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Chemically modified multiwall carbon nanotube composite electrodes: An assessment of fabrication strategies

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ABSTRACT

Chemically modified electrodes have been widely used to enhance electrochemical monitoring of analytes that are not easily detected using traditional base conductive materials. We have investigated different fabrication approaches to chemically modify multi-wall carbon nanotube (MWCNT) composite electrodes with Prussian blue (PB). Composite electrodes were made where Prussian blue was mixed with MWNCTs, where Prussian blue was coated on MWCNT composite electrodes and where MWCNTs were modified by generating PB on the surface of MWCNTs. Our findings indicate that MWCNT modified PB electrodes provided good sensitivity for the detection of glutathione and exceptional stability; whilst MWCNT coated PB electrodes provided excellent sensitivity but poor stability. Such findings provide important implications on the fabrication, suitability and use of chemically modified electrodes for electroanalysis.

1. Introduction

Chemically modified electrodes have been widely used as they offer the ability to tailor the physiochemical properties of the electrode in order to facilitate electrochemical reactions of analytes that may not display desirable properties with the base electrode material [1,2]. These chemically modified electrodes have displayed significant improvements over the base electrode including the ability to provide selectivity for the detection of specific analytes, prevent electrode fouling, improve the electrochemical/electrocatalytic properties and reduce the over-potential required for oxidation/reduction of a given species [2–4].

In previous studies, various different fabrication strategies for the chemical modification of electrode have been employed. These methods include adsorption of the chemical agent/s on the electrode surface as a film, direct bonding of the chemical agent/s on the electrode surface and or mixing the chemical agent/s within the conductive material to create a composite electrode [2]. The first two approaches are widely used for solid electrodes and electrodes. Many studies have examined the use of Prussian blue (PB) to modify electrodes, these have shown how the electrocatalytic behaviour of the PB on the surface of the electrode facilitates electron transfer and provided enhanced sensitivity [5–7]. These studies all show differences in the sensitivity, selectivity and stability of the fabricated electrodes when monitoring the same analyte. These differences can be attributed to variations in the fabrication methods utilised for the different electrodes [5,7–12].

Multi-wall carbon nanotubes (MWCNTs) have emerged as excellent electrochemical materials and have been widely used for sensor development [13]. One of the major issues with using nanotubes is the difficulty in incorporating this material within an electrode. Various approaches have been used including film coating of MWCNTs on solid electrodes, creating buckypaper or column and more commonly fabricating composite electrodes [14–16]. The latter type of fabrication has potential benefits as composite electrodes are known to offer enhanced electrochemical behaviour due to various electroactive sites on the surface, which provide improved mass transfer [17–19].

In this study we have examined various approaches of chemically modified electrodes using multi-wall carbon nanotubes as the base electrochemical material. Composite electrodes were fabricated as they offer the ideal spatial dimension for tissue measurements and PB was utilised as the chemical agent to modify the MWCNT composite material. To assess the various chemically modified electrodes, glutathione (GSH) was utilised. GSH has been shown to require a greater over-potential for oxidation on

Abbreviations: MWCNT, multiwall carbon nanotubes; PB, prussian blue; GSH, glutathione; SEM, scanning electron microscopy; EDX, Electron-dispersive X-ray spectroscopy; PBMix, PB mixed with MWCNT; PBMod, PB modified with MWCNT; PBCoat, PB coated on MWCNT electrode.

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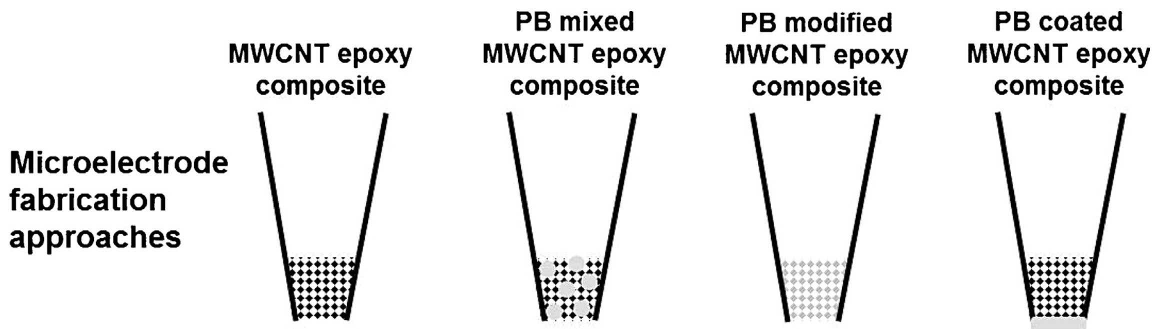

Fig. 1. Schematic diagrams of the various fabrication strategies utilised for formation of the chemically modified electrode.

conventional carbon based electrodes, and therefore many studies have been published utilising the catalytic activity of chemically modified electrodes to reduce the over-potential required for the oxidation of GSH and to facilitate monitoring of GSH [20–23]. Three different approaches of fabrication were compared for the detection of GSH. These involve a composite material made from a mix of PB powder with MWCNT, a composite material made from chemically forming PB in the presence of MWCNT and creating a film membrane of PB on a MWCNT composite electrode. Each of these approaches was compared to a control MWCNT composite electrode for their sensitivity and stability for the detection of glutathione.

2. Experimental

2.1. Materials

Potassium chloride, Prussian blue, potassium ferricyanide, iron (III) chloride, glutathione and hydrochloric acid (Sigma-Aldrich, USA), epoxy resin and hardener (Robnor Resins Ltd UK) were used as received. MWCNT-epoxy composites sensors were prepared from 30–50 nm diameter MWCNT with a length of 10–20 μm (CheapTubes, VT, USA).

2.2. Scanning Electron Microscope (SEM) and Electron-dispersive X-ray spectroscopy (EDX)

SEM was performed on a Carl Zeiss SMT Ltd SIGMA VP Field Emission Scanning Electron Microscope (FESEM) employing secondary electrons for the analysis. EDX was done with AZTEC software v2.2, created and provided by Oxford Instruments Analytical Limited. The energy dispersive (ED) analysis we carried out using back-scattered electrons on powder samples.

2.3. Preparation of prussian blue modified MWCNT

1.00 g of MWCNTs were dispersed in an aqueous solution of an equi-volume mixture of 0.1 M $FeCl_3$ and 0.1 M $K_3Fe(CN)_6$ in 10 mM HCl. This solution was then stirred for 30 minutes. The MWCNTs were filtered and washed with 10 mM HCl and distilled water in succession then allowed to dry. Final weight was approximately 1.40 g (28.5% PB).

2.4. Electrode fabrication approaches

Electrodes were made from are conductive MWCNTs, where epoxy resin was utilised as the non-conductive binder component

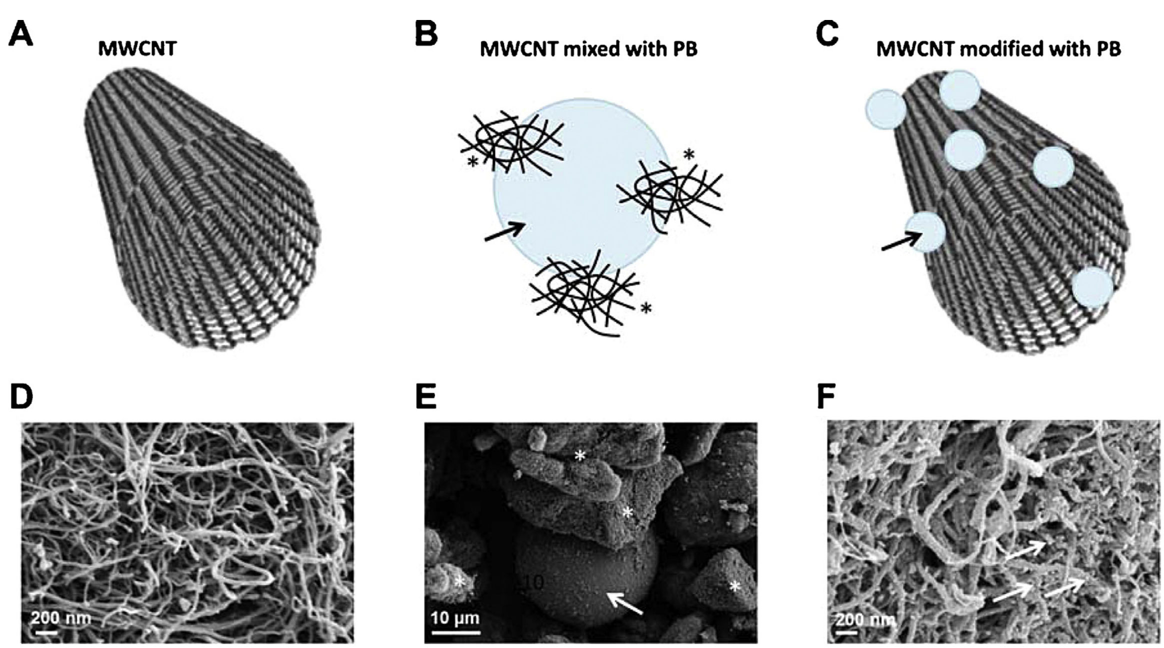

Fig. 2. Characterisation of multi-wall carbon nanotube (MWCNT) materials consisting of Prussian blue (PB). Schematic diagrams of the material are shown in A–C based on the SEM images obtained in D–F. Data is shown for the MWCNT material alone (A & D), a mixture of MWCNT with PB (B & E) and MWCNT modified with PB (C & F). The arrows indicate the presence of the PB particles/spheres on within the two materials and the star symbol indicates the large agglomerate bundles of MWCNTs.