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Immobilization of redox mediators on functionalized carbon nanotube: A material for chemical sensor fabrication and amperometric determination of hydrogen peroxide

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Abstract. Chemical functionalization of single-walled carbon nanotubes with redox mediators, namely, toluidine blue and thionin have been carried out and the performance of graphite electrode modified with functionalized carbon nanotubes is described. Mechanical immobilization of functionalized single-walled nanotube (SWNT) on graphite electrode was achieved by gently rubbing the electrode surface on carbon nanotubes supported on a glass slide. The electrochemical behaviour of the modified electrodes was investigated by cyclic voltammetry. The SWNT-modified electrodes showed excellent electrocatalytic effect for the reduction of hydrogen peroxide. A decrease in overvoltage was observed as well as an enhanced peak current compared to a bare graphite electrode for the reduction of hydrogen peroxide. The catalytic current was found to be directly proportional to the amount of hydrogen peroxide taken.

Keywords. Immobilization; functionalized; single-walled carbon nanotube; chemical sensor; determination; hydrogen peroxide.

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1. Introduction

Carbon nanotubes have been the target of numerous investigations since their discovery because of their remarkable properties such as high electrical conductivity, high surface area, significant mechanical strength, antifouling and good chemical stability. Because of these special properties of carbon nanotubes they can be used as catalyst [1], templates for nanostructures [2], nanoprobes in scanning probe microscope [3], and transistors [4]. The carbon nanotubes have been successfully applied on electrodes as novel CMEs [5,6] because of their ability to promote electron-transfer reactions in electrochemical reactions. However, the purified carbon nanotubes flocculate often in aqueous or common organic solvents, which limit their further manipulation and application. Recent studies demonstrated the excellent electrocatalytic ability and antifouling properties of carbon nanotubes on the electrochemical devices. Both multi-walled and single-walled carbon nanotubes were used to fabricate carbon nanotube electrodes. Several authors have reported the excellent electrocatalytic properties of nanotubes in the redox behaviour of different molecules and biomolecules. Wang and co-workers have reported the advantages of using glassy carbon modified with single- and multi-walled carbon nanotubes on the voltammetric behaviour of NADH [7], insulin [8], carbohydrates [9], hydrogen peroxide [10] and 2,4,6-trinitrotoluene [11].

Functionalized carbon nanotubes offer enormous potential as components of nanoscale electronics and sensors. If it were possible to chemically modify the surface of the nanotube in a controlled manner, this would afford a number of opportunities for tailoring the structural and electronic properties. Chemically modified carbon nanotubes can easily be fixed on a surface via chemical bonds from the surface of the nanotube. Organic molecules like dyes, proteins or nucleic acids may be coupled with functionalized nanotubes for sensor applications [12]. There have been some important works about the electrocatalysis of CNTs [13–16] and chemical sensors [13,17,18]. The prospect of these applications has led to successful functionalization of single-walled (SWNT) and multi-walled (MWNT) carbon nanotubes [19]. SWNTs are receiving ever-increasing attention in recent years and to achieve their full potential, it will be necessary to bring about chemical modification on their basic nature. Several attempts have been made to achieve bonded functionalization of SWNTs. For example, fluorination of SWNTs [20], 1,3-dipolar addition [21], derivatization of small diameter SWNTs [22], glucosamine attachment [23], and side-wall carboxylic acid functionalization of SWNTs [24] have been shown to occur.

Determination of hydrogen peroxide is very important due to its existence in biological systems as it is often a by-product of enzymatic reactions. In this preliminary work we describe our efforts in the functionalization of SWNT with redox mediators such as toluidine blue and thionin and then using the functionalized SWNTs for chemical sensor fabrication and for the electrocatalytic detection and determination of H_2O_2.

2. Experiment

Reagents and equipment

Single-walled carbon nanotubes with 95% purity (10–20 nm dia. and 1 μm length) were obtained from Aldrich. The redox mediators toluidine blue (TB) and thionin (Thi) were obtained from Himedia. All other chemicals and reagents used were of analytical grade. Double distilled water was used to prepare all the solutions.

Electrochemical measurements were carried out in a conventional three-electrode cell using EG&G PAR Electrochemical system (Model 263 A) equipped with GPIB (IEEE-488) interface port and IBM personal computer. The graphite electrodes modified with functionalized CNTs were used as the working electrodes; a platinum wire and saturated calomel electrode (SCE) were used as the counter and reference electrodes respectively.

Functionalization of SWNT

The SWNT samples were functionalized as follows:

(i) *Carboxylation*: SWNT (0.2 g) as purchased were sonicated in conc. HCl for 15 min. After washing with water the black solid was heated at 225°C for 18 h. The metal impurities were removed by HCl extraction. The thermal treatment has been repeated at 325°C for 1.5 h and at 350°C for 1 h followed by sonication in HCl. The carboxylated SWNTs were filtered, washed with double distilled water and dried [25].

(ii) *Acylation*: The carboxylated nanotubes (50 mg) were stirred in 15 ml of $SOCl_2$ (containing 1 ml dimethyl formamide) at 45°C for 16 h. After the acyl chlorination, the SWNTs were filtered, washed with 3 ml of CH_2Cl_2, and dried under vacuum at room temperature for ∼20 min.

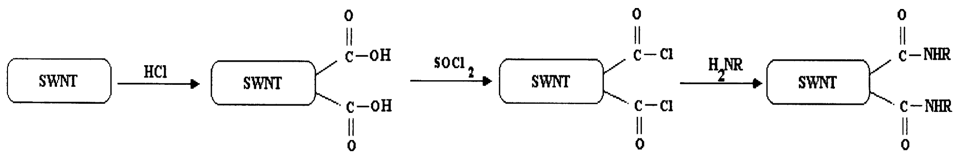
(iii) *Amidation*: The acyl-chlorinated nanotubes were suspended in 20 ml DMF and divided into two parts. The first part was mixed with toluidine blue (20 mg) and the second part with thionin (20 mg). After stirring for 2 h, the excess amine was washed with DMF followed by isopropanol and then the SWNTs were separated by filtration and dried [26].

Fabrication of the modified CNT electrodes

The working electrode was constructed using the paraffin-impregnated graphite electrode which was prepared as reported in [27]. The functionalized SWNTs were then abrasively immobilized onto the graphite electrode by gently rubbing the electrode surface on glass plate containing the carbon nanotubes for 1 min. The electrode was then rinsed with double distilled water. These modified electrodes were characterized and used as chemical sensors.

3. Results and discussion

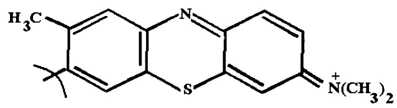
The sequence of reaction during the functionalization of SWNT is shown in scheme 1.



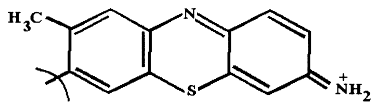
Scheme 1. Functionalization of SWNT.

The structure of the redox mediators used for preparing modified electrodes are shown below:

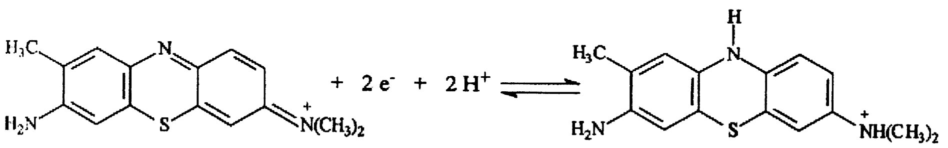
Toluidine blue:



Thionin:



The modified electrodes having mediators-immobilized SWNT at the surface were characterized by cyclic voltammetric method using 0.1 M KNO_3 as the background electrolyte. The potential was cycled between 0.2 and −0.6 V at a scan rate of 20 mV S^{-1}. The cyclic voltammogram (CV) obtained with TB-immobilized SWNT-modified electrode (TB-SWNT) is shown in figure 1 (curve c). This curve corresponds to the redox behaviour of toluidine blue, which is present on the electrode surface. When the potential is scanned from 0.2 to −0.6 V, the TB is electrochemically reduced to give the mediator in the reduced form (TB-R). When the scan is reversed at −0.6 V, the reduced form of the mediator formed on the electrode surface is oxidized to give TB. The reaction taking place at the electrode surface when the potential is scanned in the above range is shown below.



(TB-O) (TB-R)

Toluidine blue undergoes reversible electron transfer reaction and hence waves are obtained during the cathodic and anodic scans. The formal potential was found to be −350 mV. For comparison, a CV of the unmodified graphite electrode is also shown in figure 1 (curve a) where no significant current flows. When CVs were recorded with the modified electrode in the presence of various amounts of H_2O_2, an increase in reduction current was observed (curves d–g). The increase in reduction current in the presence of H_2O_2 obtained for the modified electrode is indicative of electrocatalytic reduction of H_2O_2. The reaction taking place at the electrode surface can be described as follows. Toluidine blue which is present on the electrode surface is reduced electrochemically to give TB-R (reduced form) which reduces H_2O_2 present in the solution to water and getting itself oxidized (TB-O), which is again reduced electrochemically. Thus this process is repeated a number of times, which is responsible for the catalytic current. The magnitude of the reduction current was found to be directly proportional to the amount of H_2O_2 taken. It is also to be noted that no significant reduction current for H_2O_2 was observed with bare electrode (curve b).

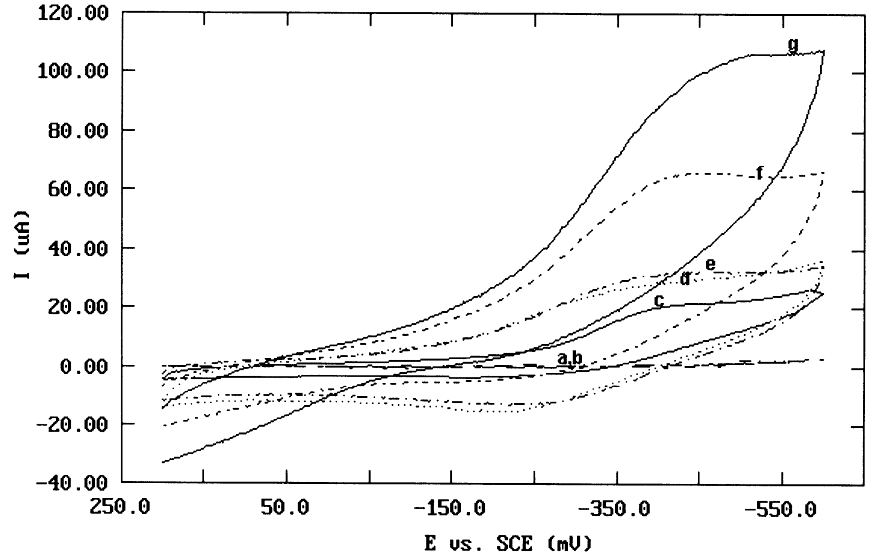
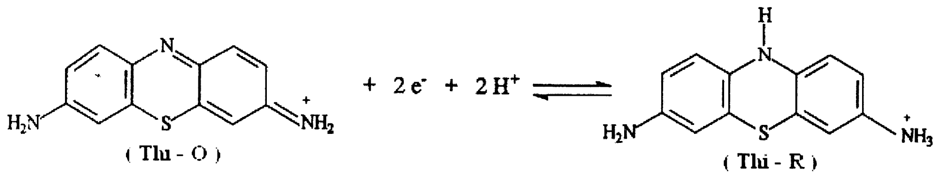


Figure 1. Cyclic voltammograms of (a) bare graphite electrode, (b) 1.02×10^{-2} M H_2O_2 at bare electrode, (c) TB-SWNT-modified graphite electrode without H_2O_2 and with (d) 6.84×10^{-6} M, (e) 2.75×10^{-5} M, (f) 3.4×10^{-3} M, (g) 1.02×10^{-2} M H_2O_2. Electrolyte: 0.1 M KNO_3; scan rate: 20 mV/s.

The cyclic voltammetric characterization of thionin-immobilized SWNT-modified electrode is shown in figure 2. In this figure, curve c corresponds to the redox reaction of thionin and the electron transfer reaction can be represented as shown below.



Similar to toluidine blue, thionin also undergoes reversible electron transfer reaction and hence both cathodic and anodic waves were obtained. The formal potential was found to be −330 mV. Curve a shows the electrochemical behaviour of the unmodified graphite electrode where no significant current flows. CVs have been recorded for the Thi-SWNT modified electrode in the presence of various amounts of H_2O_2 and the voltammograms are shown in the same figure (curves d–g). The increase in cathodic current in the presence of H_2O_2 corresponds to catalytic reduction of H_2O_2. The mechanism of catalytic reduction is similar to TB. During cathodic scanning, thionin is reduced to Thi-R (reduced form), which chemically reduces H_2O_2 to water, getting itself oxidized to Thi-O (oxidized form). This is again reduced electrochemically and this process is repeated a number of times, which results in an increased cathodic current. It is also found that as the amount

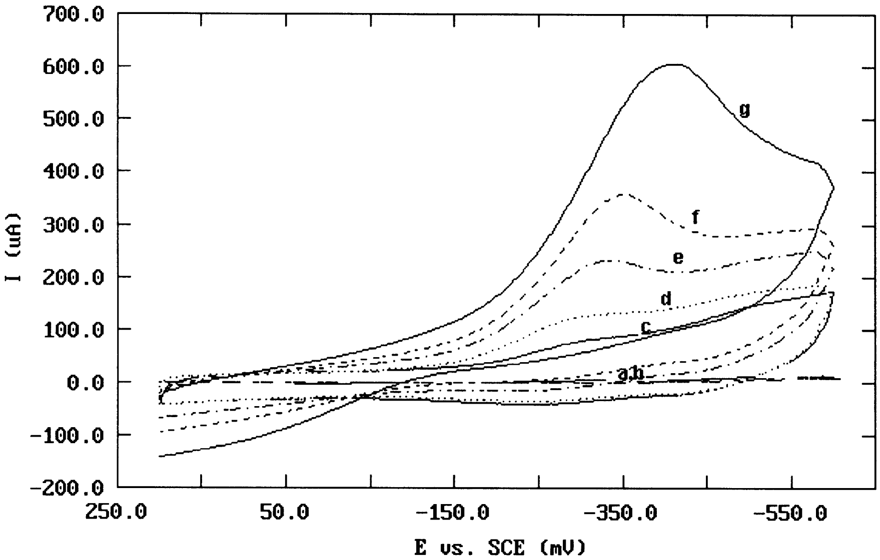
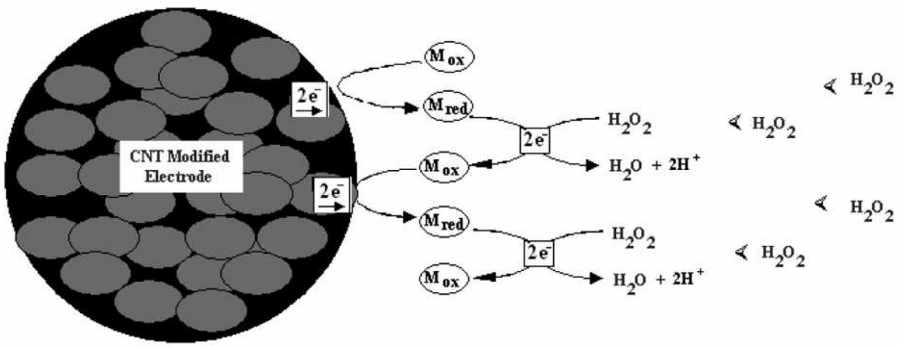


Figure 2. Cyclic voltammograms of (a) bare graphite electrode, (b) 1.02×10^{-2} M H_2O_2 at bare electrode, (c) Thi-SWNT-modified graphite electrode without H_2O_2 and with (d) 6.84×10^{-6} M, (e) 2.75×10^{-5} M, (f) 3.4×10^{-3} M, (g) 1.02×10^{-2} M H_2O_2. Electrolyte: 0.1 M KNO_3; scan rate: 20 mV/s.

of H_2O_2 increases, the catalytic current also increases. No significant current was observed for the reduction of H_2O_2 with the bare electrode (curve b). The mechanism of catalytic reduction of H_2O_2 by the immobilized mediators is shown in scheme 2.

The above preliminary results are very encouraging and give a positive proof for the immobilization of mediators on functionalized CNTs. A detailed study about the application of the sensors and the characterization of the electrode by surface analytical methods are in progress.



Scheme 2. Mechanism of catalytic reduction of H_2O_2 by the immobilized mediators.

4. Conclusion

Functionalization of SWNT with redox mediators such as toluidine blue and thionin has been achieved. The graphite electrodes were modified with functionalized SWNT by mechanical immobilization. The voltammetric response of hydrogen peroxide at functionalized CNT-modified graphite electrodes was examined and it was found that H_2O_2 undergoes electrocatalytic reduction at the modified electrodes.

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