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Fabrication of highly sensitive MnO_2/F-MWCNT/Ta hybrid nanocomposite sensor with different MnO_2 overlayer thickness for H_2O_2 detection

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ABSTRACT

In this work, we report the development of MnO_2/F-MWCNT/Ta hybrid nanocomposite sensor with different MnO_2 overlayer thickness for the detection of H_2O_2 in real samples. A novel two-step process using e-beam evaporation and spray pyrolysis deposition was adopted for the synthesis of hybrid MnO_2/F-MWCNT/Ta electrodes. SE morphology revealed smaller-sized, compact grains of MnO_2 infiltrated on the outermost walls of MWCNTs. Raman analysis confirmed the existence of carbon nanotubes with abundant structural defects of MnO_2 in the composite. The cyclic voltammetry results displayed a high peak current and narrowed over potential towards the reduction of H_2O_2. The sensor displayed a fast response (< 5 s), wide linear range (2–1510 μM) and a low limit of detection (0.04 μM) with significant anti-interfering properties, promising for the development of highly sensitive and reproducible biosensors. The three dimensional nanocomposite sensor also exhibited good recovery (> 98%), thus providing a favourable tool for analysis of H_2O_2 in milk samples.

1. Introduction

A biosensor is a self-reliant well integrated device which is effective in providing explicit quantifiable analytical information using a biological material. The bio sensing element converts a chemical event into an appropriate electrical signal that can be utilized to determine the concentrations of biomaterial [1]. The precise and low-scale detection of biomolecules, such as hydrogen peroxide (H_2O_2), melamine, amino acids etc., is of great importance in biomedicine diagnosis. Detecting H_2O_2 is a vital task for applications involving food, pharmaceutical science, clinical and environmental monitoring [2–8]. Also, several disorders such as atherosclerosis, cancer and Alzheimer's disease have been associated with cytotoxic H_2O_2 reactive oxygen species, conversely, it has been an essential component for cell growth, and migration and immune system function [9–11]. Thus, a precise and sensitive means of monitoring H_2O_2 is vital for clinical diagnostics, preservatives in food industry and patient monitoring [12–14]. Several methods of detecting H_2O_2 have been proposed, including various spectroscopic, electrochemical, optical, chemiluminescence and colorimetric [15–21]. Among these, electrochemical analysis has been validated to be an enhanced technique to analyse reactions of various analytes·H_2O_2 transductions can transpire either through electrochemical oxidation or through electrochemical reduction [22,23]. In order to overcome the limitations arising from enzyme based sensors such as operational temperature conditions and reproducibility, enzyme free sensors have been captivated for their exceptional stability in various conditions.

The emergence of extended quasi-1D carbon nanotubes material has captivated substantial attention for the fabrication of non-enzymatic electrochemical sensors due to its high chemical stability and electronic conductivity [24,25]. In the present study, we have used hydroxyl group functionalized multi-walled carbon nanotubes (F-MWCNTs). The use of functionalized MWCNTs shows improved distribution promoting chemical reactivity besides interfacial bonding for subsequent fabrication of nanocomposite [26]. Recently, H_2O_2 sensing devices based on graphene have been reported. Zhou et al., reported the electrochemical sensor based on chemically reduced graphene oxide for the detection of H_2O_2 [27]. Fugang Xu et al., reported the graphene–Pt based nanocomposite for the electrochemical detection of H_2O_2 [28]. Liu et al., developed a non-enzymatic H_2O_2 sensor using a stable aqueous dispersion of graphene nanosheets with Ag Nanoparticles [29]. However, the sensitivity and response times of these sensors were comparatively deprived and unsatisfactory for most practical applications. Hence, we attempted to blend the solid-state properties of semiconducting nanoparticle with the biofunctional properties of the organic fragment, as semiconducting material possess greater selective catalytic properties towards the electrochemical reduction of hydrogen peroxide [30–33]. Owing to the excellent catalytic activity for oxygen reduction, MnO_2 has been used to modify CNTs with high sensitivity and good cyclic stability. Also, surface coating of CNTS with optimum MnO_2 thickness

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is necessary to improve the efficiency towards the catalytic disproportionation of H_2O_2 generated at the surface of CNTs. Hence, in the present work, we investigate the influence of thickness of MnO_2 overlayer on the properties of CNTs/Ta electrodes·H_2O_2 sensors based on MnO_2 were reported for electrochemical sensor electrode fabrication [34–36]. But there are no reports on the effect of thickness of MnO_2 overlayer on the microstructural properties of carbon nanotubes for device fabrication.

Also, the distinctive characteristics of MWCNT could be devised over refractory tantalum metal, as nanotubes are connected with the conductive layer, which eradicates the difficulties caused by auxiliary buffer solution [37]. In addition, the shrewd formation of MWCNTs may be significantly improved on Ta buffer layer, as it exhibits low contact resistances and superior rate capability. These functionalities augment the transport of electron among redox centres and buffer layer, to facilitate electrochemical reactions [38]. Until now, there has been no reports on the influence of MnO_2 overlayer thickness on MWCNT/Ta electrode, especially for the fabrication of electrochemical H_2O_2 sensors. Another novelty in the present study is the use of two different deposition techniques for the fabrication of hybrid MnO_2/MWCNT/Ta electrode. For deposition of MWCNTs on Ta substrate, electron beam evaporation technique was adopted because high density vertically aligned CNTS with high purity can be fabricated at lower temperature. For the fabrication of different thickness of MnO_2 overlayer on F-MWCNTs surface, spray pyrolysis deposition route with specially designed spray gun was used. The technique has distinct features to formulate nano interfaces with multilayer deposition.

In this work, we demonstrate the electrochemical reduction of hydrogen peroxide based on MnO_2 modified MWCNT electrode fabricated on refractory tantalum. The stimulus effect of MnO_2 thickness on the properties of F-MWCNTs /Ta was investigated. The surface modification of CNTs with MnO_2 particles was examined to study its electro catalytic sensing performance towards H_2O_2 in real samples.

2. Experimental section

2.1. Apparatus and reagents

High purity (90%) functionalized multi-walled carbon nanotubes (COOH-MWCNTs: average diameter × length: 9.5 nm × 1.5 μm) and tantalum (Ta) substrates (0.5 mm thick) were procured from Aldrich chemicals. The Ta surface was buffed and rinsed with acetone in addition to deionized water. NaOH, H_2O_2, pure milk and deionized water were used for electrochemical study.

2.2. Deposition of MWCNTs over Ta substrate

The MWCNT buffer layer of 200 nm optimum thickness was fabricated on Ta substrate by electron beam evaporation (EBE) technique. The electron beam evaporation unit (Model: AUTO 306) could be operated at a high vacuum of 10^{-7} mtorr. A 6 kW electron beam gun was used as an electron source. The Ta substrates fixed on a revolving circular disc ensure construction of film with constant thickness. The chamber remained evacuated to a maximum vacuum pressure of 10^{-6} mtorr to extend the mean free path and to fabricate CNTs with good quality. Quartz crystal monitor was used to adjust the thickness of the deposited film and the rate of deposition. The crucible filled with MWCNTs powders were exposed to electron beam with a power of 100 mA, until preferred thickness was achieved.

2.3. Fabrication of different MnO_2 Over layer thickness on CNT/Ta

For the fabrication of different thickness of MnO_2 overlayer on MWCNTs matrix, a novel spray deposition route was adopted. The pyrolysis process involved the disintegration of aqueous solution of high purity potassium permaganate ($KMnO_4$ (A.R. grade, Sigma Aldrich)) dissolved in different quantities of deionized water (50, 75, 100 ml) at 1.5 M concentration. The spray parameters such as flow rate, nozzle-substrate distance and deposition time were optimized throughout the fabrication to achieve quality films. The spray gun was designed specifically with two coaxial glass tubes, the precursor solution pass through the inner tube and the air stream through the outer. A mist of uniform spray droplets were produced by Ventury effect at both tube ends. The precursor solution sprayed over the CNT/Ta electrode at an elevated temperature gives rise to desertion of the solvent. The fine droplets undergoes continual nucleation and pyrolytic decomposition, which lead to the formation of identical and well adherent MnO_2 film over the MWCNT surface.

The thickness of the different layers were measured using surface profilometer (Model: Mitutoyo SJ 301). The thickness of MWCNT film on Ta was measured to be 200 nm. The MnO_2 overlayer thickness on MWCNT was varied as 80 nm, 120 nm and 160 nm. The fabricated MnO_2/F-MWCNTs/Ta films were further characterized for its structural and morphological properties. The structural analysis was made on X pert Pro X-ray diffractometer. The vibrational spectral analysis was made on RFT FT-Raman spectrophotometer. The SEM topography of the hybrid layers were examined using a high resolution scanning electron microscope. The elemental composition were studied using an EDS spectrometer.

2.4. Electrochemical studies of MnO_2/ F-MWCNT/Ta nano interface

Electrochemical analysis was performed on an electrochemical workstation (Model: Princeton-Versa STAT 4). The system consists of three-electrodes; a platinum wire as the auxiliary electrode, MnO_2 modified MWCNTs/Ta electrodes as working electrode and Ag/AgCl electrode as the reference electrode. Except the working face, all the other sides of the Ta substrate was concealed using epoxy resin to avoid its interaction with the electrolyte solution. The influence of MnO_2 thickness on the electrochemical sensing performance of MnO_2/F-MWCNT on Ta electrode towards various H_2O_2 molar concentrations was analysed in 0.1 M of Phosphate buffer solution (PBS) at a scan rate of 50mVs^{-1} under a high purity nitrogen atmosphere. The optimized MnO_2/F-MWCNT/Ta electrode was further analysed for H_2O_2 detection in milk sample.

3. Results and discussion

3.1. Effect of MnO_2 over layer on the crystallite size and phase of F-MWCNT thin films

Fig. 1 shows the typical XRD patterns of CNT films deposited on Ta buffer layer for different thickness of MnO_2 over layer. The well crystalline characteristics of the synthesized materials could be clearly evidenced from the preferentially orientated (002) plane of CNTs (JCPDS: 89–8487). The sharp highly intense peak at (110) plane can be associated with the pure body-centered tetragonal α-MnO_2 phase, with the lattice constants of a = 0.9785 nm, c = 0.2863 nm in the space group I4/m (JCPDS44-0141). In addition to this, the reflections of (110), (200) and (211) planes of Tantalum (JCPDS no. 80–1098) was recorded. Due to the buffer layer of functionalized MWCNTs, the (110) plane of MnO_2 was assumed to be perpendicular to the surface of the substrate. The intensity of (110) plane enhanced significantly when the MnO_2 over layer thickness was increased to 120 nm, which suggests that the crystalline quality of the films can be improved by the diffusion of Mn^{2+} ions into functional groups existing on the surface of CNTs. This implies that the energy contribution of Mn ions to F-MWCNTs was maximum at the thickness of 120 nm in contrast to those of the other MnO_2/CNT samples. However, the intensity of MnO_2 (110) plane decreased when the thickness of MnO_2 layer increased to 160 nm. This may be attributed to the presence of large number of unreacted Mn atoms on the surface of F-MWCNTs in 80 and 160 nm thick MnO_2 layer,