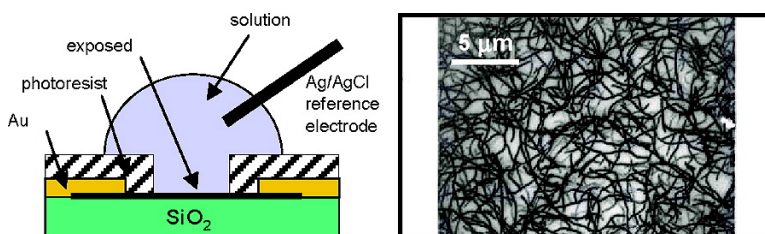


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Electrochemical and Conductivity Measurements of Single-Wall Carbon Nanotube Network Electrodes

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Single-wall carbon nanotubes (SWNTs) are fascinating molecules composed of a graphene sheet rolled into a seamless cylinder, ca. 1 nm in diameter. Their nanoscale size and unique electrical properties have prompted investigations into their electrochemical behavior. Previous electrochemical studies of SWNTs have involved a variety of different electrode arrangements and pretreatments. Common preparative methods have included depositing (or growing) the SWNTs on a conducting electrode surface¹ or mixing the SWNTs in an inert matrix to form a paste electrode.² In nearly all reported cases, the SWNTs are subject to a harsh acid clean prior to use, resulting in oxidative functionalization of the surface. The effect of the various pretreatment procedures on the electrochemical response of carbon nanotubes has recently been questioned.³ Moreover, to date, none of the reported electrochemical investigations have addressed the fact that in a typical SWNT sample, one in three is metallic (mSWNTs), whilst the remainder are semiconducting (sSWNTs).⁴

In this communication, a novel experimental arrangement for investigating the electrochemical behavior of SWNTs is reported, namely, two-dimensional networks of pristine SWNTs on an insulating support. Crucially, we demonstrate the significance of both mSWNTs and sSWNTs in determining the resulting electrochemical behavior of the SWNT network electrode (NE). The fabrication of the NE is described in detail in Supporting Information. Briefly, SWNTs were grown by catalyzed chemical vapor deposition on an SiO₂ substrate. Two contact electrodes (15 nm Cr, 100 nm Au) were patterned on the substrates after SWNT growth, creating a gap of 90 μm width and 1 mm length. A layer of photoresist (SU1815; Shipley) was then spin coated on top, and a 20 \times 400 μm area was photolithographically removed from the gap region, leaving exposed SWNTs, supported on an inert substrate and connected to the insulated contact electrodes. Au band test samples were also fabricated by exposing a similar region on a contact electrode, without SWNTs present.

A schematic of the NE and a FE-SEM image of the exposed SWNTs are given in Figure 1. The FE-SEM image shows that the sample is composed of a dense, multiply interlinked, random network of SWNTs. The contrast in the FE-SEM image is due to charging artifacts⁵ and, hence, does not show the true diameter of the SWNTs. Nanotube diameters were measured by AFM and found to be in the range of 0.8–3 nm, indicating SWNTs. 1–10 SWNTs were found in each 1 μm square, implying an average spacing of 0.1–1 μm . The lengths of the SWNTs were typically in the range of 2–20 μm , although a few longer SWNTs with lengths of a few hundred microns were also present, which could span the entire gap between the two contact electrodes. The majority of the SWNTs in the gap were, however, connected to the Au electrodes via multiple SWNT contacts.

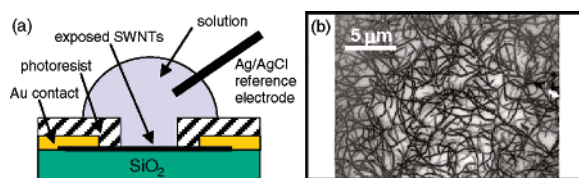


Figure 1. (a) Schematic and (b) FE-SEM image of the SWNT electrode.

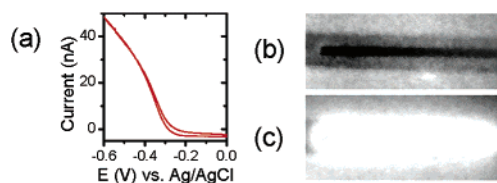


Figure 2. (a) CV at 10 mV s⁻¹ for the reduction of 1 mM BQ (in 0.2 M KNO₃ and 2 μM fluorescein); 500 μm wide confocal microscopy images obtained (b) before stepping the NE potential to -0.6 V, and (c) 8 s later.

Electrochemical measurements were made by placing a drop of solution (ca. 30 μL) containing the electroactive mediator of interest over the exposed area. A potential, $E(V)$, was applied between the working electrode (the SWNT network contacted via one of the Au contact electrodes) and an Ag/AgCl reference electrode, which was positioned within the solution droplet.

The electrochemical activity of the SWNT network was visually confirmed using confocal fluorescence microscopy to monitor the evolving three-dimensional pH gradient for electrochemical reduction of benzoquinone (BQ) in the presence of fluorescein. Figure 2a shows a cyclic voltammogram (CV) recorded at the SWNT electrode for the reduction of 1 mM benzoquinone (BQ) in a solution containing 2 μM fluorescein and 0.2 M KNO₃. The resulting CV shows pseudo-steady-state behavior. The absence of a significant limiting plateau is likely to be due to reduction of oxygen at more negative potentials as it was difficult to deaerate the solution droplet with the experimental arrangement adopted.

An optical image of an NE is shown in Figure 2b; the contact electrodes are apparent at the top and bottom of the image, as is the exposed zone (darker region) in the center of the gap. Figure 2b was taken immediately prior to a step in electrode potential from 0.0 to -0.6 V, which was sufficient to reduce BQ at a diffusion-controlled rate. This reductive process consumes protons which locally increases the pH (initial pH \approx 5.4), causing fluorescein to fluoresce with greater intensity, which can be visually mapped using a confocal microscope.⁶ Figure 2c was taken 8 s later and demonstrates the increase in fluorescence only in the exposed region (a more complete time sequence of images is shown in Supporting Information). Additionally, this observation indicates that even though the majority of SWNTs are connected to the Au electrodes via SWNT–SWNT contacts, the resistance is not high enough to suppress electrochemical activity. Repeated experiments on SWNT samples confirmed these observations. Similar results were obtained

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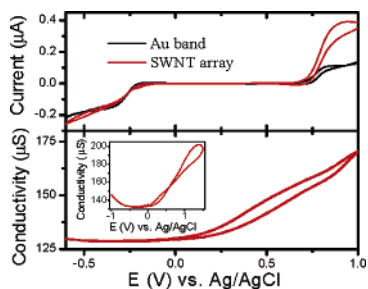


Figure 3. (a) CVs at 10 mV s^{-1} for the oxidation and reduction, respectively, of $5 \text{ mM Fe(phen)}_3^{2+}$ and $5 \text{ mM Ru(NH}_3)_6^{3+}$ in 0.2 M KNO_3 for the Au band and SWNT network electrode. (b) Conductivity of the NE as a function of the electrode potential in the above solution.

for the Au band electrodes. The electrochemical response of both electrodes was found to be stable over both prolonged periods of time and wide potential windows (up to $\pm 1.5 \text{ V}$ versus Ag/AgCl), demonstrating that the photoresist acted as an effective and stable insulator.

Figure 3a shows CVs recorded at 10 mV s^{-1} on a Au microband and an SWNT NE for the oxidation of Fe(phen)_3^{2+} and reduction of $\text{Ru(NH}_3)_6^{3+}$ (both present in the same solution, each at concentrations of 5 mM in 0.2 M KNO_3). With the experimental arrangement adopted, we were unable to avoid evaporation; hence, we used a dual redox mediator solution to allow intercomparison of the anodic and cathodic currents. For the Au electrode, the limiting currents for the two redox mediators (ca. $+0.8 \text{ V}$ for Fe(phen)_3^{2+} and -0.45 V for $\text{Ru(NH}_3)_6^{3+}$) were in the ratio of $\sim 1:1.6$, respectively, due to the difference in the diffusion coefficients of the two mediators.⁷ Similar CV behavior was observed at a $7 \mu\text{m}$ diameter carbon fiber ultramicroelectrode. Strikingly, at the SWNT NE, the limiting current for Fe(phen)_3^{2+} oxidation was significantly greater than expected based on the limiting current for $\text{Ru(NH}_3)_6^{3+}$ reduction.

To complement these results, simultaneous electrochemical and conductivity measurements were made on the NE (experimental details in Supporting Information). The two contact electrodes enabled the conductivity of the SWNT array to be measured in a standard two terminal device geometry, while the Ag/AgCl reference electrode allowed the solution potential to be controlled independently of the SWNT network. In this configuration, the solution acts as a “wet gate”, electrostatically doping the SWNTs. Previous experiments using wet gates on SWNTs have shown the capacitance between SWNTs and the electrolyte solution to be high, making the solution a very effective gate electrode.⁸ Even though the conductivity of SWNTs has been previously studied in aqueous environments,^{8,9} these measurements represent the first correlation of conductance with SWNT electrochemical activity.

Figure 3b shows the effect of varying $E(V)$ on the conductance of the SWNT network (under the same solution conditions as Figure 3a). Increasing $E(V)$ corresponds to the solution potential decreasing relative to the SWNT network and is thus equivalent to a decreasing “gate potential”. The observed response can be separated into transistor-like behavior on top of a constant background. The increase in conductance as $E(V)$ increases (i.e., decreasing gate potential) is consistent with the presence of sSWNTs, which are

usually found to be “p-type” doped.¹⁰ The inset to Figure 3b shows conductivity measurements taken over a wider range of $E(V)$ values, which are sufficient to electrostatically dope the sSWNTs to ambipolar conduction,¹⁰ demonstrating the efficacy of the wet gate. The high background conductance in Figure 3b is due to both the mSWNTs, whose conductance is roughly independent of gate potential, and those SWNTs not exposed to solution.¹¹

The conductance measurements help explain the anomalous difference in the limiting currents for the two different redox couples at the NE. At the limiting potential for Fe(phen)_3^{2+} oxidation [$E(V) \approx 0.8 \text{ V}$], both the mSWNTs and the sSWNTs conduct and contribute to the electrochemical signal. However, at the limiting potential for $\text{Ru(NH}_3)_6^{3+}$ reduction [$E(V) \approx -0.45 \text{ V}$], the sSWNTs are depleted of charge carriers, and hence, *do not* contribute to the electrochemical response. The observed increase in oxidation current compared to the reduction current supports the expectation that in the network, only one in three SWNTs is metallic.⁴ Thus, the electrochemically active area of the SWNT network is strongly dependent on the applied potential and electroactive mediator employed. Importantly, the density of SWNTs constituting the network must also be considered. For all samples investigated herein, the density was sufficiently high so that both sSWNTs and mSWNTs were above the percolation threshold.¹² Through correct choice of mediator and electrode potential, mSWNTs can be electrochemically addressed independently of sSWNTs.

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Supporting Information Available: Details of SWNT growth procedure and SWNT network electrode fabrication. Confocal microscopy demonstrating directly the electrochemical activity of the exposed region only. Experimental details of conductivity measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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