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Single Walled Carbon Nanotube Channel Flow Electrode: Hydrodynamic Voltammetry at the Nanomolar Level

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The use of single walled carbon nanotube (SWNT) band electrodes in a channel flow cell, for low concentration detection, with hydrodynamic voltammetry is reported. A two dimensional SWNT network electrode is combined with a one piece channel flow cell, fabricated by microstereolithography. This configuration provides well defined hydrodynamics over a wide range of volume flow rates ($0.05 - 25$ mL min^{-1}). Limiting current measurements, from linear sweep voltammograms, are in agreement with the channel electrode Levich equation, for the one electron oxidation of ferrocenylmethyl trimethylammonium hexaflorophosphate (FcTMA$^+$), over a wide concentration range, 1×10^{-8} M to 2×10^{-5} M, with a detection limit of 5 nM. Application of this hydrodynamic configuration to the voltammetric detection of dopamine is also demonstrated.

Keywords: channel flow electrode, hydrodynamic electrode, single walled carbon nanotubes, dopamine, band electrode

Introduction

Hydrodynamic control is an important approach for increasing detection sensitivity in electroanalysis [1]. Popular hydrodynamic techniques include the rotating disc electrode (RDE) [2,3] and the channel flow electrode (CFE) [4,5]. Hydrodynamic electrodes are attractive for electroanalysis as they readily yield steady-state mass transport limited responses, free from heterogeneous kinetic limitations, which is particularly attractive for electroanalysis. With conventional linear sweep voltammetry (LSV), such electrodes typically allow detection down to the micromolar level.

To subtract background contributions from the voltammetric response and increase detection sensitivity further, hydrodynamic *modulation* methods have been developed, for example modulating the rotation speed of the RDE [6] or pulsing solution through a CFE [7,8]. Hydrodynamically modulated jet electrodes [9,10] and microring electrodes [11,12] have also been introduced. In general, concentration detection in the range $10^{-7} - 10^{-8}$ M is typically achieved [7,13].

Recent work has shown that single walled carbon nanotubes (SWNTs), arranged in a planar, low surface coverage (< 1 %) random network, on an insulating substrate, are extremely promising electrodes for low concentration detection [14]. Voltammetric and chronoamperometric studies have shown that these SWNT electrodes provide greatly reduced background currents by up to three orders of magnitude compared to conventional solid electrodes of the same geometric area [14]. This is a direct result of the low surface capacitance of SWNTs, when prepared in the pristine state, and their low surface coverage on the insulating substrate. Importantly, diffusional overlap between neighbouring SWNTs, on the timescale of a typical voltammetric measurement, results in the faradaic current being dependent only on

the geometric area of the substrate, whilst the background current is dependent on SWNT surface coverage, only [15].

The CFE configuration is particularly attractive, as it can be combined readily with *in-situ* spectroscopic methods [16,17] and is suitable for flow injection and on-line analysis [18,19]. Hitherto, SWNT electrodes of the type described here, have only been employed in quiescent solutions. Deployment in a hydrodynamic system would be beneficial in opening up the possibility of on-line flow analysis and many hydrodynamic voltammetric techniques.

In this communication we show that SWNT network band electrodes can be employed in channel flow (using flow cells produced by microstereolithography (MSL)[20]) and that the response is well-defined. Furthermore, it is possible to achieve voltammetric detection limits that are far superior to other types of hydrodynamic electrodes employed and compete favourably with the best attained using hydrodynamic modulation [7,13].

Experimental

SWNT networks were grown onto Si/SiO_2 substrates by catalysed chemical vapour (cCVD) deposition using a Co catalyst and a hot wall growth system [21]. SWNT coverage and height were characterised by atomic force microscopy (AFM) (Multimode, Nanoscope IIIa controller, Veeco). Electrical contacts were made by evaporating Cr (10 nm) / Au (120 nm) bands (Moorfield Minibox Evaporator) onto the sample. The area of the band electrode was defined by a rectangular photoresist mask (S1818, Microposit), 1.5 mm (width) x 0.5 mm (length) [21], placed within 3 mm of the gold band contact, as illustrated in Figure 1(a).

Solutions of ferrocenylmethyl trimethylammonium hexaflorophosphate (FcTMA$^+$), synthesised in-house, in 0.01 M KNO$_3$ (99.999% Sigma Aldrich), and dopamine hydrochloride (Sigma Aldrich) in 0.01 M phosphate buffered saline solution (PBS) were used for voltammetric experiments. The channel flow cell of width and length, w_{ch} = 3 mm and l = 3.5 mm respectively, was created in-house by MSL, as reported previously [20] and positioned over the SWNT band electrode as illustrated in Figure 1 (a). The channel height, $2h$ = 192 μm, was measured by white light interferometry (Wyko NT-2000 Surface Profiler, WYKO Systems). Analyte solutions were delivered via a Gilson 305 HPLC pump which provided volume flow rates up to 25 mL min^{-1}. Cyclic voltammetry (CV) and LSV were performed in a 2-electrode configuration (due to the low currents passed) using a CHI750C potentiostat, at 10 mV s^{-1} scan rate, with a saturated calomel reference electrode (SCE). To minimise the effect of analyte adsorption onto the walls of the delivery system, the channel flow cell was soaked for 1 hour in a 2.5 x 10^{-5} M solution of the analyte of interest and then rinsed copiously with the appropriate supporting electrolyte.

Results and Discussion

The SWNT networks were characterised in terms of network density and SWNT height using AFM. To ensure the networks used were well above the metallic percolation threshold (3 μm$_{SWNT}$ μm^{-2}) [22] only samples with a network density of ≥ 4 μm$_{SWNT}$ μm^{-2} were employed herein, such as that shown in Figure 1(b). SWNT heights of between 0.8 nm and 3 nm were measured using AFM.

As shown previously [20], the limiting current response at a band electrode of the dimensions specified, in the channel geometry with the flow rates employed, should be accurately predicted by the Levich equation (equation 1) [4]

$$i_{\lim} = 1.165 n F c_{\mathrm{b}} D^{2/3} U^{1/3} h^{-1/3} w x_{\mathrm{e}}^{2/3} \qquad \text{(eq 1)}$$

where $i_{\lim}$ is the limiting current, n the number of electrons transferred in the redox reaction, c_b and D are the bulk concentration and diffusion coefficient of the species of interest respectively, U is the mean fluid velocity (cm s^{-1}), and w and x_{E} are the electrode width and length respectively. U is related to V_f through:

$$U = V_f / 2 h w_{ch} \qquad \text{(eq 2)}$$

Typical LSVs recorded at a scan rate of 10 mV s^{-1} for the one electron oxidation of 2.1 x 10^{-5} M FcTMA$^+$ in 0.01 M KNO$_3$ over the V_f range 0.2 – 25 ml min^1, recorded using a SWNT network band electrode of nominal area w = 1.5 mm and x_e = 0.5 mm, are shown in Figure 2(a). These display the expected increase in limiting current with solution velocity. Figure 2(b) shows that there is excellent agreement between the experimental limiting currents (■) and the predictions of the Levich equation (dashed line) over the V_f range 0.5 mL min^{-1} – 25 mL min^{-1}. This suggests that the SWNT network band electrode is well-defined and the ~ 1 µm recess, created when exposing the SWNT network during photolithography, does not affect the flow hydrodynamics. [23,24].

To explore low concentration detection, CVs were recorded at 10 mV s^{-1}, for the oxidation of FcTMA$^+$ (in 0.01 M KNO$_3$) in the concentration range 1 x 10^{-8} M – 1 x 10^{-6} M using a V_f = 25 mL min^{-1} (to maximise the current signal). Typical voltammograms are shown in Figure 2(c). Also shown is the background CV response (dashed line) recorded at 10 mV s^{-1} scan in 0.01 M KNO$_3$ only. Figure 2(c)

shows that it is just possible to discern the response due to the oxidation of 1.3×10^{-8} M FcTMA$^+$ against the background signal, with an estimated limit of detection of 5×10^{-9} M FcTMA$^+$ [25] and a sensitivity of 14.8 mA M^{-1}. Figure 2(d) shows a linear relationship between limiting current and FcTMA$^+$ concentration over the range 1×10^{-8} M $- 1 \times 10^{-6}$ M, as expected based on equation 1.

Attention turned to the electrochemical detection of the neurotransmitter dopamine, of importance because the detection of dopamine in electrochemical flow cells (*e.g.* HPLC with electrochemical detection) is used as a means of quantifying dopamine levels in digested tissue samples [26]. Figure 3(a) shows CVs for the electrochemical oxidation of 1.33×10^{-7} M (lowest curve), 5.0×10^{-7} M and 1.0×10^{-6} M (highest curve) dopamine at a scan rate of 10 mV s^{-1} using V_f = 25 mL min^{-1}. The CVs exhibit more sluggish kinetics that for FcTMA$^+$ oxidation, as seen previously at SWNT network electrodes under quiescent conditions [21] and is expected for carbon electrodes unless the electrode surface is pretreated [27,28]. However, importantly, clear limiting current plateaus are evident.

The relationship between the limiting current and the bulk concentration is linear over the range of 1×10^{-7} M $- 1 \times 10^{-6}$ M, with a sensitivity of 16 mA M^{-1} and a detection limit of 5×10^{-8} M [25], as shown in Figure 3(b). The limiting current, however, is only 60% of that predicted by the Levich equation for the cell employed (for $n = 2$, $D = 6 \times 10^{-6}$ cm^2 s^{-1}) [29,30]; this is likely to be due to fouling effects that are wide known for dopamine [27,28,30,31]. However, the response could be used quantitatively as it was consistent over several different samples.

Conclusion

SWNT network band electrodes have been successfully combined with MSL-fabricated one piece channel flow units to produce flow cells which have well-defined mass transport and are capable of low concentration detection. Excellent agreement has been found between experimental and theoretical (Levich) limiting currents from LSV runs for the one electron oxidation of FcTMA$^+$ over the flow rate range 0.5 mL min^{-1} – 25 mL min^{-1}, with a limit of detection of 5 x 10^{-9} M at a flow rate of 25 mL min^{-1}. This detection sensitivity compares very favourably with the best achieved even using complex hydrodynamic modulated flow techniques, due to the very low background currents of the SWNT network electrodes. The limiting current response for dopamine oxidation is linear with respect to concentration over the range of 1 x 10^{-7} M to 1 x 10^{-6} M, and a limit of detection of 5 x 10^{-8} M is estimated for dopamine in this configuration.

Acknowledgements

FIGURES

Figure 1. (a) Schematic of the channel flow cell positioned on the SWNT band electrode. The dotted white line represents the boundary of the channel and arrows show direction of flow (not to scale). (b) Typical FE-SEM image of a SWNT network of density ~8 µm µm^2; scale bar is 2 µm.

Figure 2. (a) LSVs taken at 10 mV s^{-1} in 2.1 x 10^{-5} M FcTMA$^+$ and 0.01 M KNO$_3$ at flow rates of 0.2, 1.0, 2.0, 5.0, 10.0, 15.0, 20.0 and 25.0 mL min^{-1} and (b) linear fit of the experimental limiting current response (■) to the Levich equation (dashed line) for V_f = 0.5 mL min^{-1} – 25 mL min^{-1}. (c) CVs taken at 10 mV s^{-1} with V_f = 25 mL min^{-1} in 1.56 x 10^{-7} M (upper curve), 5.2 x 10^{-8} M and 1.3 x 10^{-8} M FcTMA$^+$ in 0.01 M KNO$_3$ (lower curve) and 0.01 M KNO$_3$ only (- - -). (d) Agreement of the experimental data with the Levich predicted response (dashed line). For all experiments, x_e = 0.5 mm, w = 1.5 mm, $2h$ = 192 µm and D = 6 x 10^{-6} cm^2 s^{-1}.

Figure 3. (a) CVs recorded at 10 mV s^{-1} with V_f = 25 mL min^{-1} in 1.0 x 10^{-6} M (upper curve), 5.0 x 10^{-7} M and 1.33 x 10^{-7} M (lower curve) dopamine and 0.01 M PBS. (b) A linear relationship of limiting current and concentration is seen, which is lower than that predicted by the Levich equation (dashed line).

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