Supporting Information

Synthetic procedures

Shortened carbon nanotubes by gas-phase oxidation ($MWNT_{60\%shortened}$) [1]

MWNT (100 mg, as-received) were placed into an alumina crucible and annealed in air at 500 ^{o}C and the decrease in mass recorded. Samples heated for 40 minutes showed a *circa* 60 % decrease in mass and were termed 'annealed MWNT;' samples heated for 20 minutes showed a *circa* 30 % decrease in mass and were termed 'part-annealed MWNT.' The obtained solids were then sonicated in concentrated hydrochloric acid (37 % HCl, 50 mL) at room temperature for 30 minutes, diluted with deionised water (250 mL), filtered with a 0.45 μm diameter pore polytetrafluoroethylene (PTFE) membrane (*Aldrich*) 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 (~ 40 mg or 70 mg for annealed and part-annealed MWNT respectively).

Oxidation of nanotubes in nitric acid (MWNT-COOH) [2]

Annealed $MWNT_{60\%shortened}$ (25 mg) were sonicated in nitric acid (2.6 M HNO_3, 50 mL) at room temperature for 15 minutes and then refluxed at 120 ^{o}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. Any residual water was removed by drying under vacuum to yield a black solid (23.67 mg, 94.6 %).

Thiolation of oxidised carbon nanotubes (MWNT-SH) [3]

Oxidised MWNT-COOH were suspended in a solution containing 2-aminoethanethiol ($H_2N(CH_2)_2SH$, 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 THF and deionised water and finally sucked dry. Any residual water was removed by drying under vacuum to yield a black solid (7.70 mg, 84.3 %).

Preparation of charge-doped carbon nanotubes ($[MWMT]^{-}$) [4]

Sodium metal (100 mg, 4 mmol) was added to a solution of naphthalene (385 mg, 3 mmol) in distilled THF (50 mL) and refluxed under nitrogen at 70 ^{o}C for 2 hours. The obtained dark green solution (sodium naphthalate) was then added to annealed $MWNT_{60\%shortened}$ (5 mg) and stirred under nitrogen for 8 hours at room temperature. The obtained green/black suspension was filtered with a 0.45 μm diameter pore PTFE membrane under vacuum, rinsed thoroughly with distilled THF and finally sucked dry. Any residual water was removed by drying under vacuum to yield a black solid. This was repeated for oxidised and thiolated MWNT.

Preparation of surfactant-wrapped carbon nanotubes ($[MWNT]_{SDS}$) [5]

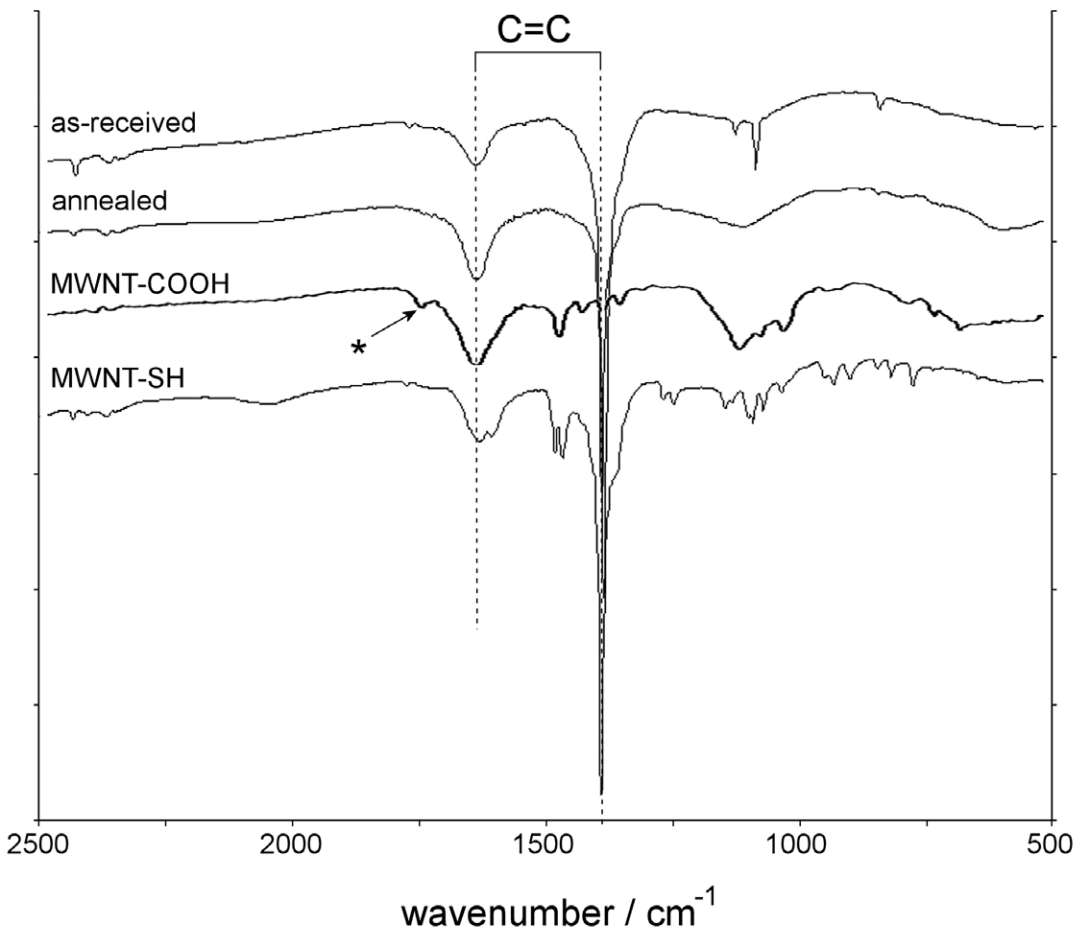
Sodium dodecyl sulphate (SDS, 20 mg, 1 wt%) and annealed $MWNT_{60\%shortened}$ (1.08 mg) were sonicated in deionised water (2 mL) for 30 minutes at room temperature to yield a light grey suspension. This was repeated for oxidised and thiolated MWNT-COOH and MWNT-SH respectively.

1 J. G. Wiltshire, A. N. Khlobystov, L. J. Li, S. G. Lyapin, G. A. D. Briggs and R. J. Nicholas, *Chem. Phys. Lett.*, 2004, **386**, 239.
2 J. Zhang, H. Zou, Q. Qing, Y. Yang, Q. Li, Z. Liu, X. Guo and Z. Du, *J. Phys. Chem. B*, 2003, **107**, 3712.
3 Z. Liu, Z. Shen, T. Zhu, S. Hou, L. Ying, Z. Shi and Z. Gu, *Langmuir*, 2000, **16**, 3569.
4a A. Penicaud, P. Poulin, A. Derre, E. Anglaret and P. Petit, *J. Am. Chem. Soc.*, 2005, **127**, 8.
4b P. Petit, C. Mathis, C. Journet and P. Bernier, *Chem. Phys. Lett.*, 1999, **305**, 370.
5 D. A. Britz and A. N. Khlobystov, *Chem. Soc. Rev.*, 2006, **35**, 637.

Spectroscopic characterisation

Infra-red spectroscopy (FTIR)

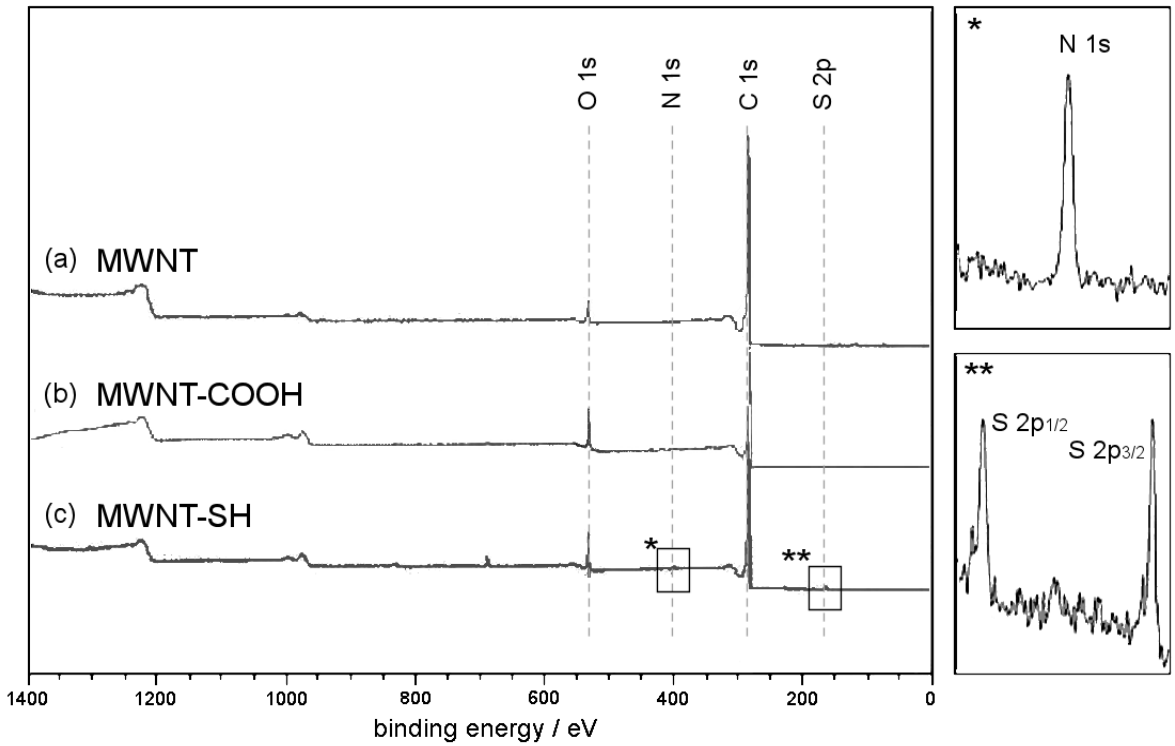
Infra-red spectra were measured as KBr discs using a Nicolet 380 FT-IR spectrometer over the range 400 - 4000 cm^{-1}. No evidence of oxygen-containing groups is seen for the air-annealed nanotubes and it is only after nitric acid oxidation that a small carbonyl signal due to carboxylic acid groups is observed. The exhibition of a characteristic peak at 1736 cm^{-1} (SI figure 1, *), corresponding to a $\upsilon_{C=O}$ stretching vibration associated with the –COOH functional group, verifies the successful incorporation of carboxylic acid functionality for MWNT-COOH. It is interesting to note that the spectrum of the air-annealed tubes is largely featureless showing only two distinct C=C bands. This implies the tubes are clean and contain little or no solvent after annealing.



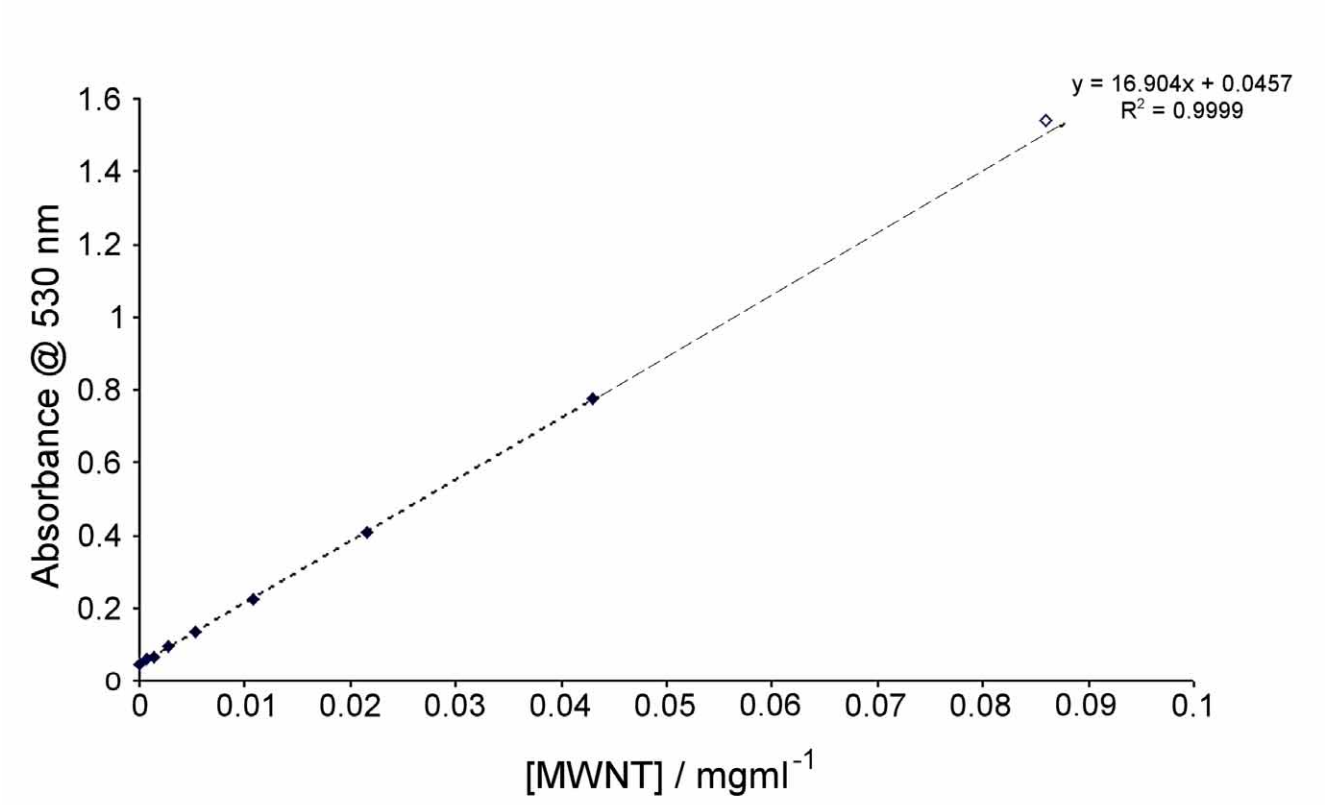
S.I. Figure 1. Comparison of FTIR spectra for $MWNT_{as\text{-}received}$, $MWNT_{annealed}$, MWNT-COOH and MWNT-SH. The * marks the position of a –COOH carbonyl stretching vibration.

X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectra were recorded using a Kratos AXIS ULTRA with monochromated Al *Kα* radiation (10 kV anode potential, 15 A emission current) in fixed analyser transmission mode (80 eV pass energy). XPS analyses of annealed $MWNT_{60\%shortened}$, oxidised MWNT-COOH and thiolated MWNT-SH (S.I. Figure) revealed the presence of nitrogen and sulphur, two elements indicative of the aminoalkanethiol linker, solely in thiolated MWNT-SH, confirming the successful introduction of thiol-functionality to the nanotube framework.

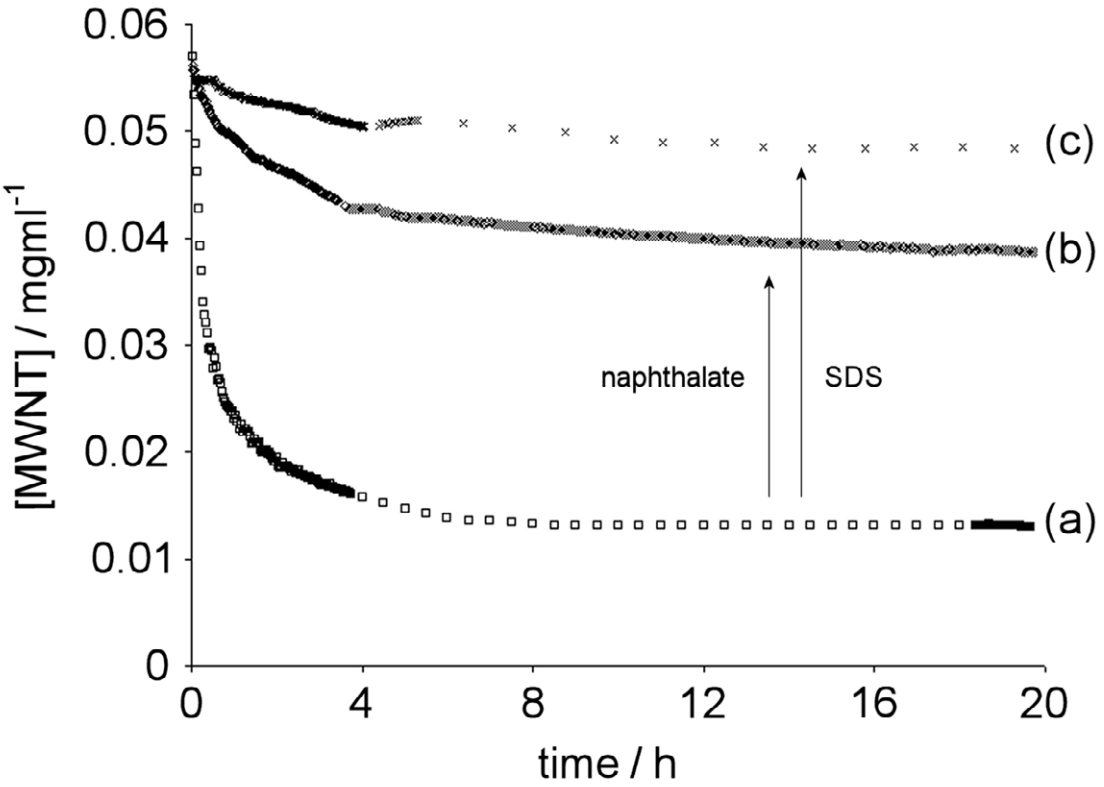


S.I. Figure 2. Comparison of XPS spectra and determined elemental ratios for MWNT before and after functionalisation: (a) annealed $MWNT_{60\%shortened}$; (b) annealed, oxidised MWNT-COOH; (c) annealed, oxidised, thiolated MWNT-SH. Insets are the N (*) and S (**) peaks.

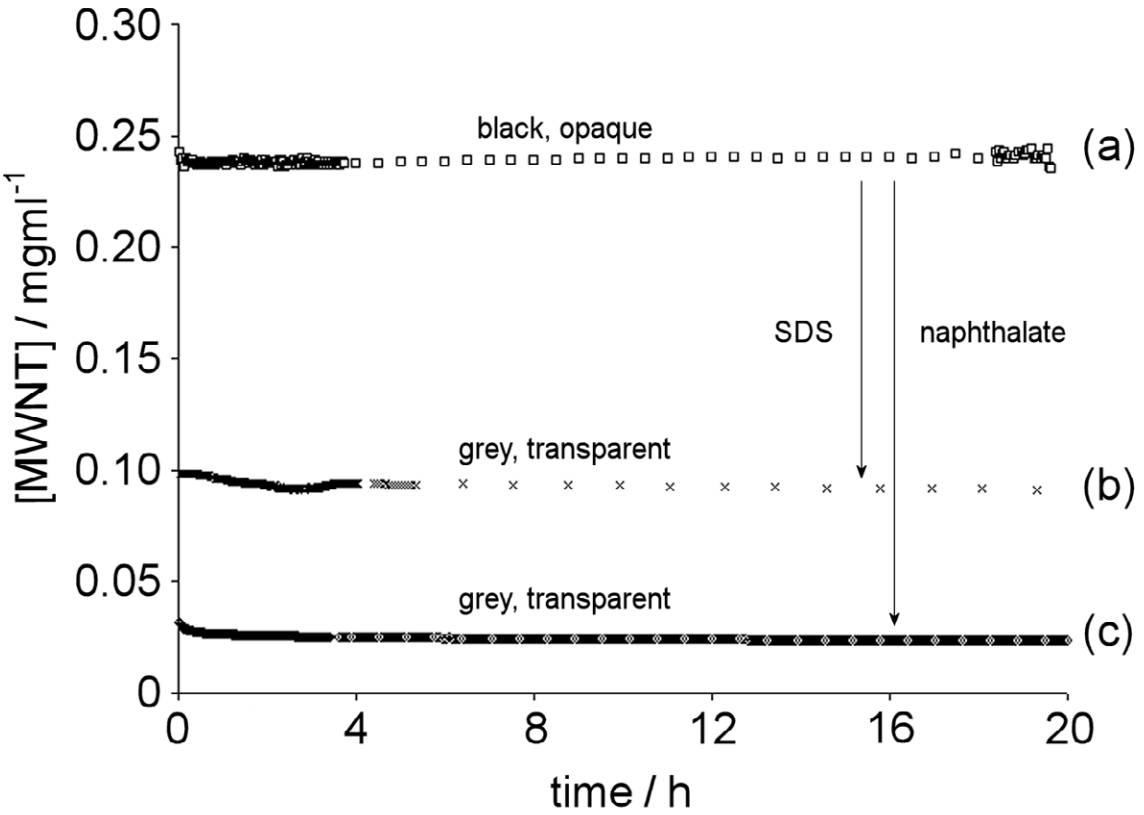


S.I. Figure 3. Demonstration of the determination of the extinction coefficient of a MWNT suspension by UVvis spectroscopic analyses of an aqueous dilution series. The best fit line ($R^2 = 0.9999$) is calculated through those points below A = 1 (a small positive deviation from the Beer-Lambert relation is observed in the final point at higher concentration). The concentration of an unknown MWNT suspension can thus be calculated through measurement of its optical density (absorption). The absolute concentration of the suspension used in the series was determined through filtration & gravimetry.

Concentration profiles



S.I. Figure 4. Concentration profiles showing the change in stability of annealed $MWNT_{60\%shortened}$ before (a) and (b) after charging nanotubes with sodium naphthalate or (c) SDS wrapping.



S.I. Figure 5. Concentration profiles showing the change in stability of MWNT-COOH before (a) and (b) SDS wrapping or (c) after charging nanotubes with sodium naphthalate.