Talanta 80 (2010) 2016–2022

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

SiO_2 coated Fe_3O_4 magnetic nanoparticle dispersed multiwalled carbon nanotubes based amperometric glucose biosensor

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ARTICLE INFO

Article history:
Received 22 August 2009
Received in revised form 31 October 2009
Accepted 2 November 2009
Available online 10 November 2009

Keywords:
Amperometric
Vibrating sample magnetometer
Bioelectrode
CNTs
Biosensor

ABSTRACT

A new type of amperometric glucose biosensor based on silicon dioxide coated magnetic nanoparticle decorated multiwalled carbon nanotubes (Fe_3O_4@SiO_2/MWNTs) on a glassy carbon electrode (GCE) has been developed. MWNTs have been synthesized by catalytic chemical vapour decomposition (CCVD) of acetylene over rare earth (RE) based AB_3 alloy hydride catalyst. The as-grown MWNTs have been purified and further functionlized. Functionalized MWNTs have been decorated with magnetic Fe_3O_4 nanoparticles which have been uniformly coated with biocompatible SiO_2 using a simple chemical reduction method. The characterization of magnetic nanoparticle modified MWNTs have been done by X-ray diffraction (XRD), Fourier transform infra red spectroscopy (FT-IR), scanning electron microscope (SEM), transmission electron microscope (TEM), vibrating sample magnetometer (VSM), energy dispersive X-ray analysis (EDX) and UV–vis spectroscopy. Amperometric biosensor has been fabricated by the deposition of glucose oxidase (GOD) over Nafion-solubilized Fe_3O_4@SiO_2/MWNTs electrode. The resultant bioelectrode retains its biocatalytic activity and offers fast and sensitive glucose quantification. The performance of the biosensor has been studied using cyclic voltammetry and amperometry and the results have been discussed. The fabricated glucose biosensor exhibits a linear response from 1 μM to 30 mM with an excellent detection limit of 800 nM indicating the potential applications in food industries.

1. Introduction

Magnetic core–shell Fe_3O_4@SiO_2 nanoparticles as specially immobilizing carrier of biomolecules have aroused great interest in current researches. The inner iron oxide core with outer shell of silica not only stabilizes the nanoparticles in solution but also provides sites for surface modification with various biomedical ligands in biomedical applications. The coating of silica on the magnetic nanoparticles facilitated the dispersion of nanoparticles [1,2]. Due to their unique physical, chemical, and mechanical properties, superparamagnetic composite nanoparticles (NPs) hold much promise for biosensor applications [3–5]. Superparamagnetic iron oxide core of individual NPs becomes more efficient at dephasing the spins of surrounding water protons, enhancing spin–spin relaxation times (T_2 relaxation times) so that the NPs act as magnetic relaxation switches (MRS) [6]. Carbon nanotubes (CNTs) are one of the most studied nanomaterials for application in biosensor technologies, by immobilizing bioactive molecules on their surfaces through covalent or non-covalent bonds. The nanodimensions of CNTs guarantee a very large active surface area and are especially suited for the conception of miniaturized sensors. In addition to this, high porosity and reactivity makes them ideal candidates for the storage of neutral species as well as electron donors when used as electrodes in electrochemical reactions [7–9].

Compared with the corresponding CNTs-free biosensor, the CNTs-doped counterpart exhibited enhanced stability and sensitivity. Surface functionalization aids CNTs to become biocompatible, improving their solubility in physiological solutions and selective binding to biotargets. CNTs functionalization with biomolecules may occur by adsorption, but covalent tethering provides better stability, accessibility, selectivity and reduced leaching, and usually occurs by an amidation reaction [10]. CNTs are also used for dramatically amplifying enzyme-based bioaffinity electrical sensing of proteins and DNA [11]. Compared with single walled nanotubes (SWNTs), much cheaper multiwalled nanotubes (MWNTs) produced by chemical vapour deposition have more structural defects and thus provide more sites for biomolecule immobilization [8]. Non-covalently functionalized CNTs may also immobilize glucose and small molecules [12].

Nanocomposite materials may play an important role for improving functionalized electrodes envisaging commercial applications. Nanoparticles, especially metal nanoparticles, are an emerging issue in biosensor design, and they have been combined with CNTs to modify a glassy carbon electrode, thus improving the

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doi:10.1016/j.talanta.2009.11.010

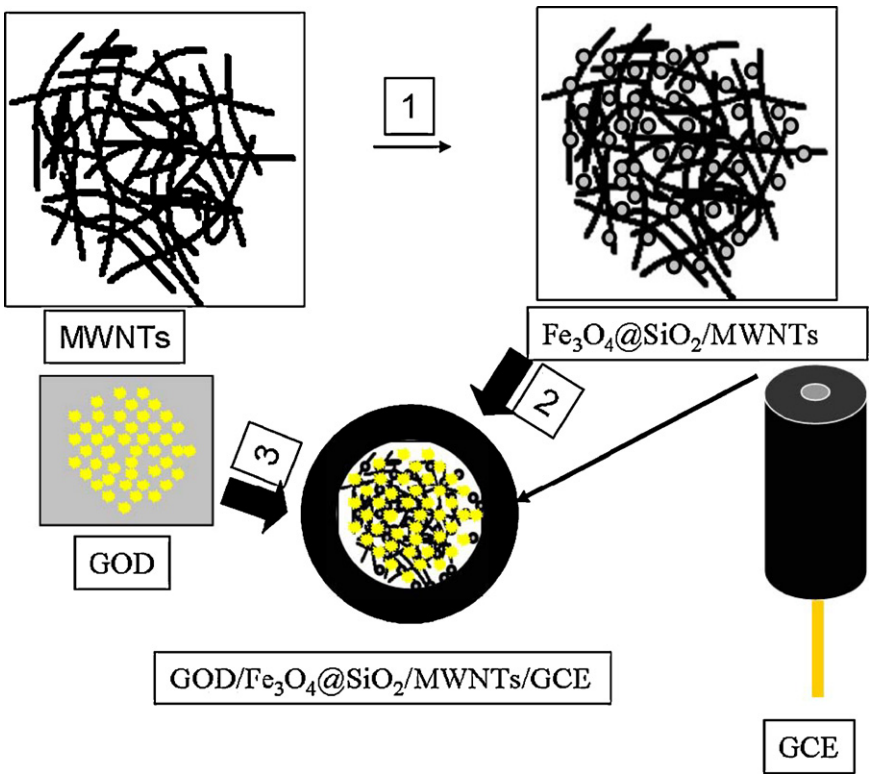

Fig. 1. Schematic of fabricated GOD/Fe_3O_4@SiO_2/MWNTs/GC electrode.

electroactivity and selectivity for glucose [13]. Metal nanoparticles have been applied as catalysts in numerous biosensor applications, due to their superior stability and complete recovery in biochemical redox processes. However, other groups showed that immobilization of the Au nanoparticles (or other metal nanoparticles) on the electrode surface would also cause similar catalytic effect on the electrochemical responses. Amperometric detection of glucose was developed using Au nanoparticles and CNT-multilayer membranes [14].

An electrochemical study with cyclic voltammetry and impedance analysis confirmed that glucose oxidase molecules suffer minimal structure changes after being immobilized on the surface of CNTs, retaining the ability to interact with small biomolecules (e.g., ethidium bromide) [7]. In this present study, MWNTs functionalized with nitric acid, in order to introduce carboxylic acid groups, have been used for the preparation of Fe_3O_4@SiO_2/MWNTs-based electrodes. Prior to immobilization, glucose oxidase (GOD) was physically adsorbed on these modified electrodes. Here, we show a good performance, fast response, nice stability and reproducibility, and a low detection limit of Fe_3O_4@SiO_2/MWNTs nanocomposite based on the reduction of H_2O_2 by immobilizing glucose oxidase on the composite.

2. Experimental

2.1. Materials

Glucose oxidase (GOD, from *Aspergillus niger*), tetraethoxysilane (TEOS) were purchased from Sigma. 0.1 M phosphate buffer solution (PBS, pH 7) prepared using potassium phosphate dibasic anhydrous and potassium dihydrogen orthophosphate. Ferric chloride ($FeCl_3{\cdot}6H_2O$), ferrous sulphate ($FeSO_4{\cdot}7H_2O$), ethanol and ammonium hydroxide (25%) were of analytical grade and deionised (dI) water was used throughout.

2.2. Sample preparation

Carbon nanotubes were synthesized by catalytic chemical vapour deposition over an alloy hydride catalyst. Rare earth based AB_3 alloy hydride was made by arc melting followed by several cycle of hydrogen absorption/desorption process. The catalyst was kept inside a furnace and acetylene (carbon precursor) was allowed at a temperature range 650–750 °C, in an inert atmosphere. Pyrolysis of acetylene was taken place at that temperature and MWNTs start growing. The as-grown MWNTs were purified before using for any applications. The amorphous carbon can be removed by heating the as-grown sample in oxygen atmosphere. Refluxing in concentric acids has been shown to be an

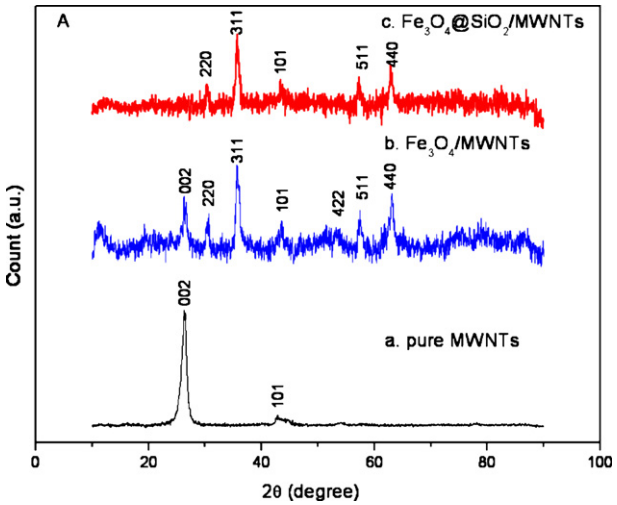

Fig. 2. X-ray diffractograms of (a) pure MWNTs, (b) Fe_3O_4/MWNTs and (c) Fe_3O_4@SiO_2/MWNTs.