#### **Supporting Information**

# **Electrochemistry at Carbon Nanotube Forests: Sidewalls and Closed Ends Allow Fast Electron Transfer**

## Thomas S. Miller, Neil Ebejer, Aleix G. Güell, Julie V. Macpherson and Patrick R. Unwin

### Section 1: SWNT forest growth and characterisation

SWNT forests were grown on silicon wafers (n-type, 525  $\mu$ m thick, IDB Technologies Ltd, UK) which had been sputtered (Plassys (MP 900S)) with a 10 nm layer of aluminium (Al) and cleaved into ~ 1 cm × 1.5 cm pieces. The individual substrates were ashed in an oxygen plasma for 2 minutes (K1050X plasma system, Emitech, UK; O2 pressure  $6 \times 10^{-1}$  mbar) and sputtered (Quorum Technologies SC7640 sputter coater, fitted with a Co target, 99.95%, Testbourne Ltd. UK) with Co. Once prepared, the substrates were heated to growth temperature (*TG*) in a CVD oven consisting of a 1" diameter quartz tube (Enterprise Q ltd.) passing through a tube furnace (Lindberg/Blue M, Thermo-Fisher Scientific, US). Heating was performed under hydrogen flow (99.995%, BOC). After *TG* was reached, argon (99.9995%, BOC) was bubbled through ethanol (99.99%, Fisher Scientific) at 0 °C before being introduced into the CVD system as the source of carbon. In both cases, the flow rates of the process gasses were controlled using mass flow controllers (MKS Instruments UK Ltd, UK). Growth was sustained for 40 minutes before the Ar-EtOH flow was stopped and the oven was allowed to cool under hydrogen flow.



Fig S1. Graphic representation of the growth scheme

FE-SEM images were acquired using a Zeiss SUPRA 55 VP FE-SEM using a 1 kV accelerating voltage. TEM images were taken using a Jeol 2000FX TEM. SWNTs were deposited onto lacey carbon film coated TEM grids (Agar Scientific) by rubbing the grid onto the side of the forest. This was found to introduce less contamination than solution based methods. XPS spectra were taken using a Scienta ESCA300 photoelectron spectrometer, with a monochromated rotating anode Al K $\alpha$  X-ray source at the National Centre for Electron Spectroscopy and Surface analysis, Daresbury Laboratory, UK.

### Section 2: Micro-Raman Microscopy of SWNT forests

Micro-Raman spectra were collected using a Renishaw inVia Raman microscope fitted with a CCD detector and a 633 nm HeNe laser with a spot size of 3  $\mu$ m with a 5 % attenuation. By

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tilting the sample we were able focus onto the sidewalls, allowing us to obtain Raman spectra of this face. The shape and location of the G band  $(sp^2)$  at 1589 cm<sup>-1</sup>, in both spectra in Figure S2, is indicative of SWNTs.<sup>1,2</sup> Whilst small D peaks  $(sp^3 \text{ carbon})$  are visible, G / D ratios for the ends and the sidewalls, 7:1 and 9:1 respectively, indicate significantly higher quality forests (*i.e.* cleaner, lower defect density) than those previously described in the literature.<sup>2,3</sup>



Fig S2. Micro-Raman spectra of an intact SWNT forest focusing on the sidewalls and tube ends.

#### **Section 3: Voltammetric Measurements**

To produce an electrical contact to the SWNT forest, a 200 nm thick gold film was evaporated onto half of the sample, covering both the tops and sides, by means of a shadow mask, leaving the rest of the sample intact for electrochemical analysis. The sample was then mounted to align either the top of the forest or the sidewalls, for electrochemical interrogation. The pipet tips were produced by pulling theta glass borosilicate pipets (Harvard Apparatus) using a Sutter instruments P2000 laser puller. Pipets were filled with the solution of interest and Ag/AgCl quasi-reference electrodes were placed in each barrel. Pipets of inner diameter ~400 nm were routinely employed herein and were accurately characterised using FE-SEM. The pipet was translated towards the surface using a piezoelectric actuator (Physik Instrumente (PI) Nanocube), in conjunction with in-house written software (LABVIEW). During approach, a potential bias, corresponding to the diffusion-limited oxidation/reduction potential of the mediator of interest was applied to one barrel of the capillary, whilst the SWNT forest substrate was held at ground. A current was sensed as soon as the meniscus at the end of the capillary established contact with the SWNT forest substrate; at this point the approach was automatically stopped. All electrochemical experiments were performed at room tempertaure, 293 K, and potentials quoted against Ag/AgCl (50mM KCl).

Figure S3 shows typical CVs recorded on the sidewall and closed ends of the SWNT forest for oxidation of the redox mediator  $FcTMA^+$ .

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*FigS3.* CVs of 2 mM FcTMA<sup>+/2+</sup> oxidation in 50 mM KCl at a scan rate of 100 mV s<sup>-1</sup>. Red lines indicate forest sidewalls, blue lines, the forest closed ends.

#### References

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