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Electrochemical impedance spectroscopy at single-walled carbon nanotube network ultramicroelectrodes

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ABSTRACT

Electrochemical impedance spectroscopy (EIS), coupled with chemical vapour deposition (CVD) grown single-walled carbon nanotube (SWNT) network disk-shaped ultramicroelectrodes (UMEs), gives stable, very well-defined and highly reproducible EIS responses for electrolysis of a simple outer sphere redox couple ($FcTMA^{+/2+}$). The resulting EIS data can be fitted accurately using a simple electrical circuit model, enabling information on double-layer capacitance, diffusion coefficient of the electroactive species and the rate constant of ET (k^0) to be extracted in a single EIS experiment. These values are replicated for a range of mediator concentrations and UME sizes (in the range 25–100 μm diameter) demonstrating the robustness of the method. These initial studies bode well for impedance based electroanalysis using SWNT network UMEs.

1. Introduction

Two-dimensional (2D), planar and electrically connected, single-walled carbon nanotube (SWNT) networks, grown using chemical vapour deposition (CVD) on an inert substrate, are emerging as powerful electrode materials for many applications [1,2]. The advantages of CVD grown 2D SWNT networks are multi-fold: the SWNTs do not require further purification; metal catalyst content is limited typically to one nanoparticle per SWNT, located at the end of the SWNT; the substrate is insulating and thus the electrochemical response is due to the SWNTs only, providing impressive signal to background ratios; and the SWNT network format is well-defined, of high uniformity and known surface coverage [3].

It has been shown that disk-shaped ultramicroelectrodes (UMEs) fabricated from SWNT networks of low surface coverage (<1%) offer superior characteristics over conventional metal UMEs of the same size and dimensions [1]. SWNT disk UMEs yield a voltammetric response governed by the area of the support, rather than the area of the SWNTs themselves, due to overlap of neighboring diffusion fields, on typical voltammetric timescales [1]. The low intrinsic capacitance of the cCVD grown SWNTs [4] and much reduced surface area lead to much faster response times and unprecedented low background currents compared to conventional solid metal UMEs [1,2] enabling trace level cyclic voltammetric (CV) detection.

Electrochemical impedance spectroscopy (EIS) is a powerful technique for studying interfacial charge-transfer [5]. The entire electrochemical response, including the rate constant of the electrochemical reaction, double-layer capacitance as well as the diffusion coefficient of the redox species in solution may be measured simultaneously in one experiment [6]. In recent work, EIS has been used as a technique complementing CV for the characterisation of the electrocatalytic activity of modified carbon nanotube electrodes on conducting supports [7–11]. However, studies have been limited to qualitative interpretation of EIS spectra to assess electron transfer (ET) behaviour at these electrodes [7–12].

By combining EIS with the SWNT network UMEs it should be possible to quantitatively characterise both Faradaic and non-Faradaic processes. Using SWNT disk UMEs of different sizes and different mediator concentrations, we show that parameters such as double-layer capacitance, standard rate constant of ET (k^0) and diffusion coefficient of the redox species can be readily calculated.

2. Experimental

2.1. SWNT growth and UME fabrication

SWNT networks of <1% surface coverage and density ~3 μm μm^{-2}, were grown directly onto Si/SiO_2 substrates by CVD, using a procedure described in detail elsewhere [3]. SWNT disk-shaped UMEs were fabricated from these networks using a lithographic procedure described in [1]. Briefly, a gold contact is evaporated onto the SWNT network and the surface insulated with photoresist. A disk of the desired diameter is defined using photo-

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lithography, exposing SWNT networks to the solution containing the redox species. A field emission-scanning electron microscopy (FE-SEM) image of a SWNT disk UME is given in Fig. 1a. Due to charging, the lateral dimensions of the SWNTs in the FE-SEM images will always appear significantly larger than they actually are, resulting in a false impression for the fractional surface coverage, *f*. For an accurate characterisation of SWNT height and *f*, atomic force microscopy (AFM) must be used, as shown in Fig. 1a. Micro-Raman spectra of SWNT networks on insulating Si/SiO_2 surfaces were recorded using a Renishaw in Via Raman Microscope with incorporated Leica microscope. A 514.5 cm^{-1} (2.41 eV) excitation wavelength of an Ar laser, at 10 mW power, focused in a ~2.5 μm diameter spot was used. Fig. 1b shows a typical Raman spectrum. Peaks marked with * belong to the Si substrate. The shape of the G-band (1500–1700 cm^{-1}) and the presence of the radial breathing mode (RBM) (100–200 cm^{-1}) positively identifies the sample to contain SWNTs, in agreement with the AFM data and our previous work [1,3].

2.2. Solutions

Aqueous solutions were prepared using Milli-Q reagent water (Millipore Corp.). Solutions for CV and EIS consisted of (ferrocenylmethyl) trimethylammonium, $FcTMA^+$, hexafluorophosphate in 0.1 M NaCl (99 + %, Sigma–Aldrich). $FcTMA^+$ hexafluorophosphate was prepared via the metathesis of the corresponding iodide salt (99%, Strem) with ammonium hexafluorophosphate (99.5%, Strem).

2.3. CV and EIS measurements

A two electrode droplet cell set-up was employed [1]. A chlorinated silver wire, Ag/AgCl was used as a reference electrode (RE). Measurements were carried out with a Gamry Reference 600 workstation (Gamry, USA) equipped with a PCI4/300 potentiostat in conjunction with EIS 300 software. EIS data were measured at frequencies in the range 100 kHz–1 Hz, at 5 mV wave amplitude and at the formal potential of the redox couple. Experimental data of the impedance plot were analyzed by applying the non-linear least squares fitting to the appropriate theoretical model (*vide infra*) represented by an equivalent electrical circuit.

3. Results and discussion

The analysis of the diffusion process to a disk UME subjected to an AC flux perturbation has been described theoretically by Baranski [5], who proposed an equivalent circuit to analyze experimental results. A similar circuit, represented in Fig. 1c, has been used to fit EIS data at the SWNT UMEs, with the only modification being the addition of a contact resistance, R_c, to describe the resistance between the gold contact and the SWNT network [5]. R_{ct} is the charge-transfer resistance; R_u is the uncompensated resistance and is the sum of the resistance of the electrolyte solution and that of the SWNT network, the latter which dominates [3]; C_s is the stray capacitance which develops between wires connecting the working electrode to a current transducer and between these wires and the solution and C_{dl} is the double-layer capacitance. For capacitance, absolute values are quoted herein (Farads, F) rather than F per unit area given that for 1D SWNTs, normalizing by electrode area is not appropriate.

The diffusional impedance to the UME is represented by a parallel combination of Warburg impedance, Z_W, and R_{nl}, a resistance related to non-linear (hemispherical) diffusion. At high frequencies, diffusion is linear and semi-infinite, corresponding to Z_W, whereas at low frequencies, diffusion becomes hemispherical (in contrast to that at a macroelectrode) and is described by R_{nl}.

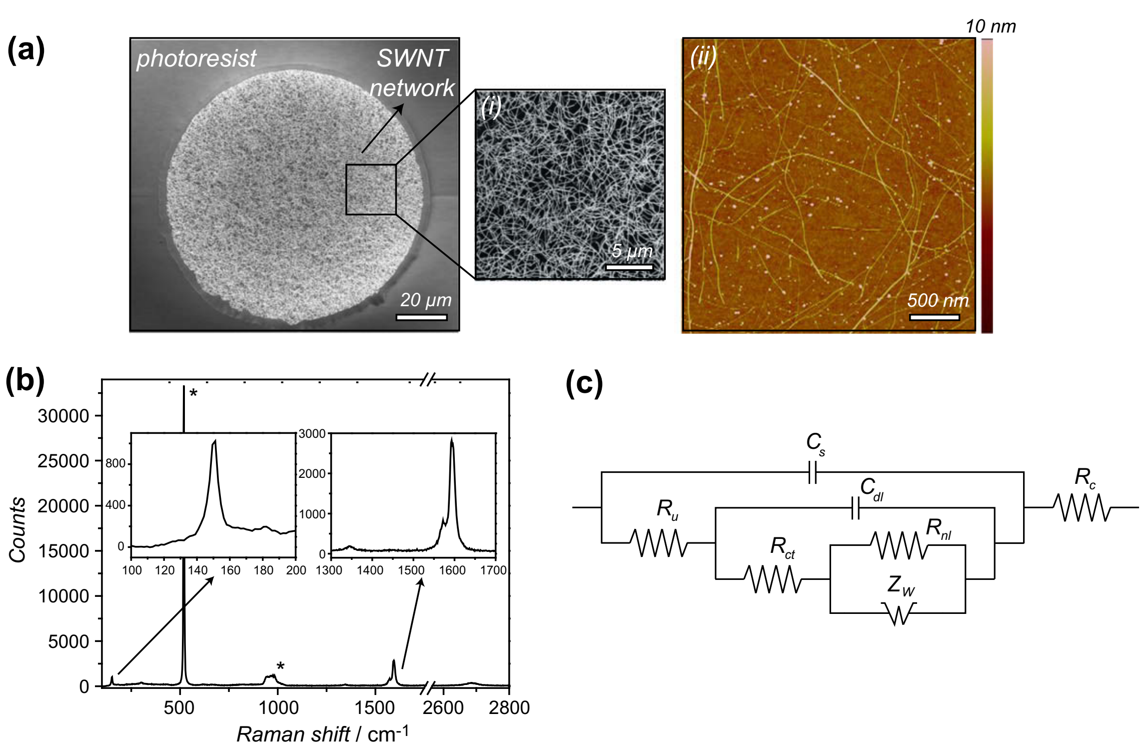

Fig. 1. (a) FE-SEM image of a 100 μm diameter SWNT network UME. High-resolution (i) FE-SEM image and (ii) topographic height AFM image of the SWNT network (on insulating SiO_2) of <1% surface coverage. Due to charging effects in the FE-SEM image, only AFM can be used to determine the true SWNT dimensions. (b) Typical Raman spectrum of a SWNT network on a Si/SiO_2 substrate; peaks marked with * belong to the substrate. The spectrum was taken using a 514.5 nm excitation wavelength focused in a ~2.5 μm spot. Insets represent magnified regions of the spectrum: the RBM, in the 100–200 cm^{-1} region and the G-band in the 1500–1700 cm^{-1} region, both positive identifiers of the presence of SWNTs. (c) Equivalent circuit used to fit the EIS data.