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Utilization of highly purified single wall carbon nanotubes dispersed in polymer thin films for an improved performance of an electrochemical glucose sensor

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ABSTRACT

In this work we report the improved performance an electrochemical glucose sensor based on a glassy carbon electrode (GCE) that has been modified with highly purified single wall carbon nanotubes (SWCNTs) dispersed in polyethyleneimine (PEI), polyethylene glycol (PEG) and polypyrrole (PPy). The single wall carbon nanotubes were purified by both thermal and chemical oxidation to achieve maximum purity of ~98% with no damage to the tubes. The SWCNTs were then dispersed by sonication in three different organic polymers (1.0 mg/ml SWCNT in 1.0 mg/ml of organic polymer). The stable suspension was coated onto the GCE and electrochemical characterization was performed by Cyclic Voltammetry (CV) and Amperometry. The electroactive enzyme glucose oxidase (GOx) was immobilized on the surface of the GCE/(organic polymer–SWCNT) electrode. The amperometric detection of glucose was carried out at 0.7 V versus Ag/AgCl. The GCE/(SWCNT–PEI, PEG, PPY) gave a detection limit of 0.2633 μM, 0.434 μM, and 0.9617 μM, and sensitivities of 0.2411 ± 0.0033 μA mM^{-1}, $r^2 = 0.9984$, 0.08164 ± 0.001129 μA mM^{-1}, $r^2 = 0.9975$, 0.04189 ± 0.00087 μA mM^{-1}, and $r^2 = 0.9944$ respectively and a response time of less than 5 s. The use of purified SWCNTs has several advantages, including fast electron transfer rate and stability in the immobilized enzyme. The significant enhancement of the SWCNT modified electrode as a glucose sensor can be attributed to the superior conductivity and large surface area of the well dispersed purified SWCNTs.

1. Introduction

Carbon based nanoparticles have revolutionized the field of nanoelectronics and electrochemical sensors due to their excellent electronic properties [1–3]. Specifically, single wall carbon nanotubes (SWCNTs) have played a major role owing to their superior conductivity leading to faster electron transfer at the electrode surface, especially in biochemical reactions [4,5] while offering the advantage of increasing the surface area of the electrode. Another added advantage of using CNTs in electrochemical sensors is that it reduces the distance between the surface of the electrode and the active site of the enzyme thus increasing the sensor response [6,7]. Several factors hamper the electronic properties of SWCNTs such as, the presence of impurities, like amorphous carbon and residual metal catalysts, and the dispersibility in organic and inorganic solvents. SWCNTs have been purified by various techniques like treatments with harsh acidic environments, which not only shorten the tubes but also disrupt the electronic properties. As such, a selective purification step is very essential that does not disrupt the electronic properties. The dispersion issues can be excluded by functionalizing the CNTs [8–10]. Non-covalent functionalization has gained considerable attention through the successful modification of CNTs with polymer films that have been shown to restore the electronic properties and disperse the CNTs mainly by π-stacking [11]. Various approaches have been made to improve the sensitivity and limit of detection of electrochemical glucose sensors that are assayed based on voltammetric techniques [12]. Among these include dispersion and functionalization of CNTs in various polymers/solvents like Teflon [13], chitosan [14], nafion [15], bromoform [16], and mineral oil [17,18]. Another strategy is to use conducting polymers as a dispersant which offers a second advantage of immobilizing the redox enzyme [19].

Here we report the advantage of using a purification step that would not disrupt the electronic properties of SWCNTs and the purified SWCNTs

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were dispersed in three different organic polymers; polyethyleneimine (PEI), polyethylene glycol (PEG), polypyrrole (PPy) providing an excellent platform for immobilizing glucose oxidase (GOx). This approach does not require supplementary use of polyelectrolytes and any previous treatment of the glassy carbon electrode (GCE). The purified SWCNTs, due to their exquisite electrical properties, provide excellent signal amplification, eliminate fouling of the electrode and effectively immobilize GOx leading to a highly sensitive and robust glucose sensor.

2. Materials and methods

2.1. Reagents

Single wall carbon nanotubes, polyethyleneimine (MW 25,000), polyethylene glycol (MW 35,000), pyrrole (MW 67.09), 30% hydrogen peroxide, hydrochloric acid, potassium ferricyanide, potassium nitrate, and GOx derived from *Aspergillus niger* were purchased from Sigma-Aldrich (St. Louis, MO, USA). The polycarbonate membrane was purchased from Millipore (Billerica, MA, USA, 2013) (cat no ATTP04700). The glassy carbon electrode, platinum counter electrode and Ag/AgCl reference electrode were purchased from BAS Inc (West Lafayette, IN, USA). The β-D-glucose was purchased from Fisher scientific (300 Industry Drive, Pittsburg, PA) (MW 180.16). The 0.1 M phosphate buffer was purchased from Bio-rad (1000 Alfred Nobel Drive, Hercules, CA) All other chemicals were prepared/diluted in de-ionized (DI) water (ρ = 18 MΩ).

2.2. Purification of SWCNTs

The raw SWCNTs (~49% pure) were purified in a 2 step process. Briefly, the 100 mg raw SWCNT was heated in air in a furnace at 470 °C for 90 min. This oxidation step removed most of the amorphous carbon. The temperature chosen was due to the oxidation temperature of the amorphous carbon being 450 °C. The heat treated SWCNTs were then dispersed in a 40 ml mixture of 30% H_2O_2 and 8 N HCl in a 1:1 ratio. The solution was sonicated in a water bath for 6 h at 40 °C. After the end of every hour, 20 ml of the mixture (1:1) was added to the original solution replenishing the reactants. At the end of 6 h, the solution that contained SWCNTs was added to 500 ml of ice cold water, gently, and then filtered using a 0.08 μM polycarbonate membrane. This filtration was done several times until the pH of the filtrate was nearly 7. The purified SWCNTs were then dried in oven at 120 °C to remove the residual solvent.

2.3. Characterization of SWCNTs

The raw and purified SWCNTs were characterized by Field Emission Scanning Electron Microscopy (FESEM, Hitachi S4700) and Thermogravimetric analysis (TGA, Perkin Elmer TGA6). Briefly, the raw and purified SWCNTs (0.1 mg/ml) were dispersed in ethanol and sonicated for 30 min. 50 μL was dropped onto the stub for FESEM analysis. For TGA analysis, 10 mg of SWCNTs was oxidized in a ceramic sample holder from room temperature to 1000 °C at the rate of 5 °C per min.

2.3.1. Preparation of GCE/(SWCNT/PEI)

The GCE was polished with alumina slurries of 0.30 and 0.05 μm for 3 min each and sonicated in ethanol for 5 min. The purified SWCNTs (1.0 mg/ml) were dispersed in PEI (1.0 mg/ml, prepared in 50:50 v/v ethanol/water) followed by sonication for 30 min. The dispersed SWCNTs (40 μL) was pipetted onto the surface of the polished GCE and allowed to dry for 90 min at room temperature.

2.3.2. Preparation of GCE/(SWCNT/PEG)

The GCE was polished in the same way as mentioned earlier. The purified SWCNTs (1.0 mg/ml) were dispersed in PEG (1.0 mg/ml, prepared in 50:50 v/v ethanol/water) followed by sonication for 30 min. The dispersed SWCNTs (40 μL) were pipetted onto the surface of the polished GCE and allowed to dry for 90 min at room temperature.

2.3.3. Preparation of GCE/(SWCNT/PPy)

The GCE was polished in the same way as mentioned earlier. The purified SWCNTs (1.0 mg/ml) were dispersed in pyrrole (0.1 M in

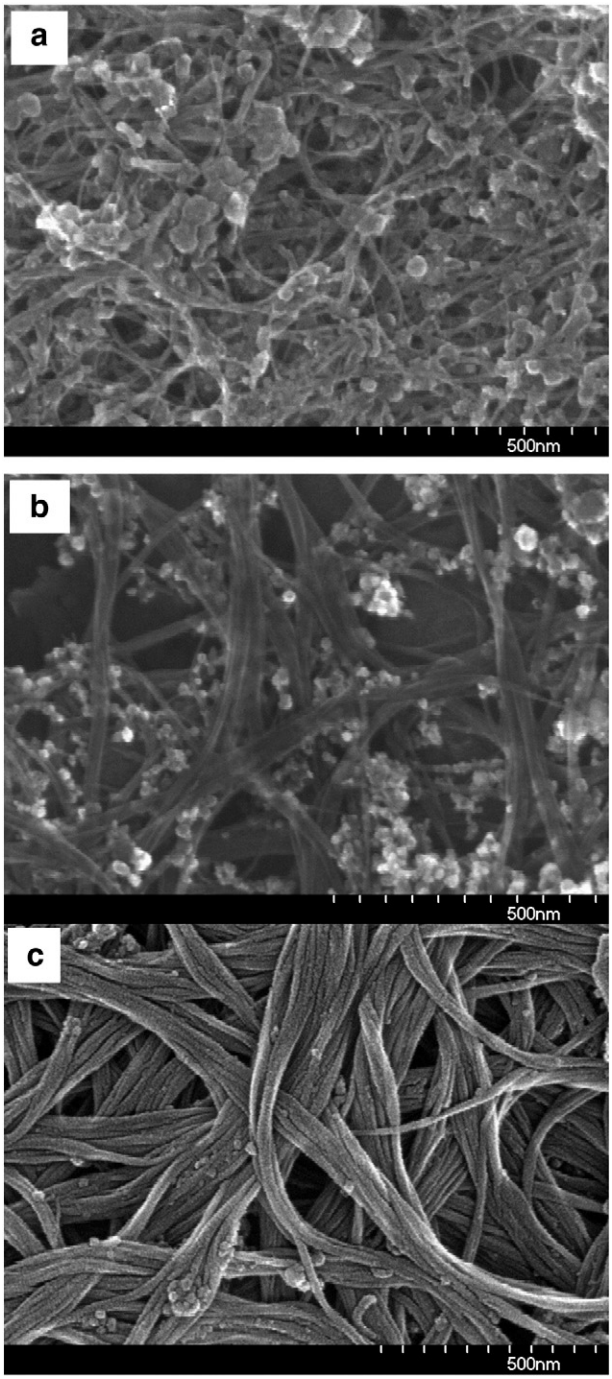

Fig. 1. FESEM image of the raw SWCNT (a), heat treated SWCNT (b) and purified SWCNT (c).