

Assembly, Structure and Electrical Conductance of Carbon Nanotube – Gold Nanoparticle 2D Heterostructures

Electronic Supporting Information: Detailed synthetic procedures, discussions of film cohesion, morphology, sampling, interfacial entrapment & additional electrical data.

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Shortened carbon nanotubes by gas-phase oxidation

MWNT (100 mg, as-received) were placed into an alumina crucible and annealed in air at 500 °C and the decrease in mass recorded. Samples heated for 40 minutes showed a *circa* 60 % decrease in mass and were termed ‘annealed MWNT’. The obtained solids were then sonicated in concentrated hydrochloric acid (37 % HCl, 50 mL) at room temperature for 30 minutes (to remove metallic catalyst residues), diluted with deionised water (250 mL), filtered with a 0.45 µm diameter pore polytetrafluoroethylene (PTFE) membrane under vacuum, rinsed thoroughly with deionised water and ethanol and sucked dry. Residual water was removed by drying under vacuum to yield a black solid.

Oxidation of nanotubes in nitric acid

Annealed MWNT (25 mg) were sonicated in nitric acid (2.6 M HNO₃, 50 mL) at room temperature for 15 minutes and then refluxed at 120 °C for 48 hours. The obtained black

suspension was diluted with deionised water (100 mL), filtered with a 0.45 μm pore diameter PTFE membrane under vacuum, rinsed thoroughly with deionised water and ethanol and finally sucked dry.

Preparation of thiol-functionalised carbon nanotubes

Oxidised MWNT were suspended in a solution containing 2-aminoethanethiol (57 mg, 0.7 mmol), dicyclohexylcarbodiimide (DCC, 100 mg, 0.5 mmol) and tetrahydrofuran (THF, 20 mL), sonicated for 15 mins and then stirred for 24 hrs at room temperature. The obtained black suspension was filtered with a 0.45 μm diameter pore PTFE membrane under vacuum, rinsed thoroughly with tetrahydrofuran and deionised water and finally sucked dry.

Synthesis of gold nanoparticles

Gold colloids were prepared by a modified aqueous citrate reduction method whereby tannic acid was used as an additional reducing agent. Briefly, in separate flasks, hydrogen tetrachloroaurate solution (1 wt%, 150 ml) and a mixture of tannic acid (1 wt%) and trisodium citrate solutions (1 wt%) were heated in an oil bath to 85 °C before mixing together. The combined mixture was then heated for 1 hour or until the reaction had completed, as indicated by an unchanging ruby red colour to the solution. The colloids were used as prepared.

Substrate preparation

Clean silicon wafers (100 orientation, Si-Mat) coated with a thin (25 nm) thermal oxide layer were cut into chips $\sim$ 5 mm square and used as is. Smart (Windsor Scientific) multi-electrode arrays (MEA) were purchased with 7 variable gaps ranging from 5 μm to 200 μm . These were sonicated (pulsed-mode) in isopropyl alcohol for 15 minutes to remove any residual resist. After rinsing and drying under nitrogen these were stored for use.

Assembly of networks at liquid-liquid interfaces

MWNT/nanoparticle networks were prepared using a variety of solvent systems. In all cases, water was the sub-phase, into which gold colloids were added. The super-phase was either n-pentane, n-hexane, n-heptane, toluene or diethyl ether. Solvents were HPLC grade or better with dry residue less than 0.0005%, purchased from Sigma-Aldrich and used as received. CNT suspensions were sonicated for 15 minutes to disperse aggregates and then centrifuged for 5 minutes at 8500g. The dark gray supernatant was decanted and used for film assembly. The procedure was performed as follows. To a volume of water (1 - 2.5 ml) a solution of aqueous gold colloid was added followed by an aqueous suspension of thiol-functionalised MWNT (MWNT-SH). An immiscible liquid phase (pentane or toluene, 1ml) was added to form an interface. Ethanol was then injected added rapidly through the superphase, upon which the network visibly began to form at the interface. Film growth at high ethanol volume fractions completed within 2 minutes.

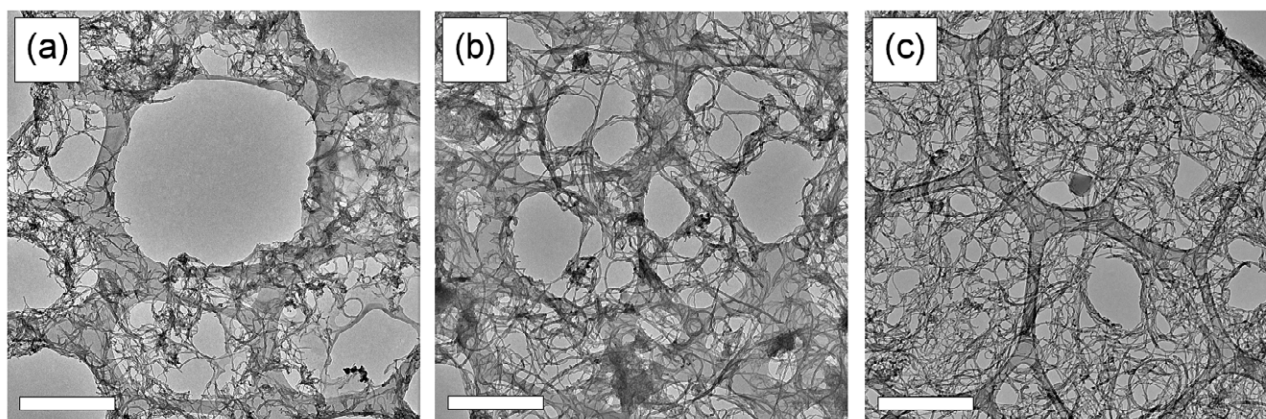
Deposition of networks onto substrates & MEA

Evaporation of the superlayer was then allowed under ambient conditions until an air-water interface, analogous to LB experiments was obtained. The floating network was then dip-coated onto silicon/silica wafers or MEA using a parallel pickup technique. This involves lowering the sample substrate, upside-down, with the desired face parallel to the interface. As the substrate comes into contact with the network it transfers quantitatively onto the substrate face. Devices were then rinsed with water (18.2 MΩ.cm) and immersed in water for 18 hours to dissolve any unbound salts or other material. The chip was then removed, rinsed and dried under flowing nitrogen. Devices were then immersed in the non-aqueous phase (corresponding to that used during film growth) and soaked, rinsed and dried in a similar way. Finally, washed chips were sealed in quartz tubes which were then evacuated (10^{-5} Torr) and heated to 200 °C overnight. These chips were removed from the tube and stored prior to analysis.

Film strength & cohesion

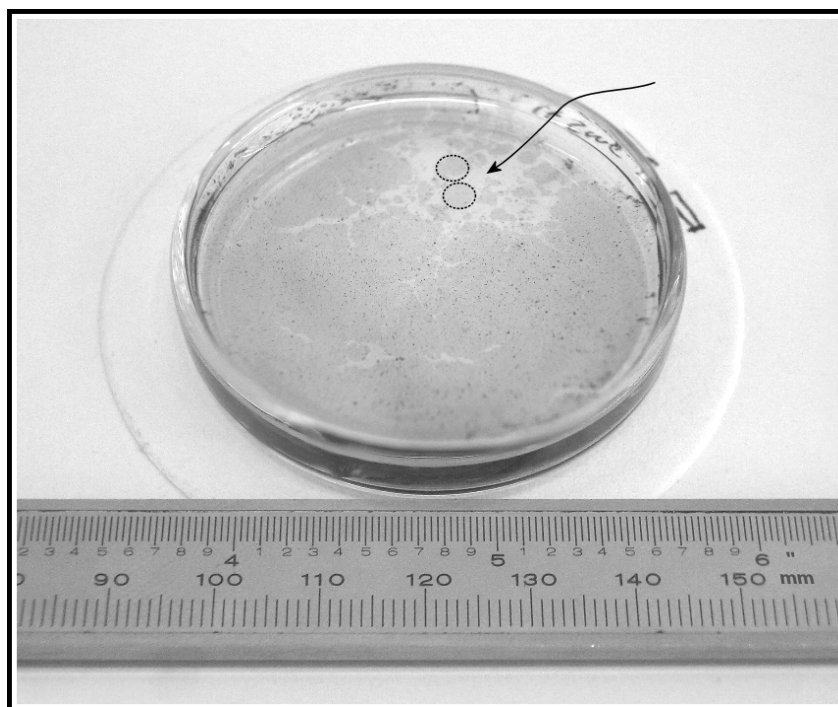
The nanotube films were sufficiently mechanically robust for the lift-off from the interface and deposition on solid substrates or TEM specimen grids. MWNTs are

interwoven into a thin sheet which are held together presumably by inter-tube van der Waals (vdW) interactions, similar to those causing formation of bundles of single-walled nanotubes (SWNT). However, unlike SWNT bundles, the MWNT do not show a tendency to form parallel sidewall-sidewall vdW interactions and generally cross each other to form a structure with many interstices or pores rather than a dense mat. Nanotube functionality has an effect on the network cohesion. Annealed MWNT are able to bridge small gaps in the support film but presumably only vdW forces play a role. The strongest films are seen for carboxylic acid (-COOH) functionalised MWNT where additional cohesion can be brought about through hydrogen bonding between neighbours. Thiolated tubes, although not as robust as the acid case are better than purely annealed nanotubes and it is thought that weak hydrogen bonding may occur through residual, unmodified acid groups. Disulphide bridges (-S-S-) may also form between thiol groups in close proximity.



SI Figure 1: Series of TEM images for films prepared from (a) annealed, unfunctionalised MWNT, (b) thiolated MWNT and (c) carboxylic acid functionalised tubes, in order of increasing film cohesion. The annealed nanotubes can be seen to bridge small gaps in the carbon support film, thiolated tubes can bridge larger gaps and acid functional tubes are self-supporting over even very wide holes. Scale bars are 1 micron.

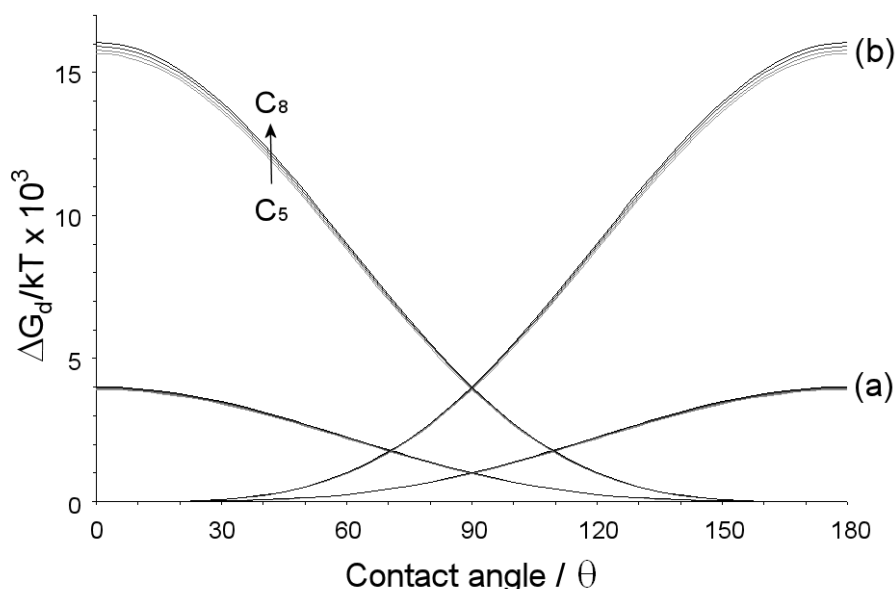
Film bulk morphology & sampling



SI Figure 2: Photograph of a large area network of unfunctionalised MWNT floating on a liquid interface. The fractured region marked with an arrow is where sampling has been performed. Two circular (3 mm diameter) islands are marked which have been sampled from the surface with a Pt sample loop and redeposited on the surface demonstrating that quantitative sampling may be performed. Due to disturbance of the surface during sampling the film has broken into large cm scale islands. Smaller fragmentation (not visible here) is evident under microscopic examination. Scale is shown in mm (and inches) in the foreground.

Interfacial Entrapment

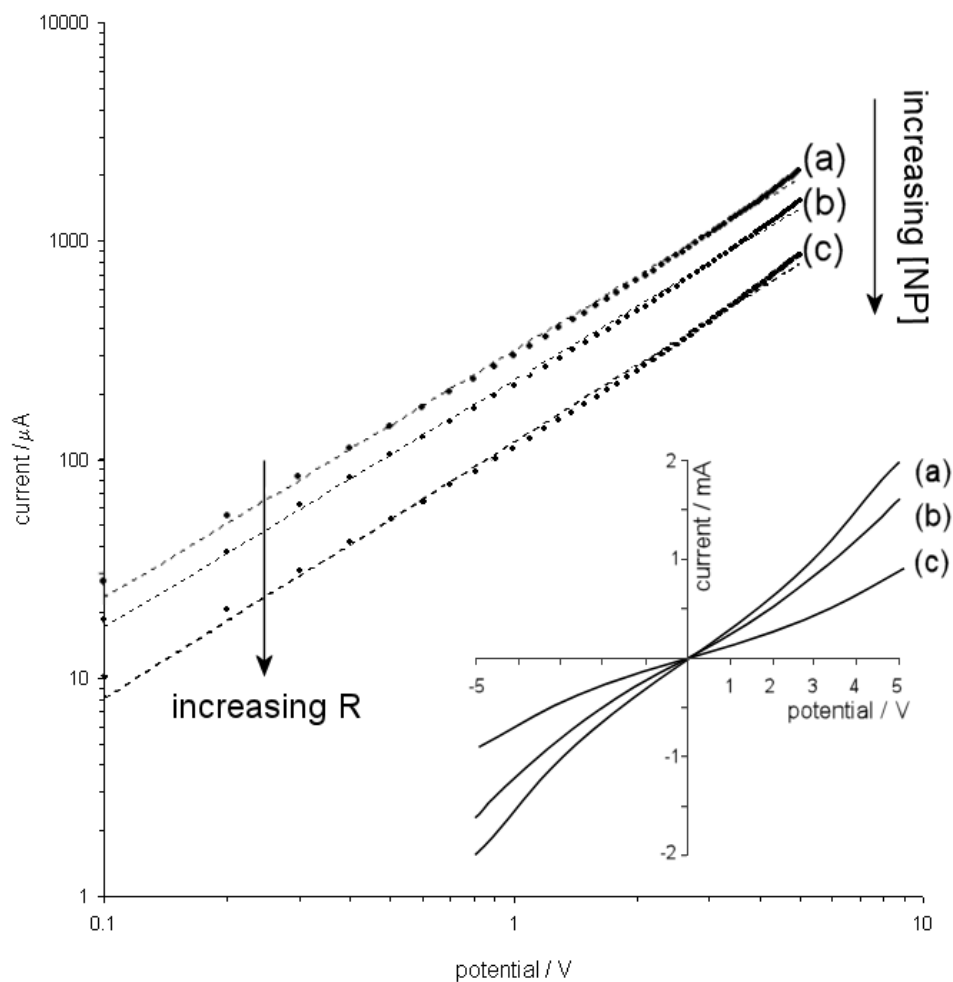
For those particles that are not completely wet by either phase, *i.e.* those systems where the ternary contact angle is between 30 ° and 150 °, the detachment energy is tens, hundreds or even thousands of times kT (the thermal energy). This barrier to removal increases with particle size and also with a particle's aspect ratio. Thus MWNT with aspect ratios on the order of 100 (length / diameter) are likely to be trapped irreversibly. The addition of a non -solvent will aid this process as will the interaction between particles, such as between MWNT and nanoparticles. This may increase the likelihood of their interfacial entrapment by charge transfer away from the particles or displacement of citrate molecules leading to a change in the interfacial tension of the particle in the system.



SI Figure 3: Plot showing the results of a calculation ** of the free energy of detachment of a particle from an interface *vs.* the contact angle (through the aqueous phase) for spherical nanoparticles with diameters of (a) 10 nm and (b) 20 nm. Data is shown for series of interfacial tensions for n-alkane / water interfaces from pentane to octane. The two branches of each plot are for detachment into the aqueous or oil phase.

B.P. Binks, T.S. Horozov, in *Colloidal Particles at Liquid Interfaces*, (Eds.: B.P. Binks, T.S. Horozov), Cambridge University Press, Cambridge, **2006, pp. 1-77.

I(V) data for varying NP content



SI Figure 4: Log-log plots of $I(V)$ data (across a $5\ \mu\text{m}$ gap) for networks prepared from bulk solutions with (a) a 10:1 ratio, (b) a 10:1 ratio with a 3-fold higher concentration, and (c) 80:1 ratio of gold NP and thiolated MWNT, and corresponding to the films shown in **Figure 4** of the main paper. Resistances are $3.2\ \text{k}\Omega$, $4.1\ \text{k}\Omega$, & $8.0\ \text{k}\Omega$ respectively for plots (a), (b) and (c) and increase with increasing nanoparticle composition. Insets show the full $I(V)$ curves.