

Effect of Different CNT's Oxidation Methods on Thiocoline Detection by Surfactant Modified Graphite Electrodes

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Abstract:

Carbon nanotubes are regarded as promising building blocks for the construction of novel biosensors due to their unique properties like fast electron transfer, high electrocatalytic effect and good biocompatibility. In the present study, the effect of different chemical oxidation's methods of multi-walled carbon nanotubes (MWCNTs) on the electrochemical behavior of modified graphite electrodes has been investigated. The MWCNTs were oxidized by using three kinds of oxidants: a) concentrated nitric acid (65 wt %), b) mixture of concentrated sulfuric acid (98 wt %) and nitric acid (65 wt %) (3:1), and c) hydrochloric acid (2M) followed by acid mixture of (b). The results of oxidation procedures were characterized by infrared spectroscopy. Graphite electrode surface was modified with cationic, anionic, and non-ionic surfactants. The obtained results showed that amperometric responses of functionalized CNTs were enhanced with cationic surfactant-modified electrodes. The sensitivity of nitric acid treated CNT/DTAB/graphite electrode has been enhanced by 47% and its detection limit has reduced to 0.01 mM for amperometric thiocholine detection.

Keywords: Multi-walled carbon nanotubes, Modified graphite electrode, Functionalization, Surfactants, Thiocholine detection

1. INTRODUCTION

One of the major products of thiocholine ester (TChE) hydrolysis with acetylcholinesterase (AChE) enzyme is Thiocholine (TCh). Therefore, detection of TCh and determination of its concentration can be used to evaluate the activity of AChE, as a common biomarker for the biological effect of organophosphates, carbamates and other pesticides [1,2]. Electrochemical method is one of the most considerable subjects in enzyme detection, due to its low detection limit, high selectivity, and high sensitivity [3]. The true arrangement of enzymatic

reactions with the electrochemical method of scanning electroactive enzymatic product, such as thiocholine, results to the development of enzyme based electrochemical biosensors [4].

The main objective of the present paper is to develop a carbon nanotube (CNT) modified electrode for highly sensitive monitoring of enzymatically generated thiocholine products. There are two different classes of CNTs: single-wall carbon nanotubes (SWCNTs) and multiwall carbon nanotubes (MWCNTs). The MWCNTs are made-up of highly ordered pyrolytic graphite (HOPG), whose open-end is comparable to the edge plane of HOPG, and the side-wall arrangement is similar

to the graphite basal plane of HOPG [5]. Since the electron transfer on edge-plane graphite is faster than that on the basal plane graphite, the open ends of the CNTs should have fast electron transfer rates [6]. While, the side-walls present very slow electron transfer rates similar to the graphitic basal plane [5]. The possibility of the promotion of electron transfer as well as CNTs high surface area makes them a unique candidate for biochemical sensing system [7]. However, commercially available CNTs have some disadvantages as follows:

- 1) they contain amorphous carbon and metal catalysts, which probably have negative effects on their electrocatalytic activity;
- 2) they have poor dispersion in all types of solvents, which is especially important for biological applications. Therefore, these products should always be purified and functionalized before bringing into use. Functionalization of MWCNTs with poly (amidoamine) dendrimer [8], partial oxidation of CNTs to produce oxygen-containing groups [9], covalent modification of CNTs with hydrophilic groups and non-covalent functionalization of CNTs with surfactants or hydrophilic polymers are some examples of such efforts [10]. Several methods such as oxidative treatment using concentrated HNO_3 or mixture of concentrated H_2SO_4 and HNO_3 have been proposed to enhance the dispersion ability of CNTs in water [4].

Recently, Dutsyuk et al. showed that chemical oxidation of MWCNTs plays a fundamental role in their reactivity properties [11]. They found that nitric acid treated material under reflux conditions suffered the highest degree of degradation. However, basic oxidative treatment led to the complete removal of amorphous carbon and metal oxide impurities without any damage to structural integrity [10]. Vesali-Naseh et al. studied functionalization of CNTs using dielectric barrier discharge (DBD) plasma [12]. Based on their studies, it is found that plasma treatment mainly functionalizes the surface of the CNTs, whereas in case of chemical treatment, changes in the bulk of the CNTs might occur [12].

Recently, Kim et al. [13] have been used ammonium hydroxide/hydrogen peroxide mixture for treatment of MWCNTs and showed that, due to the minor

damages of the graphitic sidewalls, the resulting composite with epoxy as matrix, have enhanced electrical conductivity [13].

In the present work, we carried out an organized study of the chemical oxidation of MWCNTs, treated by various chemical reagents, which possess different degrees of oxidation power. Based on the obtained results, we report a more suitable and efficient acid treatment method for functionalizing MWCNTs in electrochemical biosensor applications. MWCNTs were treated by three oxidants and their electrochemical behavior was investigated using amperometry in thiocholine solution. In addition, the effect of different surfactants on bare electrode and MWCNT modified electrode was studied.

2. MATERIALS AND METHODS

2.1. Materials

Multi-walled carbon nanotubes (MWCNTs, > 90% purity) were obtained from Research Institute of Petroleum Industry (Tehran, Iran). Acetylthiocholine iodide (purity > 99%), and acetylcholine-esterase were purchased from Sigma (Steinheim, Germany). Dodecyl trimethylammonium bromide (DTAB), sodium dodecyl sulfate (SDS), Triton X-100 and paraffin were purchased from Merck (Darmstadt, Germany). Other reagents were commercially available and were of analytical grade. Solutions were prepared with ultra pure water (18 M Ω .cm).

2.2. Methods

Substrate solution of acetylthiocholine iodide was prepared in 0.1 M phosphate buffer with a final concentration of 0.1 M and was kept at -20°C in aliquots. The thiocholine (TCh) solution was prepared by the enzymatic reaction of AChE and acetylthiocholine iodide solution for 30 min in 0.1 M phosphate buffer (pH 7.4), which was used as supporting electrolyte. All electrochemical experiments were carried out using a Potentiostat/Galvanostat (model 263-A, EG&G, USA), a single-compartment electrochemical cell equipped with a auxiliary platinum rod electrode, an Ag/AgCl reference electrode (containing 3 M KCl) and a

paraffin-impregnated graphite working electrode with a disk diameter of 4 mm that was modified with surfactant and MWCNTs as described in follows.

2.2.1. Purification and functionalization of MWCNT

In order to remove the probable amorphous carbons and metal catalysts, 500 mg of the MWCNTs was heated in an oven at 400°C under nitrogen atmosphere for 8 h. The air oxidized MWCNTs were functionalized by combinations of nitric acid (HNO₃), sulfuric acid (H₂SO₄), and hydrochloric acid (HCl). These acids were used as oxidizing agents in order to create oxygenated groups, such as –COOH and –OH groups, on MWCNTs' surface [14]. The methods used for functionalization are as follows:

A) Chemical modification with nitric acid, CNT1: 10 mg air oxidized MWCNT was heated in 4 mL HNO₃ 65% at 70°C for 6 h and dispersed by ultrasonication for 30 min. Then, MWCNTs were washed by repeated centrifugation at 10000 rpm for 10 min followed by re-dispersion of the precipitate in doubled distilled water, until the pH of the solution became neutral. Afterwards, MWCNTs were dried in an oven at 60°C for 12 h.

B) Chemical modification with nitric acid/sulfuric acid mixture, CNT2: 10 mg of heated MWCNT was dispersed in the mixture (3:1) of 4 mL of concentrated sulfuric acid (98%) and nitric acid (65%) for 5 h. The other steps including heating, ultrasonication, washing and drying were similar to the preparation of CNT1.

C) Chemical modification with HCl - nitric acid/sulfuric acid mixture, CNT3: 10 mg of heated MWCNT was dispersed in 4 mL HCl (2M) and heated for 6 h at 70°C. Then the MWCNTs were separated and dried at 60°C. Dried MWCNTs were dispersed in 4 ml mixture of concentrated H₂SO₄ and HNO₃ (3:1, 98 wt% and 65 wt%, respectively) at 70°C for 6 h. Other steps including ultrasonication, washing and drying, were similar to CNT1 preparation.

2.2.2. Characterization of MWCNTs

Fourier transforms infrared (FT-IR) spectra of

pristine and oxidized MWCNTs were recorded on a Mattson 1000 FT-IR spectrometer (UK), using the potassium iodide disc method, to define the structure of the functionalized MWCNTs.

2.2.3. Modification of electrode with surfactants

The working electrode was constructed using a graphite rod that was removed from a battery. The rod was cleaned and heated in HNO₃ (30%) at 70°C to remove industrial oil and washed with double distilled water. Then, the rod was put in heated liquid paraffin to make paraffin-impregnated graphite electrode. Prior to modification, the graphite electrode was carefully polished with sand paper and rinsed with double-distilled water. 2 μL aliquot of 50 mM surfactant (DTAB, SDS, Triton X-100) solution was casted on the electrode surface and dried at room temperature. After drying, the surface was rinsed thoroughly with double distilled water.

2.2.4. Immobilization of MWCNTs on electrode surface

0.5 mg of the functionalized MWCNTs was abrasively immobilized onto the graphite electrode by gently rubbing the electrode surface on glass plate containing the CNTs, for 1 min. Then, the electrode was then rinsed with double distilled water to remove the non-immobilized MWCNTs.

2.2.5. Electrochemical measurements

Amperometric measurements were performed using an electrochemical analyzer (EG&G, USA). The electrochemical cell consisted of the MWCNT/graphite working electrode (or bare graphite electrode), a silver/silver chloride reference electrode and a platinum wire counter electrode. Amperometric measurements were performed in 3 mL electrochemical cell containing 1 mM phosphate buffer. In each injection, 1 μL of 1mM tiochrome solution was injected to the electrochemical cell. The desired working potential of 100 mV was applied and transient currents were allowed to decay to a steady-state value.

3. RESULTS AND DISCUSSION

3.1. FT-IR spectra of pristine and oxidized MWCNTs

To characterize the structure of functionalized MWCNTs, FT-IR spectrums of pristine CNT, CNT treated with HNO_3 (CNT_1), $\text{HNO}_3\text{-H}_2\text{SO}_4$ (CNT_2) and $\text{HCl} / \text{HNO}_3\text{-H}_2\text{SO}_4$ (CNT_3) are shown in Figure 1. The appearance of the peaks (1700, 1520 and 1159 cm^{-1}) in the IR spectrum of pristine CNT (Figure 1-a) indicates the presence of carboxylic and carboxylate oxygen-containing groups on the surface of the CNTs, as reported by Liu et al. [4]. These groups might be introduced during modification. The FT-IR of the functionalized MWCNTs (Figure 1-b,c,d) shows the presence of sharper peaks when compared to the pristine CNT.

The absorption band at $3365\text{--}3590\text{ cm}^{-1}$ has been attributed to hydroxyl groups (O-H, -OH)

stretching vibration, coming from acid treatment process. In addition, other bands at $1400\text{--}1730\text{ cm}^{-1}$ corresponding to -C=O , -COO^- , and -COOH groups were all reinforced after acid treatment, especially those corresponding to C=O groups at 1729 cm^{-1} . These results are in good agreement with the results reported by Chiu and Chang [14]. Appearing more carboxyl and hydroxyl groups on HNO_3 -treated CNTs as compared to other functionalized MWCNTs, is representative of more achievement through this method.

3.2. Electrochemical Behavior and Amperometric Responses of Thiocholine

The oxidation process of thiocholine can be described as [5]:

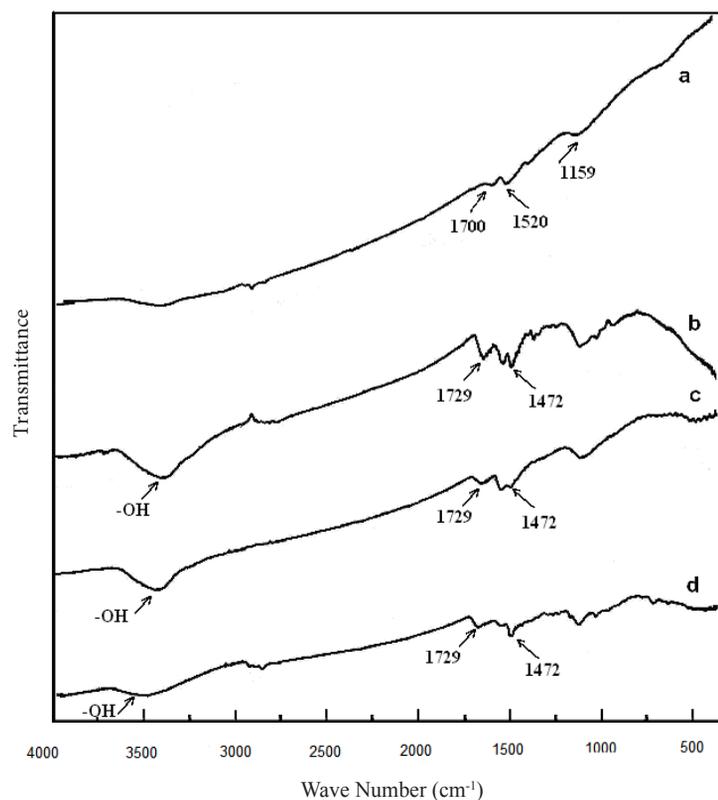
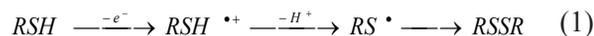


Figure 1: FTIR spectra of a) pristine CNT, b) CNT treated with HNO_3 (CNT_1), c) CNT treated with $\text{HNO}_3\text{-H}_2\text{SO}_4$ (CNT_2), d) CNT treated with HCl and $\text{HNO}_3\text{-H}_2\text{SO}_4$ (CNT_3)

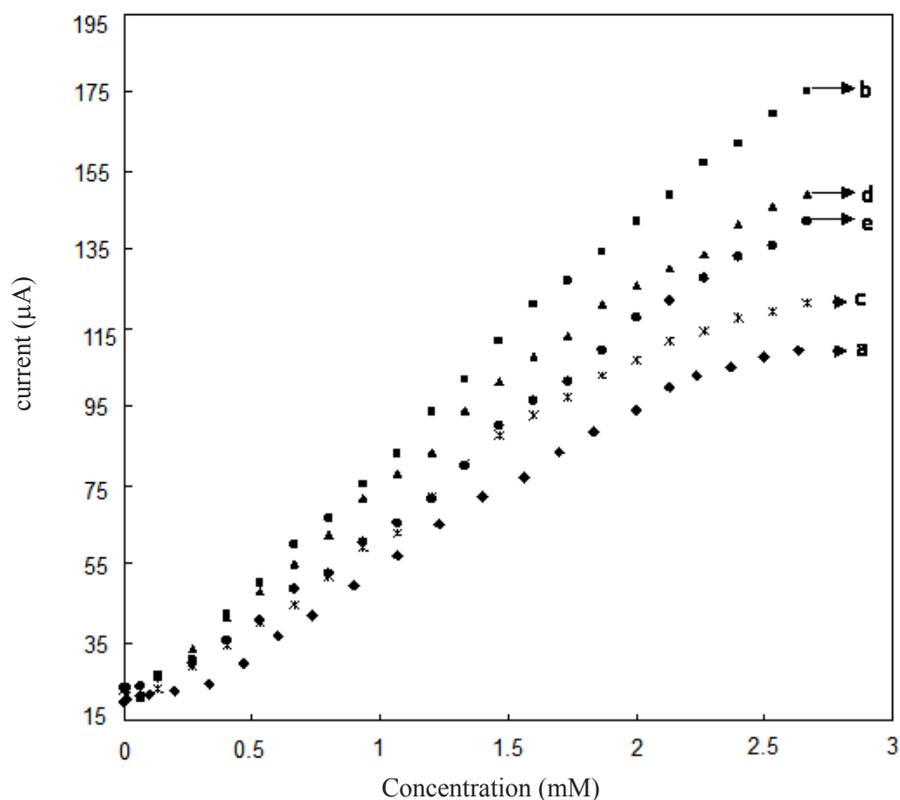


Figure 2: Amperometric response of various concentrations of thiocholine oxidation on, a) bare graphite electrode, b) pristine CNT/Graphite electrode, c) CNT₁/Graphite electrode, d) CNT₂/Graphite, e) CNT₃/Graphite, in PBS buffer (pH=7.4, 0.1M)

where the RS' species undergoes rapid dimerization to form a disulfide species, results to an anodic oxidation peaks at about 700 mV on graphite electrode. The results of amperometric measurements of thiocholine by bare graphite electrode as well as the electrodes modified with pristine CNT and treated CNTs with three kinds of oxidants are shown in Figure 2. Compared to the bare electrode, an increase in the slope of amperometric curves were seen in the presence of CNTs (Figure 2-a and 2-b). The modified electrode with pristine CNT shows the higher record as compared to other modified electrodes. The electrostatic interactions between the MWCNTs and the graphite electrode could be the reason for such behavior [15, 16]. Recently, Lucrecia Carot et al. clarified the influence of electrostatic and hydrophobic interactions involved in biofunctionalization of CNTs [17]. Due to the chemical oxidation of MWCNTs and the formation of carboxyl and carbonyl groups on the side wall

and opened ends of MWCNTs, partial hydrophilic nature could be assigned to these functionalized tubes. The surface of graphite electrode used in this work, has hydrophobic and non-polar properties, which could be assigned to the presence of paraffin. Therefore, the hydrophilic MWCNTs might not perfectly immobilize on the hydrophobic substrate (electrode surface), leading to a slow electron transfer rate. Therefore, non-functionalized hydrophobic MWCNTs could entirely immobilize and promote electron transfer in comparison with functionalized MWCNTs.

The results of electrode modified with DTBA, are different (Figure 3). Here, the acid treated MWCNTs with negatively charged surface immobilize more on modified graphite with positive surface charges. DTAB, as a cationic surfactant [18], can attach to paraffin from its hydrophobic tail and to functional groups

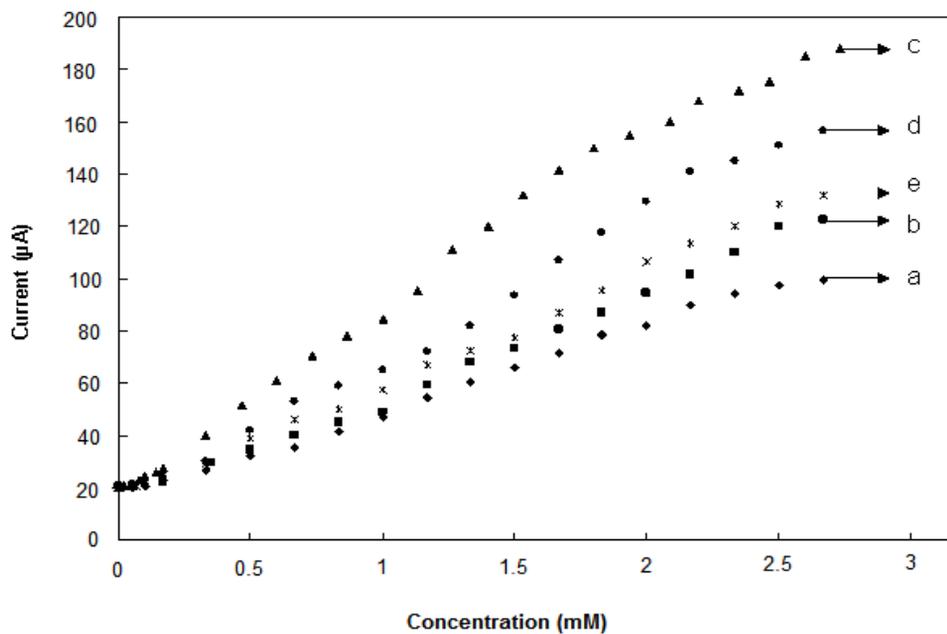


Figure 3: Amperometric response of various concentrations of thiocholine oxidation on graphite electrode modified a) with DTAB, b) with pristine CNT/DTAB, c) with CNT1/DTAB, d) with CNT2/DTAB, e) with CNT3/DTAB, in PBS buffer (pH=7.4, 0.1M).

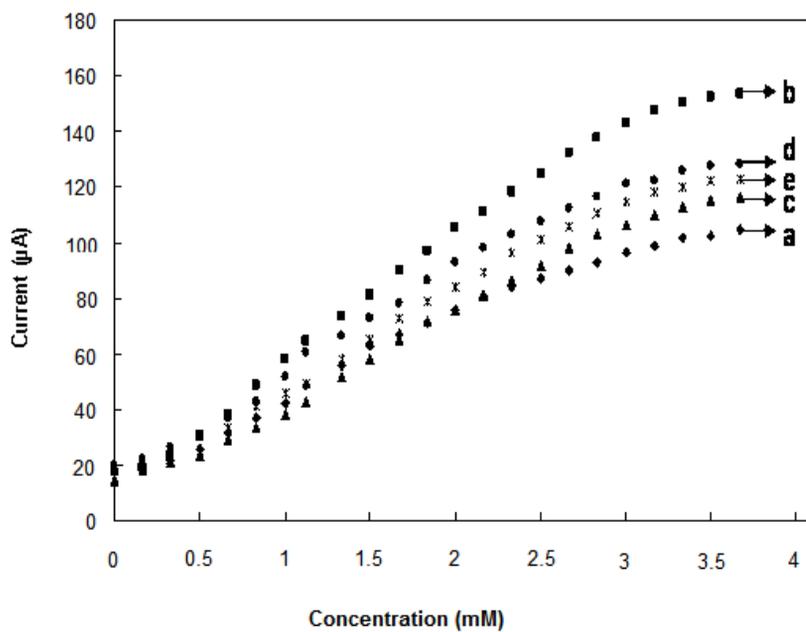


Figure 4: response of various concentrations of thiocholine oxidation on graphite electrode modified a) with SDS, b) with pristine CNT/SDS, c) with CNT1/SDS, d) with CNT2/SDS, e) with CNT3/SDS, in PBS buffer (pH=7.4, 0.1M).

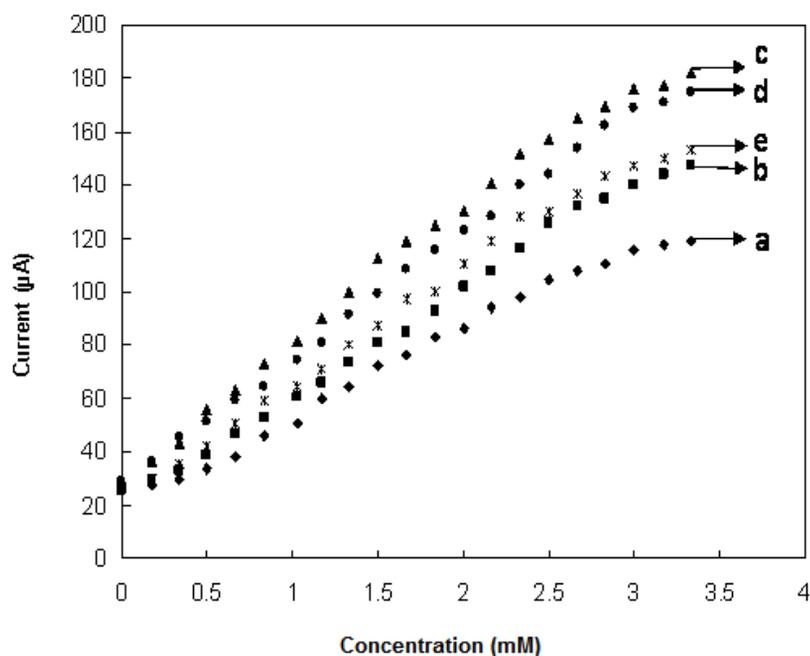


Figure 5: Amperometric response of various concentrations of thiocholine oxidation on graphite electrode modified a) with TritonX100, b) with pristine CNT/TritonX100, c) with CNT1/TritonX100, d) with CNT2/TritonX100, e) with CNT3/TritonX100, in PBS buffer (pH=7.4, 0.1M)

of MWCNTs from hydrophilic head. This attachment will improve the immobilization of functionalized MWCNTs on electrode surface. The HNO_3 -treated MWCNTs (CNT1, Fig 3c) will enhance the amperometric response for thiocholine oxidation more, as compared to the other functionalized MWCNTs. These results are in agreement with Lee and Mijovic investigations on bio-nano complexes [19]. Based on their studies, DTAB molecules display higher binding affinity toward DNA when hydrophobically attached to the single-walled carbon nanotube (SWNT) surface.

Using sodium dodecyl sulfate (SDS) as an anionic surfactant, results an electrode with negative surface charges. Based on other studies, it is known that the SDS could have a strong interaction with MWCNTs and it is incorporated within the electrode surface, by adsorption of the hydrophobic alkyl chain, leaving the negatively charged sulfate groups exposed to the bulk solution so a higher charge density contributed to the capacitive current [21]. Here, the SDS

will attach to paraffin from its hydrophobic tail and its hydrophilic end with negative charges will coat the electrode surfaces [20]. Therefore, when functionalized MWCNTs were immobilized on SDS-modified electrode surface, electrostatic repulsion between MWCNTs and SDS will lead to a weak attachment. As a result, the amperometric response to thiocholine addition for pristine MWCNTs (CNT, Figure 4b) was more than any other modified electrodes (Figure 4).

The non-ionic hydrophilic groups will appear on the electrode surface through its modification by a non-ionic surfactant, octyl phenol ethoxylate (Triton X-100). Here, a strong non-ionic bond between electrode surface and hydrophilic functionalized MWCNTs could form [22]. Therefore, treated MWCNTs showed an enhanced amperometric response in comparison with pristine MWCNTs (Figure 5). Here, the CNT1 had the better responses than the CNT2, CNT3 and CNT. Moreover, the attachment of functionalized CNTs on this electrode surface was weaker than DTAB modified electrode but stronger than SDS modified (Figure 3, 4 & 5).

In a similar work, Islam et al. reported a simple process to solubilize high weight fraction single-wall carbon nanotubes in water by the nonspecific physical adsorption of sodium dodecylbenzene sulfonate. They reported that there is a strong hydrophobic interaction between Triton X-100 and the SWNTs due to the aromatic group [22].

Comparison of maximum response of each modified graphite electrode (Figure 6), reveals that the HNO₃-treated MWCNTs (CNT1) immobilized on DTAB-modified graphite electrode exhibited the best amperometric responses for thiocholine oxidation, because of its higher sensitivity (slope of linear part) and lower detection limit. This could be related to higher immobilization of acid treated MWCNTs on this modified electrode. The sensitivity of HNO₃-treated MWCNTs /DTAB/ graphite electrode has been enhanced by 47% and its detection limit has reduced to 0.01 compared to the value of 0.07 of pristine MWCNTs / graphite electrode for amperometric thiocholine

detection. This demonstrates that functional groups on MWCNTs treated with HNO₃ made greater improvement in the electron transfer process on cationic surface of graphite electrode.

4. CONCLUSION

Functionalized MWCNT-modified graphite electrodes offer a highly sensitive and better anodic detection of enzymatically generated thiocholine products compared to the bare and pristine MWCNT-modified electrodes. Such promising profiles were attributed to the catalytic activity of edge-plane-like graphite sites and -COOH groups at MWCNTs ends. These characteristics allow fast electron transfer and provide a large working surface area. The immobilization of MWCNTs functionalized with nitric acid improved the amperometric response of oxidation of thiocholine on cationic surfactant modified electrodes up to

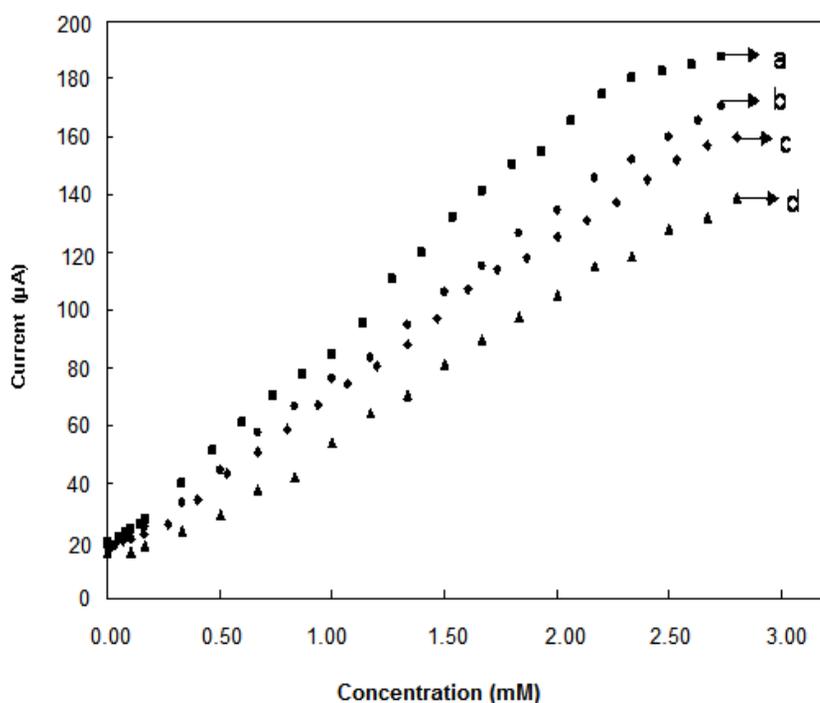


Figure 6: Comparison of maximum Amperometric response of various concentrations of thiocholine oxidation on each modified electrode, a) pristine CNT/Graphite electrode, b) CNT1/DTAB/Graphite electrode, c) pristine CNT/SDS/Graphite electrode, d) CNT1/TritonX100/Graphite electrode, in PBS buffer (pH=7.4, 0.1M)

47%. Results obtained in this study, show that the interaction between surfactant-modified electrode surface and MWCNTs cannot be underestimated, and functionalized MWCNTs have a substantial effect on electron transfer.

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