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ScienceDirect
Electrochemistry Communications 9 (2007) 2330–2333
electrochemistry communications
www.elsevier.com/locate/elecom

Single walled carbon nanotubes contain residual iron oxide impurities which can dominate their electrochemical activity

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Received 25 April 2007; received in revised form 14 June 2007; accepted 15 June 2007
Available online 30 June 2007

Abstract

We demonstrate with the electrochemical oxidation of hydrazine and the electrochemical reduction of hydrogen peroxide that residual iron impurities, likely in the form of Fe_3O_4, can dominate the electrochemical response of single-walled carbon nanotubes.
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Keywords: Single-walled carbon nanotubes; Electrochemistry; Hydrazine oxidation; Electro-catalysis; Hydrogen peroxide reduction

1. Introduction

Carbon nanotube modified electrodes continue to receive significant attention in electrochemistry because of their enhanced sensing properties [1–7]. This is in part due to the reported significant reductions in overpotentials, large surface area, increments in the magnitude of voltammetric signals and little or no observed surface fouling [8]. Additionally, carbon nanotubes facilitate electrochemistry in domains where no other electrodes can penetrate. For example, Gooding et al. has demonstrated that single walled carbon nanotubes can perform electrochemistry inside proteins [9]. This fact suggests that carbon nanotubes can be utilized for the direct mediator-free probing and sensing of bio- and redox-active compounds, especially enzymes.

Carbon nanotubes occur in two principal types: single-walled carbon nanotubes (SWCNTs) which consist of a single tube of graphite, and multi-walled carbon nanotubes (MWCNTs) which consist of several concentric tubes of graphite fitted one inside the other. The lengths of the tubes are usually in the micrometer range while the diameters of carbon nanotubes can range from just a few nanometres in the case of SWCNTs to several tens of nanometres for MWCNTs. The unique structure of carbon nanotubes means that they have high accessible surface area, low electrical resistance and high chemical stability suggesting them to be suitable electrode materials and utilised in other associated applications such as catalyst supports in fuel cell applications.

It is well established that the electrochemical activity of multi-walled carbon nanotubes is either due to edge plane like – sites/defects [10–14] or metallic impurities [15,16] depending on the electrochemical system. Capitalising on the premise that metallic impurities can dominate the response of carbon nanotubes, it has recently been shown that the electroanalytical sensing of halothane is possible [17], although the electroanalytical response was found to be approximately reproducible using a single batch of nanotubes, the variation from batch to batch was not addressed which could likely hamper realisation as a sensor for halothane. More recently Pumera [18] has revisited the problem of metallic impurities in multi-walled carbon nanotubes and concluded that the metal nanoparticles are ‘sheathed’ by graphene sheets [18].

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1388-2481/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.elecom.2007.06.024

Particularly in the area of electroanalysis, researchers have been fast to misplace claims of electro-catalysis on carbon nanotubes. Without characterisation of carbon nanotubes a fundamental understanding of the origin of the electrochemical activity cannot be attained. While the electrochemical responses of MWCNTs have been extensively explored, SWCNTs have not. The only real fundamental exploration of SWCNTs has come from the Gooding group [19], who have demonstrated the importance of oxygenated ends of SWCNTs. We have recently shown, via TEM and XPS that SWCNTs contain iron oxide, which even after acid washing is not removed. [20] However, the electrochemical response, in terms of the origin of the electrochemical activity has, to best of our knowledge, not yet been explored.

In this communication we demonstrate that SWCNTs contain significant amounts of iron, likely in the form of Fe_3O_4 which dominates the electrochemical response in respect of the electrochemical oxidation of hydrazine and the electrochemical reduction of hydrogen peroxide.

2. Experimental section

All chemicals used were of analytical grade and were used as received without any further purification. These were: hydrazine sulfate (99+% A.C.S Reagent, Aldrich) and hydrogen peroxide (50 wt.% in water, Aldrich), $Na_2HPO_4\ 7H_2O$ and KH_2PO_4 (both 99+%, A.C.S. Regent, Aldrich). All solutions were prepared with deionised water of resistivity not less than 18.2 MΩcm.

Voltammetric measurements were carried out using a μ-Autolab II (ECO-Chemie, The Netherlands) potentiostat. All measurements were conducted using a three electrode configuration. Basal plane pyrolytic graphite (BPPG) electrodes and edge plane pyrolytic (EPPG) graphite electrodes were fabricated by cutting discs of pyrolytic graphite into a 4.9 mm diameter, with the disc face parallel with the edge plane, or basal plane as required. The counter electrode was a bright platinum wire with a large surface area, with a saturated calomel electrode completing the circuit.

The BPPG electrode was prepared by first polishing the BPPG electrode surface on carborundum paper and then pressing cellotape on the cleaned BBPG surface before removing along with general attached graphite layers. The electrode was then cleaned in acetone to remove any adhesive.

The single-walled carbon nanotubes (SWCNTs) were received from Carbon Nanotechnologies Inc. (USA). These are classed as "Purified HiPCo® single-wall carbon nanotubes" which are of research grade and have been purified to remove large catalyst particles (<15 wt.% ash content) [21]. Researchers should note that the single-walled carbon nanotubes come with a disclaimer of warranties and are sold "as is" and "that there may be variations in the characteristics of Products, and CNI expressly disclaims any warranties related to any samples that CNI may from time to time provide to Purchaser" [21].

The SWCNTs were cast onto a freshly prepared BPPG. This involves first dispersing 5.8 mg of MWCNTs into 2 mL ethanol. The suspension is then placed into an ultrasonic bath for 2 min before 20 μL is pippetted onto the BPPG surface. This is allowed to volatize at room temperature producing a random distribution of carbon nanotubes on the BPPG surface.

XPS was performed in an ion pumped UHV chamber equipped with a VG nine channel CLAM4 electron energy analyser (base pressure 5×10^{-10} torr) 250 W Mg X-ray (1253.6 eV) excitation was used. The analyser was operated at constant pass energy of 100 eV for the wide scans and 20 eV for the detailed scans. Data was obtained using VGX900-W operating system. Peak areas were measured after background subtraction following methods of Shirley [22].

TEM micrographs have been taken on a JEOL 2010 instrument, which is equipped with an Oxford Instruments LZ5 windowless energy dispersive X-ray spectrometer for EDS.

3. Results and discussion

Fig. 1 displays the voltammetric response corresponding to the electrochemical oxidation of 4.8 mM hydrazine in pH 7.0 phosphate buffer solution at a SWCNT modified BPPG electrode. A clear electrochemical oxidation wave occurs at ca. +0.49 V (vs. Ag/AgCl in 3 M KCl aq.) at the SWCNT modified BPPG electrode. Comparison of this SWCNT modified BPPG electrode with that of a bare BPPG and EPPG electrode are also shown in Fig. 1, where at the BPPG and EPPG there are no electrochemical oxidation wave observed in the accessible potential window. The direct comparison of the nanotube modified electrode's response with an EPPG electrode allows one to deduce whether or not edge plane like-sites/defects are the origin of the electrochemical response [10–13]. As shown in Fig. 1, no oxidation waves corresponding to the electrochemical oxidation of hydrazine are observed using the BPPG and EPPG electrodes in the accessible potential window; clearly the origin of electro-activity of the SWCNTs are not due to edge plane like – sites/defects.

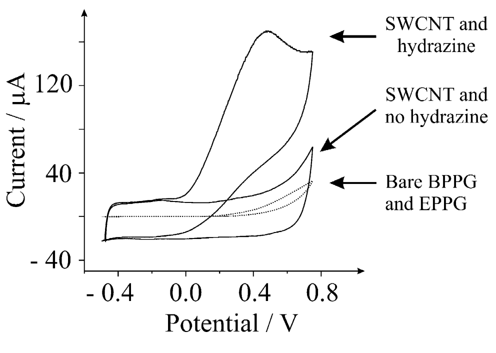

Fig. 1. Cyclic voltammograms recorded in 4.8 mM hydrazine in pH 7.0 phosphate buffer. Scan rate: 10 mV/s.

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