SUPPLEMENTARY MATERIAL

Experimental Procedures

Chemicals

Cysteamine was purchased from Sigma Chemical Company (Sydney, Australia), 1,3 dicyclohexylcarbodiimide (DCC), potassium ferricyanide and dimethyl formamide (DMF) were purchased from Aldrich Chemical Company (Sydney, Australia) and nitric acid, sulphuric acid and KCl, KH_2PO_4 were obtained from Ajax Chemicals (Sydney, Australia). The single walled carbon nanotubes (SWNT) were HiPCo tubes from Carbon Nanotechnologies Inc. (USA). All aqueous solutions were prepared with Milli-Q water.

Shortening of Nanotubes

The SWNTs were cut according to the procedure developed by Liu *et. al* [2]. HiPCo SWNTs (2 mg) were added to 10 mL of an acid mixture of 1:3 (v/v) concentrated sulfuric acid and concentrated nitric acid. The SWNT were sonicated in the acid mixture using a 55 Hz sonicator bath for the specified number of hours (between 2 and 8 hours). After sonication the mixture was diluted in 500 mL of Milli-Q water and allowed to settle overnight. The shortened SWNTs were then collected by filtration using a 0.45 μm nitrocellulose membrane (Millipore, Sydney, Australia) and washed until neutral pH was achieved. Finally the cut and washed carbon SWNTs were re-dispersed in 10 mL of ethanol.

Preparation of Nanotube Modified Electrodes

Gold electrodes were polished using 1.0, 0.3 and 0.05 micron Buehler Micropolish alumina slurry on Buehler Polishing Microcloth (Buehler, Ltd. USA) until a mirror finish was achieved and then sonicated in 55 Hz bath sonicator for 10 minutes. The electrode was then cleaned electrochemically by cycling it in 0.05 M H_2SO_4 solution between –300 mV and +1500 mV *versus* Ag/AgCl with a scan rate of 150 mV s^{-1} until reproducible cyclic voltammetry was achieved (typically 20 cycles). The clean gold electrodes were immersed in a 100 mM cysteamine solution in water for 3 hours at room temperature followed by rinsing with Milli-Q and drying under a stream of nitrogen.

The cysteamine modified electrodes were placed in a suspension of shortened SWNTs in 1 mL DMF solution containing 0.5 mg of 1,3 dicyclohexylcarbodiimide (DCC) for four hours to give an electrode modified with SWNTs aligned normal to the electrode surface.

Randomly dispersed electrodes were prepared by depositing droplets of cut SWNTs dispersed in ethanol onto a cysteamine modified gold surface and heating at 60 ^{o}C.

Electrochemical Measurements

All amperometric measurements were conducted using a BAS 100B potentiostat. The auxiliary electrode was a home-made 1 x 1 cm^2 platinum flag electrode and the working electrode was a polycrystalline gold electrode prepared as described previously [1]. All potentials were set against the Ag/AgCl reference electrode (BAS, Lafayette In, USA).

Transmission Electron Microscopy (TEM) Measurements

SWNTs (pristine or cut for the specified time) were dispersed in absolute ethanol and sonicated for 10 minutes. TEM samples were then prepared by placing a drop of the dispersion onto a standard TEM sample grid covered with carbon film and allowing the solvent to evaporate. A Philips CM 200 Field Emission Transmission microscope was used to record images. The lengths of the shortened tubes were estimated by visual inspection.

Atomic Force Microscopy (AFM) Images

Atomic force microscope images were taken using a Digital Instruments Dimension 3100 scanning probe microscope. All images were acquired in tapping mode using commercial Si cantilevers/tips (Olympus) used at their fundamental resonance frequencies, which typically varied from 275 - 320 kHz. AFM images were performed on molecularly smooth gold substrates which were freshly prepared by template stripping as described previously [3].

X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectra were collected on a VG ESCALAB 220-iXL spectrometer with a monochromated Al K_α source (1486.6 eV). The spectra were accumulated at a take-off angle of 90°. The pressure in the analysis chamber was less than 10^{-8} mbar. Spectra were analyzed using the XPSPEAK41 software.

FTIR Characterisation

The dispersion of SWNTs in ethanol was dried in an oven at 373K to evaporate the solvent. Dried SWNT powder was mixed with KBr to make the IR pellet. FTIR spectra of the SWNT samples (pristine or cut for the specified time) were collected

using a Nicolet-Avatar 320 ESP Fourier transform infrared spectrometer. All spectra shown were baseline corrected using the EZ OMIC software.

References

[1] J.J. Gooding, P. Erokhin, D.B. Hibbert, *Biosensors Bioelectronics* **15** 229 (2000).

[2] J. Liu, A.G. Rinzler, H.J. Dai, J.H. Hafner, R.K. Bradley, P.J. Boul, A. Lu, T. Iverson, K. Shelimov, C.B. Huffman, F. Rodriguez-Macias, Y.S. Shon, T.R. Lee, D.T. Colbert, R.E. Smalley, *Science* **280** 1253 (1998).

[3] J. Mazurkiewiecz, F.J. Mearns, D. Losic, L. Weeks, E.R. Waclawik, C.T. Rogers, J.G. Shapter, J.J. Gooding, *J. Vac. Sci. Technol.* B. **20** 2265-2270 (2002).

Figures

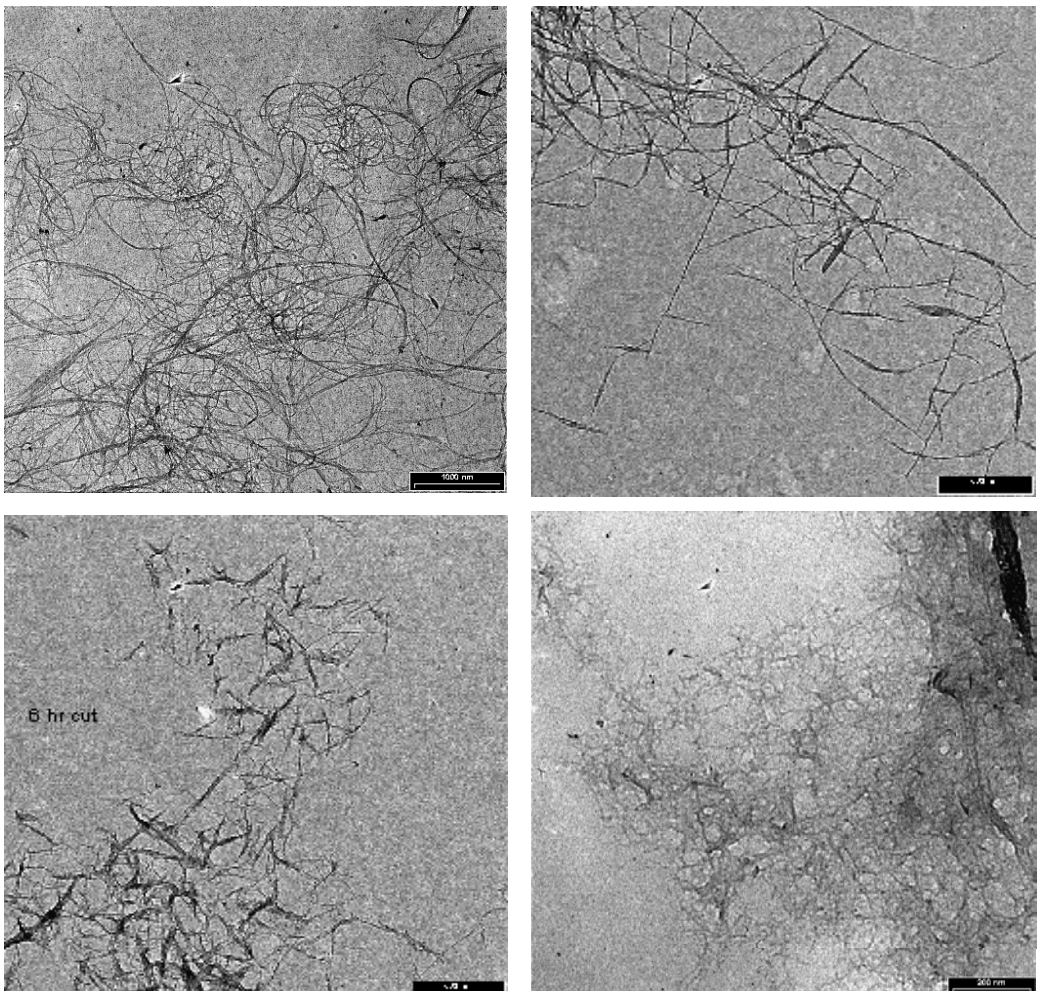

Figure S1. Transmission electron microscope images of single walled carbon nanotubes:
top left: pristine
top right: cut for 4 hours
bottom left: cut for 6 hours
bottom right: cut for 8 hours.

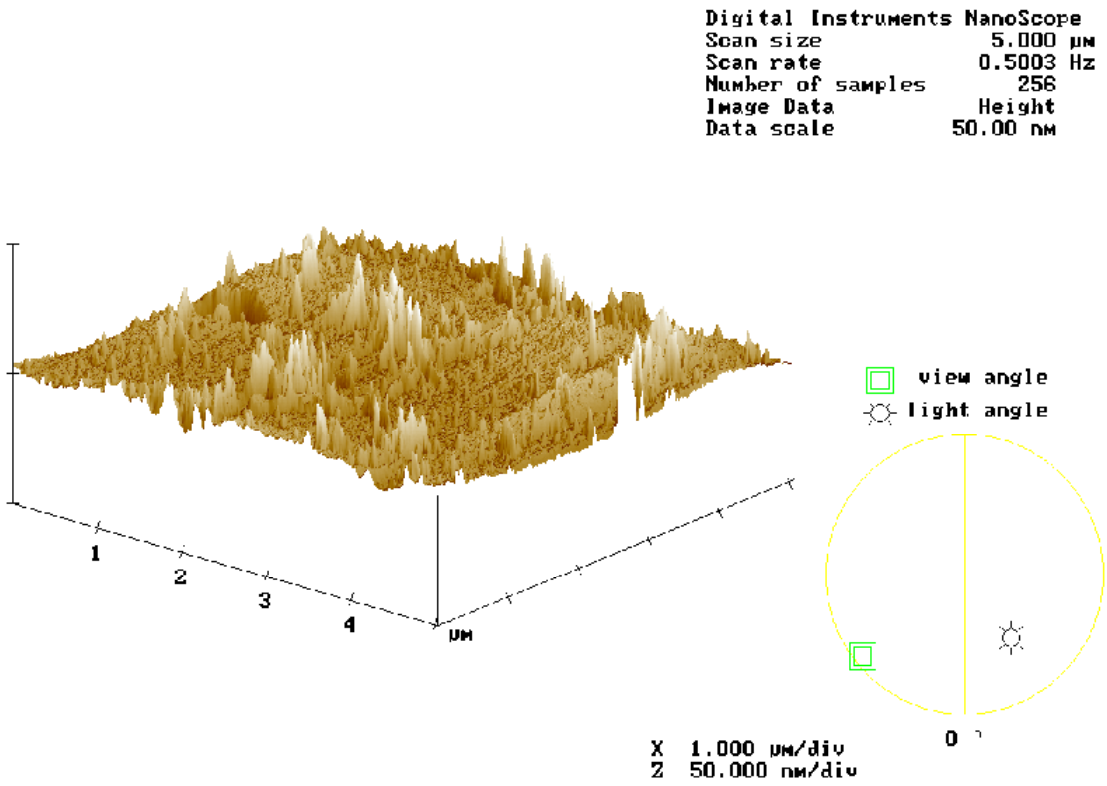

Figure S2. Tapping mode atomic force microscope image of shortened SWNT aligned normal to a smooth gold electrode surface by self-assembly. The sample was prepared by immersion of a cysteamine modified gold substrate in a solution containing SWNTs as described in the Experimental Section. The SWNTs shown here were cut for six hours.

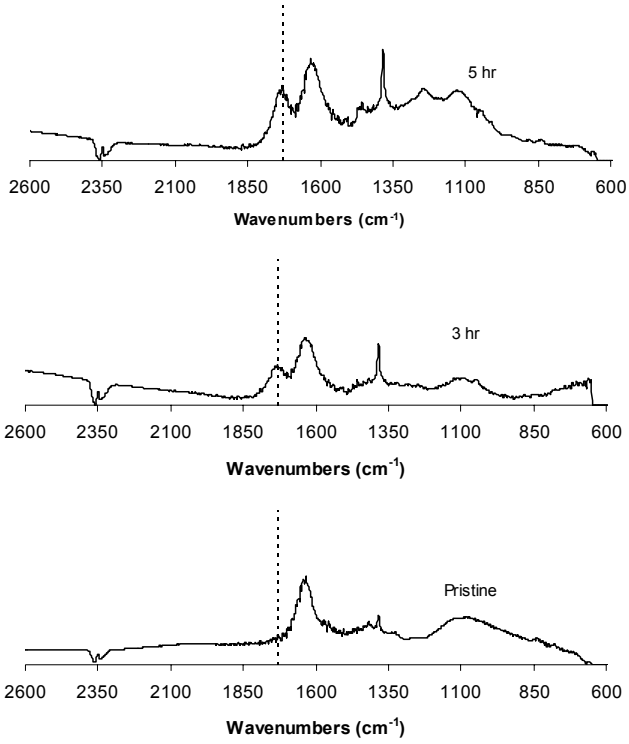

Figure S3. FTIR spectra of pristine SWNTs (bottom), SWNTs cut for 3 hours (middle) and cut for 5 hours (top). The peak centred at ~1730 cm^{-1} (dotted line) indicates the appearance of COOH groups.