Electrochimica Acta 55 (2010) 2186–2190

Contents lists available at ScienceDirect

Electrochimica Acta

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

Redox polymer covalently modified multiwalled carbon nanotube based sensors for sensitive acetaminophen and ascorbic acid detection

Nathaniel Havens[a], Phong Trihn[a], Daniel Kim[b], Manelich Luna[b], Adam K. Wanekaya[b], Amos Mugweru[a,*]

[a] Department of Chemistry and Biochemistry, Rowan University, Glassboro, NJ 08028, USA
[b] Chemistry Department, Missouri State University, Springfield, MO 65897, USA

ARTICLE INFO

Article history:
Received 25 August 2009
Received in revised form
13 November 2009
Accepted 16 November 2009
Available online 24 November 2009

Keywords:
Redox polymer
PEG-DA gel
Electrochemical catalysis
Photopolymerization

ABSTRACT

A sensitive electrochemical detection method was developed involving multiwalled carbon nanotubes (MWCNTs) covalently modified with osmium-based redox polymer. The polycationic redox polymer, poly[4-vinylpyridine Os(bipyridine)$_2$Cl]-co-ethylamine (POs-EA), was first synthesized and covalently attached to MWCNTs. The redox polymer modified MWCNTs were then trapped in a hydrogel formed from polyethyleneglycol diacrylate (PEG-DA) using 1-phenyl-2-hydroxy-2-methyl-1-propanone as a photoinitiator. Upon exposure to aqueous media, the gel swelled to allow movement of analytes in and out of the gel without having any effect on the redox polymer modified nanotube signal. Cyclic voltammetry showed reversible pairs of oxidation–reduction peaks at 0.35 V (*vs* Ag/AgCl) corresponding to the Os^{II}/Os^{III}. This assembly was able to catalytically oxidize both acetaminophen and ascorbic acid (AA). Amperometric data showed a linearity between 0 and 100 μM (R^2 of 0.999, n = 10) 0.5 mV *vs* Ag/AgCl (sensitivity 0.003 μA/μM) for ascorbic acid, while for acetaminophen the linearity was between 0 and 1.5 μM (R^2 of 0.9999, n = 8) with a sensitivity of 65 μA/μM. This sensing system was found to exhibit remarkable stability over several weeks with excellent reproducibility.

1. Introduction

Carbon nanotubes (CNTs) are promising inorganic platforms with high surface area, ideal for immobilization of different electron transfer mediators. They are also used as electrode materials in electrochemical reactions to promote electron transfer reactions, a new and unique application [1]. The applications of carbon nanotubes for fabrication of electrochemical sensors are increasingly being explored for detection of various analytes [2–10]. Some of the advantages of using CNTs include rigid structures, insolubility in organic solvents, and large surface area. For sensor fabrication, the sidewalls of CNTs can be functionalized through covalent bonding or noncovalent modification methods without changing the mechanical and electronic properties of the inner nanotube [11].

Hybrid materials consisting of conductive polymers and carbon nanotubes have been observed to induce a synergic effect of the resulting hybrid material, attributed to the fact that the conducting polymer can immobilize and connect CNTs, while the CNTs can interact with the polymer to form aggregates that are able to reduce the ion intercalation distance [12,13]. This facilitates charge transfer and increases the conductivity of the composite polymeric film. To immobilize CNTs, they are first oxidized to introduce carboxylic groups that can be used to covalently bond other molecules [14]. The CNTs can also be functionalized with amino groups to allow further covalent bonding to different molecules [15].

Acetaminophen is widely used as an analgesic antipyretic drug with action similar to aspirin. It is a suitable alternative for patients who are sensitive to aspirin and is safe up to therapeutic doses. The large scale therapeutic use of that drug has generated the need for the development of rapid and reliable methods for the determination of acetaminophen. Electrochemical methods involving composite electrodes have been used for biosensors for acetaminophen detection [16–18].

Most electrochemical studies of acetaminophen and ascorbic acid have been developed with conventional glassy carbon or carbon paste electrodes that suffer from fouling and hence require periodic polishing or activation processes. Other work in the literature has involved noncovalent bonding of nanotubes with polymers including poly(aminoquinone) [19], poly(vinylimidazole) complexed with Os(4,4′-dimethylbpy)$_2$Cl [20], polypyrrole [21,22], and poly(ethylene glycol) [23] to make the nanotubes biocompatible. Recently, we used biocompatible PEG-DA hydrogel networks to physically trap both the redox polymer and glucose oxidase on polyimide sheets for glucose sensor applications [24,25]. The osmium-based redox polymer replaced oxygen as

---

* Corresponding author at: Department of Chemistry and Biochemistry, Rowan University, 201 Mullica Hill Rd, Glassboro, NJ 08028, USA. Fax: +1 856 256 4478.
E-mail address: mugweru@rowan.edu (A. Mugweru).

0013-4686/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2009.11.054

a non-physiological electron acceptor in the reaction. In this work, we fabricated sensors using hybrid materials incorporating osmium-based polymers covalently attached to MWCNT. The MWCNT, covalently functionalized with a redox polymer, was later physically trapped in a polyethylene glycol hydrogel and tested for stability. These redox polymer modified MWCNTs were found to catalyze oxidation of acetaminophen and ascorbic acid. These materials were found to exhibit remarkable stability over several weeks. The sensitivity obtained for both acetaminophen and ascorbic acid enhanced the sensing sensitivities to the micromolar range.

2. Experimental

2.1. Material and reagents

Multiwalled carbon nanotubes (MWCNTs, 20–30 nm outer diameter), N-hydroxysuccinimide (NHS), hexafluorophosphate, sodium dithionite, ether, *N,N*-dimethylformamide, anion exchange beads, hydrochloric acid, ethyl alcohol, ethylene glycol, acetonitrile and hydrogen peroxide were purchased from VWR (West Chester, PA). Glassy carbon electrodes of diameter (area 0.07 cm^2), polishing alumina and 1 μm diamond polish were obtained from Bioanalytical Systems Inc. (West Lafayette, IN). Supplies of 1-ethyl-3-(3-diemthylaminopropyl) carbodiimide hydrochloride (EDC, 98+%), poly(4-vinyl) pyridine and poly(ethylene glycol) diacrylate (MW 575) were purchased from Sigma–Aldrich (St Louis, MO) while N-hydroxysuccinimide (NHS), hexafluorophosphate, sodium dithionite, ether, *N,N*-dimethylformamide, anion exchange beads and hydrochloric acid were purchased from VWR. Ammonium hexachloroosmate(IV) and 2-bromoethylamine hydrobromide were purchased from Alfa Aesar, while poly(4-vinyl) pyridine was purchased from Aldrich.

The polycationic redox polymer, poly[4-vinylpyridine Os(bipyridine)$_2$Cl]-co-ethylamine (noted as POs-EA), was synthesized according to a procedure described previously [26]. DAROCUR 1173 (1-phenyl-2-hydroxy-2-methyl-1-propanone, the photoinitiator) was obtained from Ciba Specialty Chemical (Tarrytown, NY). Phosphate buffered saline (PBS) consisted of 1.1 mM potassium phosphate monobasic, 3 mM sodium phosphate dibasic heptahydrate, and 50 mM sodium chloride.

Fourier transform infrared (FTIR) spectroscopy was performed on an FTS 7000 from Thermo Corporation. The spectrometer was equipped with a DTGS KBr detector in the region 400–4000 cm^{-1}. Twenty scans (4 cm^{-1} resolution) were obtained and then averaged. Scanning electron microscope images were recorded with a JEOL Scanning Electron Microscope.

2.2. Carboxylation of MWCNTs

The MWCNTs were first carboxylated by sonicating 0.7 g of the material in a 150 mL mixture of concentrated HNO_3 and H_2SO_4 (3:1, v/v) for 4 h. Afterward, the mixture was carefully added to 250 mL of de-ionized water and the reaction was allowed to cool to room temperature. The suspension was filtered through a 0.25 μm pore-size membrane filter and washed with 0.05 M NaOH followed by washing with de-ionized water to pH 7.0, then dried at 110 °C. The resulting carbon nanotubes are referred to as MWNT-COOH.

2.3. Functionalization of MWNT-COOH

For this purpose, 0.5 g of MWCNT-COOH was suspended in a solution containing 0.1 M 1-ethyl-3-(3-diemthylaminopropyl) carbodiimide hydrochloride (EDC) and 0.1 M of N-hydroxysuccinimide (NHS) in 0.1 M acetate buffer (pH 5.5) for 1 h with constant agitation. The nanotubes were centrifuged at 13,000 rpm (Sorvall Rc 5b plus, Asheville, NC), and the solution phase was discarded. The nanotubes were then mixed with 2.0 mg/mL of POs-EA in 50.0 mM phosphate buffer at pH 7.4 and incubated for 1 h. Once again, the nanotubes were centrifuged at 13,000 rpm, and the solution phase was discarded. The nanotubes were washed with de-ionized water and centrifuged several times, each time discarding the supernatant solution. The modified nanotubes, labeled as MWCNT-CO-POs-EA, were dried in ambient atmosphere and stored in the refrigerator. Fig. 1 shows a pictorial representation of the modified nanotubes.

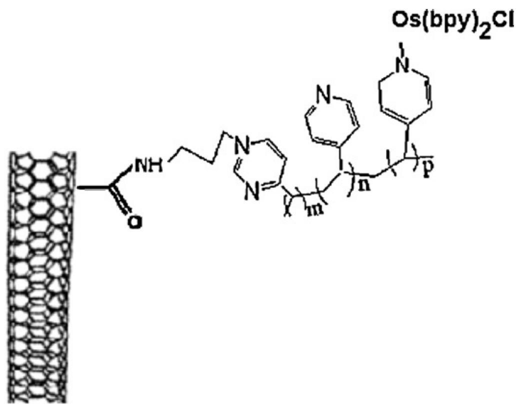

Fig. 1. Pictorial representation of carbon nanotube covalently modified with POs-EA.

2.4. Voltammetry

Cyclic voltammetry (CV) was carried out with a computer-controlled electrochemical workstation (CHI 660c, USA) with ohmic drop 98% compensated. A three electrode cell was employed with an Ag/AgCl electrode as a reference electrode, glassy carbon (GC) as working electrode and Pt wire as counter electrode, all from Bioanalytical Systems Inc. All phosphate buffers were purged with pure nitrogen for 20 min to remove oxygen and blanketed with nitrogen before making measurements. Glassy carbon electrodes (0.07 cm^2) were polished with 1 μm diamond polishing paste, then ultrasonicated in ethanol and distilled water successively for 1 min followed by rinsing in water.

2.5. Encapsulation of MWCNT-CO-POs-EA in polyethylene glycol

The formation of hydrogel from PEG-DA resulted from the free-radical polymerization of the acrylate end groups attached to the PEG derivatives. The photoinitiator dissociates when exposed to UV radiation and creates highly reactive methyl radicals that attack the unsaturated carbon–carbon double bonds of the acrylate groups to initiate free-radical polymerization. In this work, a precursor solution containing 9.5 μL of PEG-DA, 5 μL of modified MWCNT-CO-POs-EA (2 mg/mL in phosphate buffer), and 0.5 μL DAROCUR was made. The precursor solution was deposited on a clean glassy electrode and then exposed to UV light at 366 nm, 300 mW/cm^2, UV light source (UVP Inc., San Gabriel, CA) for 0.5–3.0 s.

3. Results and discussions

Previously, it has been reported that modified MWCNT can show the ability to depress the catalytic oxidation of ascorbic acid as well as other analytes [27]. In this work, MWCNT were first oxidized with nitric acid to introduce carboxylic acid functional groups. Characterization of the MWCNT with carboxylic groups was carried out using previously described procedures [10]. POs-EA synthesized in our lab was covalently attached to carboxylic acid functionalized MWCNT carbon using diimide chemistry. POs-EA