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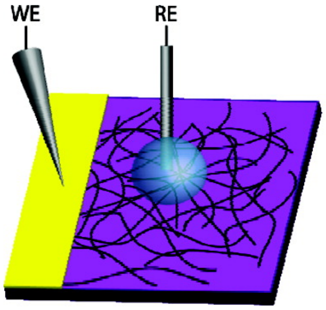

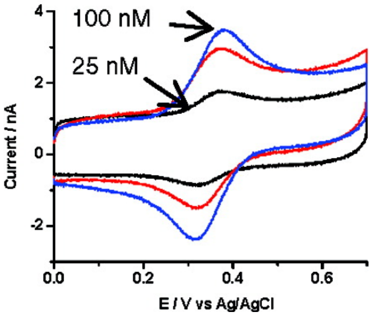

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Trace Level Cyclic Voltammetry Facilitated by Single-Walled Carbon Nanotube Network Electrodes

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Discrimination against currents which arise from background and non-faradaic processes[1] represents a significant challenge in the use of amperometry for trace level analysis. Background and non-faradaic currents typically scale with the area of the electrode and may arise, for example, from capacitative effects associated with charging of the electrode/electrolyte interface (non-faradaic), electrode surface reactions, and solvent decomposition (at the limits of the potential window). One approach to tackling this problem has been to use arrays of small area electrodes, arranged to minimize the active surface area while maximizing the current signal. Among various configurations, nanoporous filtration membranes filled with Au[2] have received considerable attention, and more recently, vertically aligned arrays of carbon nanotube bundles (50−100 nm domain size) set in epoxy resin or silicon oxide have been realized.[3]

In this paper, we report the use of pristine (non-functionalized) single-walled carbon nanotubes (SWNTs), grown in a two-dimensional network arrangement on an inert support, as an electrode material with unprecedented low background currents, which facilitates trace level (nanomolar) cyclic voltammetry (CV) measurements. SWNTs are currently attracting much interest as electrode materials. Their small size (1−3 nm in diameter) results in high mass transfer coefficients,[4] and they are characterized by high conductivity (typically one in three is a ballistic metallic conductor).[5] Although it has been suggested that electron transfer may only occur at the ends of nanotubes or at defect sites,[6] evidence is emerging that pristine SWNTs show good characteristics as an electrode material.[4,7] This is significant, as carbon is the electrode material of choice for bioelectrochemistry, with CV particularly important for chemical identification in such systems.[8] With macroscopic carbon electrodes, CV has typically been limited to a rather narrow concentration range, ca. 10 μM to 10 mM.

Electrically connected pristine SWNT networks are readily produced on insulating surfaces (Si/SiO_2) via catalyzed chemical vapor deposition at Fe nanoparticles.[9] Electrical connection is made at one side via an evaporated Au band. At sufficiently high density and on typical voltammetric time scales, the network electrode behaves like a thin metallic film, and in the pristine state, the capacitance of a SWNT is low.[10]

In previous electrochemical studies with SWNT networks, small areas were exposed to solution to minimize the effect of the network resistivity.[7] Crucially, the low current density associated with low concentration detection means that much larger network areas can be employed, thus simplifying the experimental arrangement significantly and negating the need for lithographic processing of the substrate after growth of the network. The ability to carry out CV measurements at low concentration was assessed initially using the simple outer sphere redox species (ferrocenylmethyl)trimethylammonium, $FcTMA^+$ (further details on synthesis can be found in Supporting Information), in an aqueous solution containing 0.1 M NaCl (purity >99.99%). Figure 1 shows the simple experimental setup employed for these investigations and a field emission-scanning electron microscopy (FE-SEM) image of a typical network.

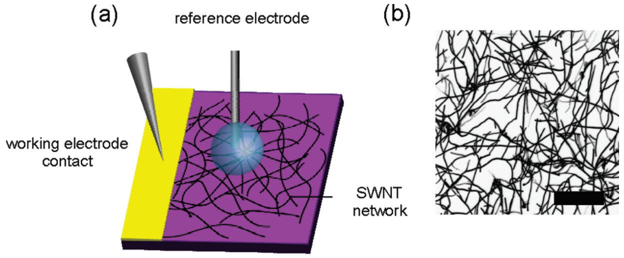

Figure 1. (a) Schematic of the setup for electrochemical measurements with SWNT network electrodes. (b) FE-SEM image of a SWNT network, density ~ 5 $\mu m_{SWNT}\ \mu m^{-2}$. Scale bar represents 2 μm. Note that FE-SEM exaggerates the width of SWNTs.

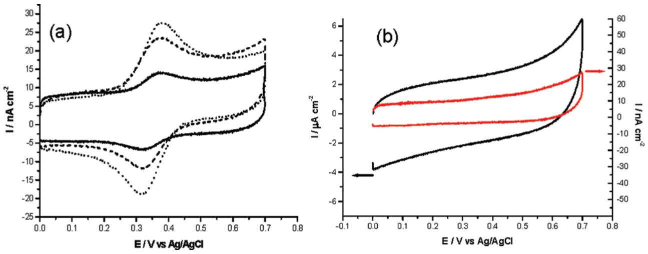

Figure 2. (a) CVs for the $FcTMA^{+/2+}$ couple (0.1 M NaCl) at concentrations of 25 nM (solid line), 70 nM (dashed line), and 100 nM (dotted line), recorded at a scan rate of 100 mV s^{-1}. (b) CV showing the background response at a GCE in a 0.1 M NaCl solution, recorded at 100 mV s^{-1}. The red line shows the background response recorded at a SWNT network (0.1 M NaCl) at 100 mV s^{-1} (note different currents scales).

The network electrode was electrically connected using a sharp prober placed on the Au contact band. SWNT networks with densities in the range of 5 ± 1 $\mu m_{SWNT}\ \mu m^{-2}$ (defined as length of SWNT per micrometer^2)[9] were employed for all experiments, corresponding to ca. 0.5 ± 0.1% surface coverage.[9] A drop of solution (10 μL; 4 mm diameter) containing the electroactive species of interest[11] was placed on the network close to the Au band but avoiding contact. A Ag/AgCl (0.1 M NaCl) reference electrode was positioned within the drop to complete the circuit, and CVs were recorded for different concentrations of $FcTMA^+$.

Figure 2a shows typical CVs recorded at a potential sweep rate of 100 mV s^{-1} for the $FcTMA^{+/2+}$ couple at concentrations of 25 nM (—), 70 nM (- - -), and 100 nM (• • •). Evidently, the response for a concentration of just 25 nM is easily discernible. It is important to note that, although the network coverage is <1% of the surface, the current response is as if the entire surface was covered. This is due to overlap of the diffusion fields between adjacent nanotubes, causing the response to be controlled by planar diffusion. However, the low surface coverage and low intrinsic capacitance of pristine SWNTs mean that the background current at the network electrode is more than 2 orders of magnitude smaller than would be expected

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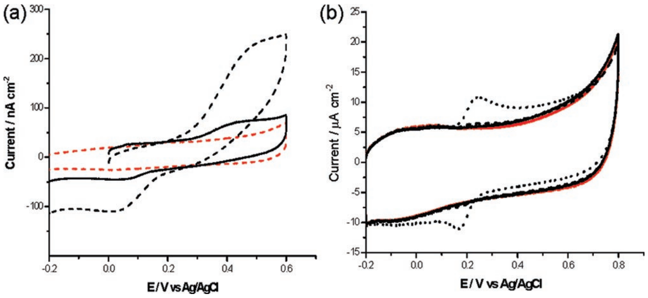

Figure 3. CVs for the oxidation of dopamine (in 0.1 M NaCl, 0.1 M acetic acid buffer, pH 5) at a scan rate of 100 mV s^{-1}: (a) a SWNT network electrode at concentrations of 100 nM (solid line) and 500 nM (dashed line); (b) a GCE at concentrations of 100 nM (solid line), 1 μM (dashed line), and 10 μM (dotted line). In both cases, the red line represents the background response without dopamine.

for a planar electrode. This point is further demonstrated in Figure 2b, which shows the CV response for a solution containing 0.1 M NaCl at a conventional glassy carbon electrode (GCE) and a SWNT network electrode.

Given a diffusion coefficient for FcTMA$^+$ of 6×10^{-6} cm^2 s^{-1}, the expected peak oxidation current density for a FcTMA$^+$ concentration of 100 nM at a uniform electrode is ∼21 nA cm^{-2} (in accordance with the Randles−Sevcik equation),[12] in good agreement with the experimentally measured peak current at the SWNT network electrode. Importantly, the peak current for the oxidation of FcTMA$^+$ was found to scale linearly with concentration over the range of 25 nM to 5 μM (see Supporting Information), as did the peak current density with the square root of the scan rate for a particular redox mediator concentration (as shown in Supporting Information). The peak−peak separations for the FcTMA$^+$ CVs shown in Figure 2 are 77 mV (25 nM), 71 mV (70 nM), and 71 mV (100 nM), reasonably close to reversible for this one-electron redox process. As the concentration was further increased, the voltammetric waves became more distorted, increasing from ∼90 mV (1 μM) to ∼240 mV (10 μM). This is not unexpected and arises primarily from ohmic effects in the network,[7,9] which become more pronounced as the current magnitude increases.

To examine the applicability of SWNT network electrodes for trace level measurements of more complex electrode processes, we investigated the CV response for the neurotransmitter, dopamine (positively charged under these solution conditions), which is oxidized in a two-electron process. Adsorption of dopamine is thought to be a key step in the mechanism.[13]

Figure 3a shows CVs recorded at a scan rate of 100 mV s^{-1} for the oxidation of dopamine, which forms dopamine *o*-quinone on the forward step, at concentrations of 100 nM (solid black line) and 500 nM (dashed line) in a solution containing 0.1 M NaCl and 0.1 M acetic acid (buffered to pH 5). For comparison, the CV response for 100 nM (solid black line), 1 μM (dashed line), and 10 μM (dotted line) dopamine at a GCE, in the same buffered background electrolyte solution, is shown in Figure 3b.

The GCE shows quasi-reversible electron transfer characteristics ($\Delta E_p \sim 80$ mV; two-electron transfer process),[14a] but this is only evident at concentrations greater than 1 μM. In contrast, although the CVs for dopamine electrolysis, at the pristine (untreated) SWNTs are electrochemically sluggish (as observed by others[14b,c]), a concentration of 100 nM can easily be measured. The baseline current, at potentials where dopamine is not oxidized, is slightly higher than for FcTMA$^+$ oxidation. However, it is significantly lower than prior reports for nanotube-modified electrodes,[15] as a consequence of the significantly reduced surface area and the initial pristine nature of the SWNTs used herein. The small increase in baseline current may be due to adsorption of dopamine on the nanotube surface increasing background and non-faradaic effects during potential scans. Nonetheless, to the best of our knowledge, these CVs show the highest detection sensitivity for dopamine at an untreated, unmodified carbon-based electrode material and highlight the promising nature of native SWNTs in electroanalysis.

In summary, SWNT networks are very effective for trace level CV measurements, offering a simple and useful route to concentration levels which have proved inaccessible to other electrode materials. With non-covalent modification of the surface, lower network densities, efforts to minimize stray capacitance, the use of pulsed potential techniques, and hydrodynamic methods, there is considerable scope for further increasing the detection sensitivity and selectivity of these network electrodes.

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Supporting Information Available: Materials, peak oxidation current versus concentration plot for CV measurements of FcTMA$^+$, and peak current versus $v^{1/2}$ dependence for the oxidation of FcTMA$^+$ (CV measurements). This material is available free of charge via the Internet at http://pubs.acs.org.

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