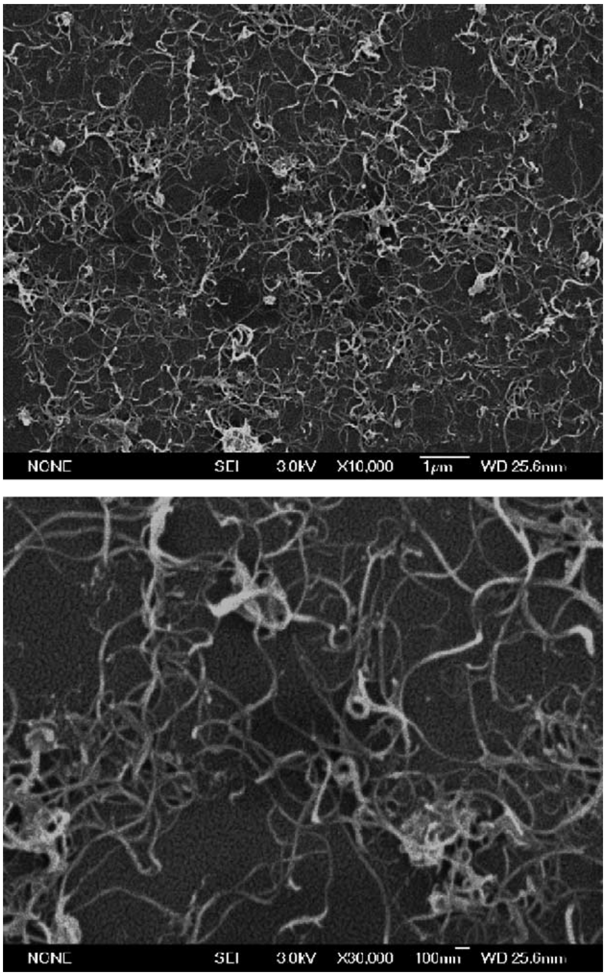

Fig. 1. SEM images of CNTs used to fabricate CNT-modified glassy carbon electrode, magnification 10,000× and 30,000×.

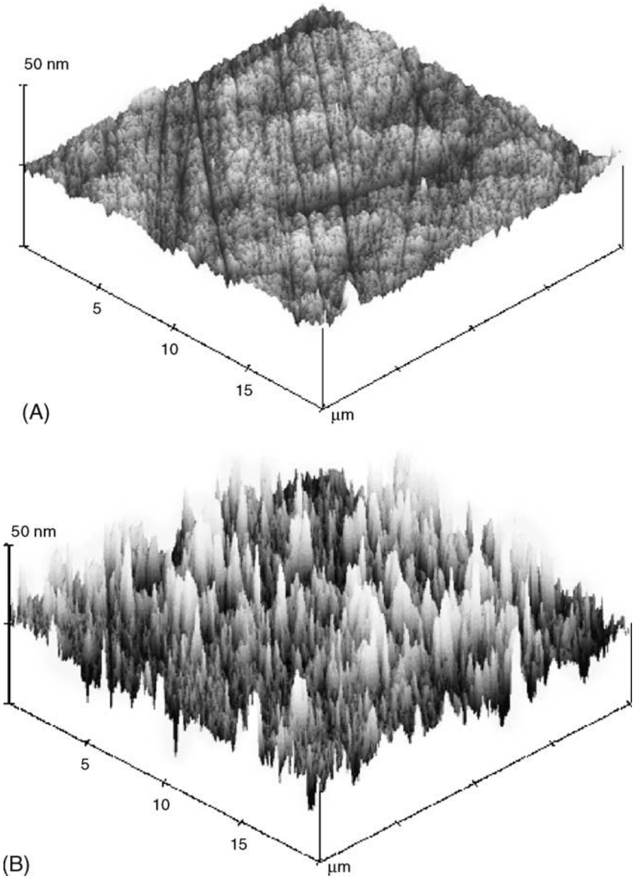

Fig. 2. AFM images of (A) unmodified GC carbon electrode and (B) MWCNT-modified GC electrode surface.

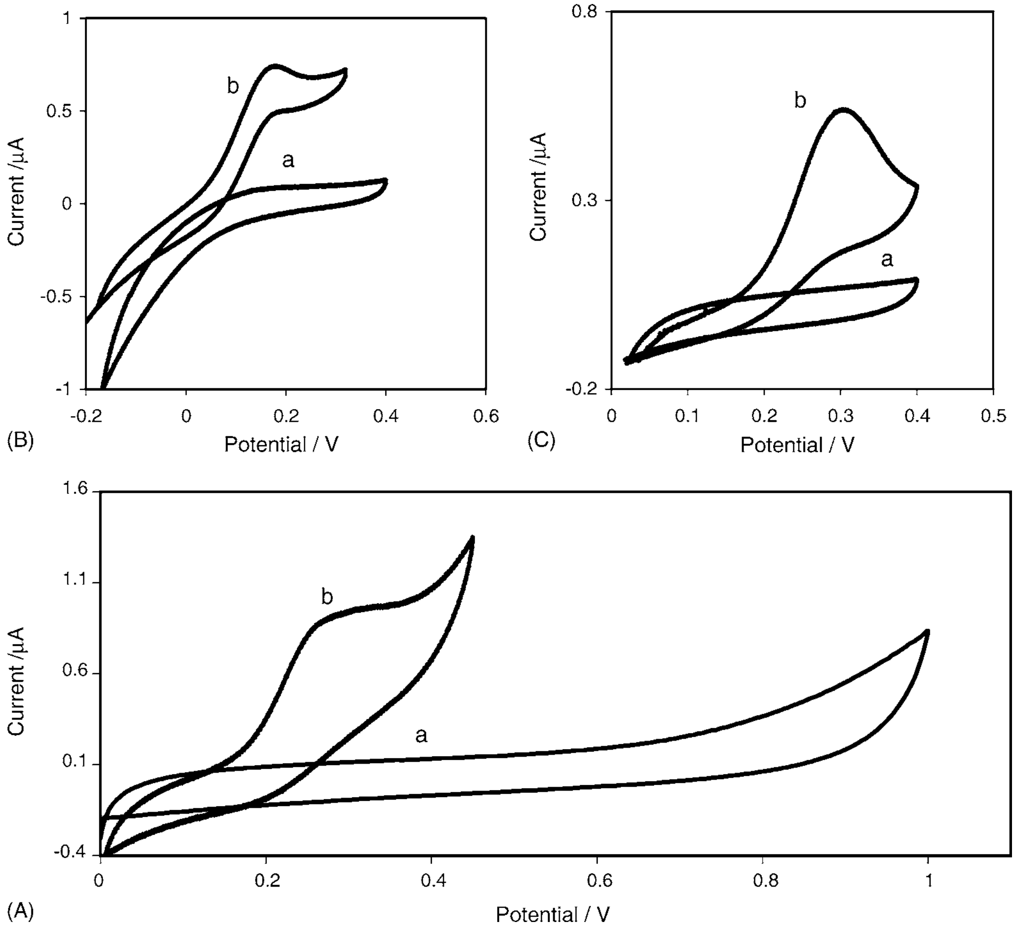

Fig. 3. (A) Cyclic voltammograms for 1 mM thiocytosine in 0.1 M phosphate buffer solution (pH 5). (B) and (C) as in (A) for 3 mM L-cysteine and 2 mM glutathione in 0.1 M phosphate buffer solution (pH 4), at unmodified (a) and MWCNT-modified GC electrode (b), scan rate: 10 mV s^{-1}.

antifouling properties for thiols and their oxidation products. Also on using the electrodes after leaving them unused for period of 2 weeks in 0.1 M phosphate buffer solution (pH 7) the peak potential for thiols oxidation was again unchanged and the current signals showed only less than 4% decrease of the initial response. In reproducibility tests, it was found that the relative standard deviation (R.S.D.) of the cyclic voltammograms peak currents of 2 mM thiol derivatives (pH 5) for five replicate measurements was 2–4%. To study the reproducibility of the electrode preparation, six modified electrodes were prepared; then their cyclic voltammograms were recorded in 1 mM thiocytosine, relative standard deviation was 5% (from measurements of anodic peak currents at 0.3 V). The modification of GC electrode without preheating with carbon nanotubes shows catalytic activity for thiols oxidation (not shown), but signals are not stable and peak current decreases after 20 repetitive cycles, also R.S.D. were more than 10% for six replicate determinations (2 mM thiols derivative). It was suggested that direct adhesion of carbon nanotubes is difficult and signals are not stable on usually polished glassy carbon electrode.

In order to optimize the electrocatalytic response of the modified carbon nanotubes GCE towards thiols oxidation, the effect of pH on the catalytic oxidation behavior was investigated. The response of thiocytosine is well behaved in buffer solution in the range of pH 2–9. As shown in Fig. 4, the peak potential shifts negatively as pH increases but the peak currents are broadly of similar magnitude. This is a consequence of the deprotonation involved in the oxidation process that is facilitated at higher pH values. The modified electrode shows stable electrocatalytic activity for thiols oxidation over this wide range of pH values studied. A plot of peak potential versus pH was found to be linear over the pH range 2–9 (inset of Fig. 4) with a gradient 59 mV/pH consisting with a two proton–two electron process. According to the results the catalytic oxidation of thiols at the modified nanotube electrodes is described by the following equation:

$$2\,\mathrm{RSH} - 2\,e^{-} \rightarrow \mathrm{RS{-}SR} + 2\,\mathrm{H}^{+} \qquad (1)$$

A similar behavior was observed for L-cysteine and glutathione. In particular, the redox reactions between thiols and the corresponding disulfides (Eq. (1)) are essential processes in many biological and chemical systems. The dependence of the voltammetric response of the modified CNT electrode to the addition of thiol concentration was investigated.

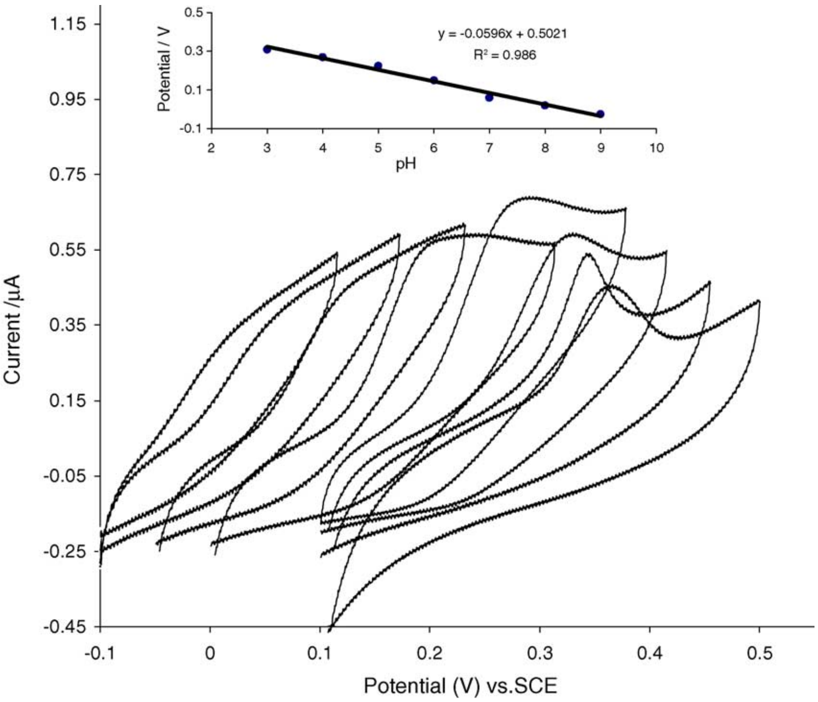

Fig. 4. The cyclic voltammetric response of MWCNT-modified GC electrode in 1 mM thiocytosine solution at different pH (from right to left, 2–8); scan rate: $10\,\mathrm{mV\,s^{-1}}$. Inset shows the variation of peak potentials vs. pH.

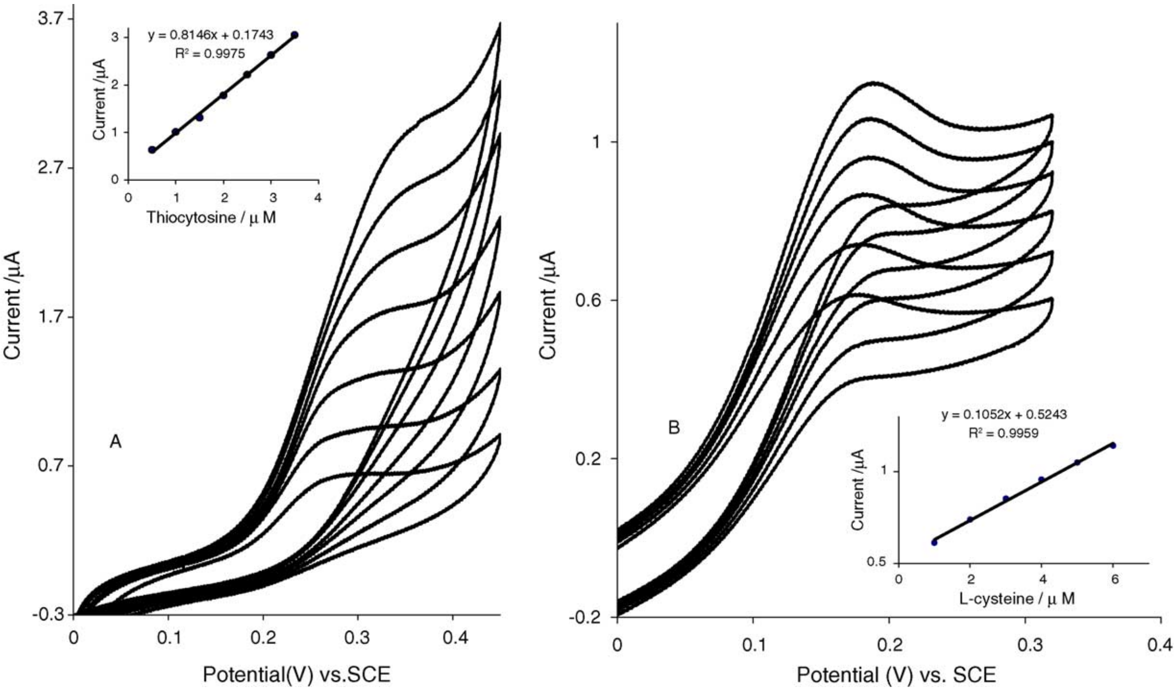

Fig. 5. (A) Cyclic voltammograms of MWCNT-modified GC electrode in 0.1 M phosphate buffer solution (pH 5) at scan rate $10\,\mathrm{mV\,s^{-1}}$ with increasing the thiocytosine concentration (from inner to outer) 0.5, 1, 1.5, 2, 2.5, 3 and 3.5 mM thiocytosine. Inset shows plot of peak current vs. thiocytosine concentrations. (B) as in (A) for 1, 2, 3, 4, 5 and 6 mM L-cysteine.

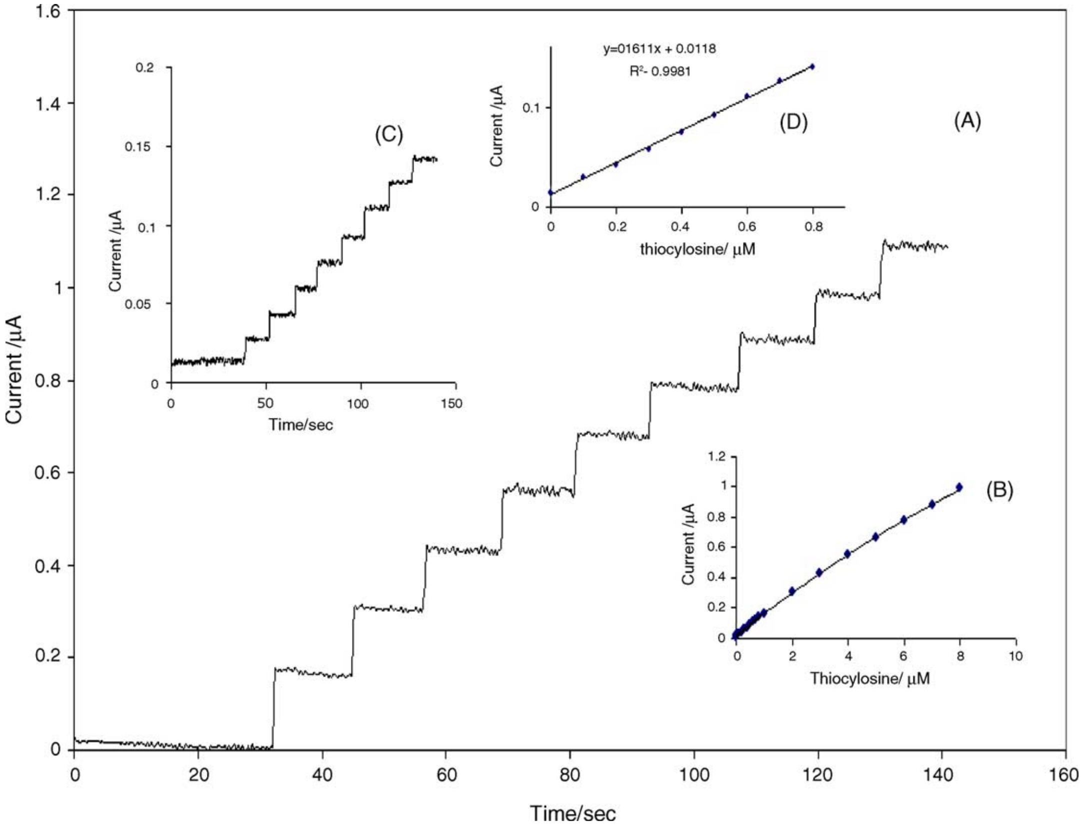

Fig. 6. Amperometric response at MWCNTs modified GC electrode, rotating modified electrode (rotation speed: 2500 rpm) held at 0.3 V in phosphate buffer solution (pH 5) for successive addition of (A) 1 µM and (C) for 0.1 µM; (B) and (D) plot of chrono-amperometric currents vs. thiocytosine concentration.

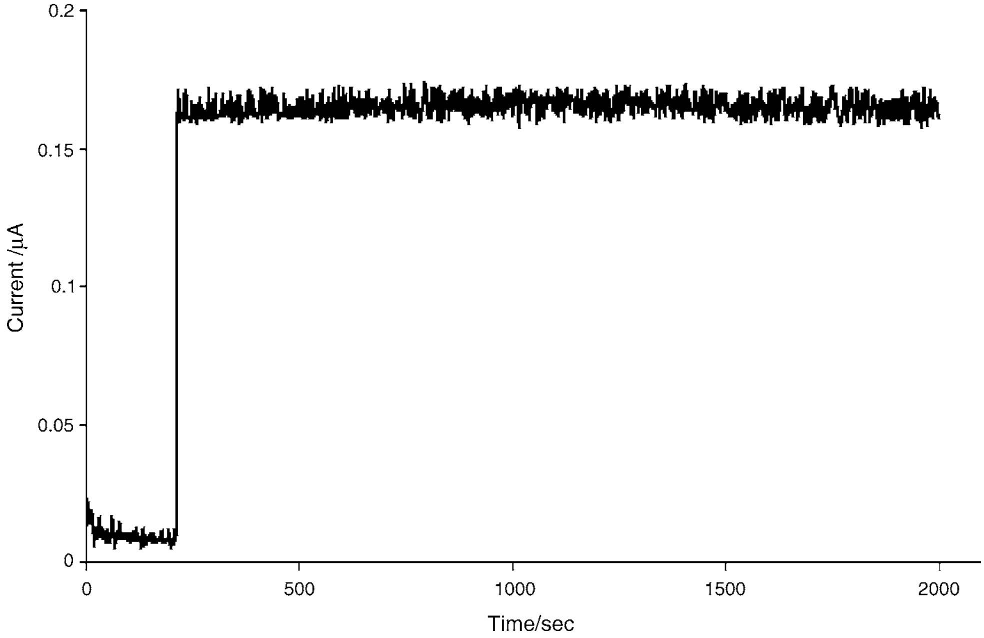

Fig. 7. Stability of the response of the MWCNT-modified electrode to 1 µM thiocytosine, other conditions as in Fig. 6.

Table 1
Analytical parameters for thiols detection with different modified electrodes

Sensitivity (nA μM^{-1})	Limit of detection (μM)	Dynamic range (μM)	Method	Analyte	Electrode	Reference
22	0.4	2–20	Amperometry	L-Cysteine	Co(II) salophen-modified carbon paste	[46]
8.9	0.2	1–12	Amperometry		Carbon electrode bulk Modified with cobalt phtalocyanine	[50]
5–53	–	10–100	SWV[a]	L-Cysteine		
5	1	6–685		L-Cysteine	Ru(II) complex-modified carbon ceramic electrode	[38]
7.5	1	5–700	Amperometry	Glutathione		
28	0.3	Up to 10	Voltammetry	L-Cysteine	Octabutylthiophtaocyanato-Co(II) modified gold electrode	[47]
–	0.018		Amperometry	L-Cysteine	Pyrroloquinoline quinone-modified electrode	[48]
	0.036	–		Glutathione		
–	2	2–2800	Amperometry	L-Cysteine	Pt microelectrode modified with carbon nanotubes	[41]
15.5	–	20–300	Voltammetry	L-Cysteine	Fullerene-C$_{60}$-modified carbon electrode	[57]
4.7	0.063	–		L-Cysteine	Coenzime pyroloqunoline quinone-modified GC electrode	[45]
0.03	11.4	–	Amperometry	Glutathione		
32.5	1.4	Up to 560	SWV	L-Cysteine	Lead ruthenate pyrochlore-modified electrode	[49]
78	0.0017	0.01–100	FIA[b]			
	0.12	0.3–1000	Liquid chromatography with flow injection amperometry	L-Cysteine	GC electrode-modified with multiwall carbon nanotubes	[58]
–	0.22	0.3–1000		Glutathione		
30.7	5.7			L-Cysteine	Born doped diamond (5-thio-2-nitrobenzoic acid as electron transfer mediator)	[59]
25.2	4.4	–	Chrono-amperometry	Homocysteine		
22.4	5.8			Glutathione		
		0.52		L-Cysteine	Gold electrode modified with phtalocyanide	[51]
–	–	2.3	SWV	Homocysteine		
–	0.002	0.04–1	Voltammetry	L-Cysteine	Nafion/Co(II) modified electrode	[52]
	1.7 pmol	1.16 nmol–1.7 pmol	FIA	L-Cysteine	Aquocobalamine-adsorbed GC electrode	[53]
1	0.175	25–1000	CZE[c] amperometry	L-Cysteine	Carbon electrode	[54]
2.5	0.0747	5–1000		Glutathione		
0.32	–	0.8–6000	Potentiometry	Thioglyconic acid	Carbon paste electrode-modified cobalt phetalocyanine	[55]
12–20	0.9	1–200	Voltammetry flow injection	L-Cysteine	BDD	[56]
12	0.21	0.1–100				
3	5.4	10–500		L-Cysteine	Glassy carbon electrode modified with multiwall carbon nanotubes	This work
3	3.3	5–100	Amperometry	Glutathione		
160	0.026	0.1–10		Thiocytosine		

[a] SWV: square wave voltammetry.

[b] FIA: flow injection amperometry.

[c] CZE: capillary zone electrophoresis.

Fig. 5 shows cyclic voltammograms of CNT-modified GCE in solutions containing different concentration of thiocytosine (0.5–3.5 mM) and the inset shows that the catalytic current is proportional to concentration. With additions of thiocytosine, the anodic peak current was observed to increase with the dependence of the peak current response to the concentration of thiocytosine found to be linear in the range 0.1–10 mM. The plots of peak currents versus L-cysteine and glutathione concentration are linear in the concentration range 0.5–20 and 0.4–12 mM, respectively. The effect of scan rate on the electro-oxidation of thiols at the modified electrode was investigated by cyclic voltammetry. The oxidation peak current of thiocytosine increased linearly with the square root of scan rates in the range 5–80 mV s^{-1}, with a correlation coefficient of 0.996. The same behavior was observed for L-cysteine and glutathione. This suggests that the process of electrode reaction is controlled by diffusion of the thiols.

3.2. Amperometric detection of thiols at modified CNT glassy carbon electrode

As discussed above, the carbon nanotube modified glassy carbon electrode has excellent and strong mediation properties and facilities the low potential amperometric measurements of thiols. Fig. 6 shows the chrono-amperometric response of thiocytosine oxidation at rotating CNT-modified GCE (rotation speed 1000 rpm), under conditions where the potential was kept at 0.3 V in phosphate buffer solution with pH 6. It is clear that during successive addition of 0.1 μM thiocytosine a well-defined response is observed. As shown the steady-state current rises with the addition of thiocytosine and quickly reaches a stable value (less than 5 s), indicating that the CNT-modified GCE has a short response time for thiol determination. The plot of currents versus thiocytosine concentration is shown in inset of Fig. 6. The calibration plot is linear over a wide concentration range; 0.1–10 μM. Linear least squares calibration of the curve over the range 0.1–0.8 μM (eight points) had a slope of 160 nA μM^{-1} with a correlation coefficient 0.998. The electrode has a detection limit of 25 nM at signal to noise ratio of 3. The results of same experiments for L-cysteine and glutathione are shown in Table 1. These analytical parameters are comparable or better than results reported for analytical determination of thiols at the surface of different modified electrodes [38,41,45–59] (Table 1) and alternative electrochemical methods for determination of thiols [60].

The results indicating detection limits are somewhat lower and our system is more sensitive than those previously reported. One of the advantages of this modified electrode for amperometric detection of thiols is its highly stable amperometric response during long period of time towards thiols oxidation. Fig. 7 shows the amperometric response of 20 μM of thiocytosine as recorded over 30 min periods. The amperometric response of L-cysteine and glutathione are stable for the same period of time. For evaluation of reproducibility of modified CNT glassy carbon electrode for thiols detection a series of replicate addition of thiocytosine at different concentrations are recorded (Fig. 8). Each replicate corresponds to five successive amperometric measurements carried out using modified CNT glassy carbon electrode in phosphate buffer solution containing thiocytosine (50–150 μM). The relative standard deviation for each concentration ($n = 5$) is less than 2%. Thus the modified CNT glassy carbon electrode was found to exhibit high sensitivity, stability at long period of time, good repeatability and fast response time for thiols determination.

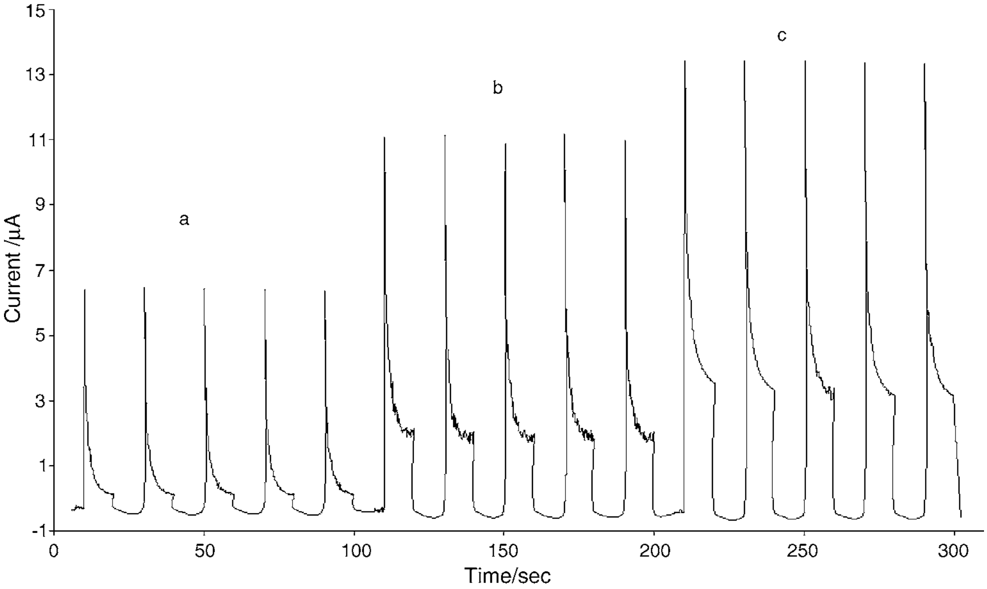

Fig. 8. Chrono-amperometric response for five replicate addition of 50, 100 and 150 μM thiocytosine to 0.1 M phosphate buffer solution (pH 5), operational potential 0.3 V.

4. Conclusion

A stable thin film of carbon nanotubes with long stability and excellent reproducibility was achieved on the surface of preheated glassy carbon electrode. The modified electrode has been shown to be promising for thiols detection with many desirable properties including, high stability, good reproducibility and repeatability, high sensitivity, low detection limit, fast response time and antifouling property for thiols and their oxidation products. A CNT-modified glassy carbon electrode was used for the fast amperometric detection of thiols at micromolar or lower concentration at wide pH range. This sensor can be used as an amperometric detector for routine analysis of thiols derivatives in flow systems when coupled to chromatographic and electrophoretic separation systems.

Acknowledgments

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