Supporting Information: A versatile, solvent-free methodology for the functionalisation of carbon nanotubes

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Experimental

All reactants were purchased from Sigma-Aldrich, UK. For use in the gas-phase setup (see Experimental section in the main text), the reactants were used as purchased. Before use in liquid-phase setup, radical inhibitors were removed by chromatographic purification over basic alumina powder.

Table S1 provides additional information about the chemical compounds grafted onto the CNTs.

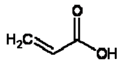
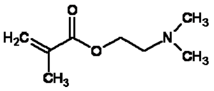
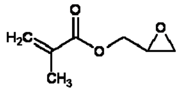
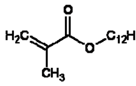
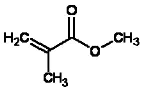
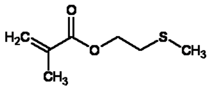
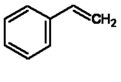
Acronym	Reactant	Washing agent	Chemical Structure
AA	acrylic acid	water	
AN	acrylonitrile	DMF	
DMAEMA	2-(dimethylamino) ethyl methacrylate	water	
GMA	glycidyl methacrylate	acetone	
IDD	1-iodododecane	toluene	$I{-}C_{12}H_{25}$
LMA	lauryl methacrylate	toluene	
MMA	methyl methacrylate	toluene	
MTEMA	2-(methylthio) ethyl methacrylate	THF	
Sty	styrene	toluene	

Table S1: Overview of organic reactants used for CNT grafting. The washing agent is a known organic solvent for the corresponding polymer.

Thermogravimetric analysis (TGA) was carried out using a Perkin-Elmer Pyris 1 TGA. Experiments were performed on (2±0.1) mg of CNT material under air flow

(flow rate 10 mL/min) applying a constant ramping rate of 10 K/min in a temperature range between 50 and 850ºC. The grafting ratio Δ, i.e. the weight of the chemisorbed organic monomer relative to the total weight of the sample, was determined from the height of the first step-like feature in the TGA weight loss profile of the grafted CNTs, as described in the Supplementary Information.

The surface coverage of the CNTs, Θ, was estimated from the ratio of the surface area of the CNTs, A_{CNT}, and the surface area of a monolayer of the grafted reactant molecules, $A_{grafted}$:

$$\Theta = \frac{A_{grafted}}{A_{CNT}} = \frac{N_A \cdot a \ \cdot n_{grafted}}{m \ \cdot S_{BET}} \qquad (1)$$

where N_A is Avogadro's number, m the weight of the CNTs, and S_{BET} the specific surface area of the CNTs as determined by BET measurements. The molar amount of monomer grafted to the surface, $n_{grafted}$ was calculated from the grafting ratio Δ. The cross-sectional area of the organic reactant, a_{react}, was estimated from the density, ρ_{react}, and its molecular weight, M_{react}, using the following equation:[1]

$$a_{reac\tan t} = 1.091 \cdot \left(\frac{\rho_{react}}{M_{react}} \right)^{2/3} \qquad (2)$$

SEM images were obtained on a GEMINI LEO 1525 FEGSEM at an accelerating voltage of 5 kV; TEM images were obtained on a JEOL 2000FX, operating at 200 kV. Samples were dispersed in methanol, and deposited onto an alumina stub or a holey carbon film, respectively. Raman spectra of CNT powders were collected in a range between 1000 and 2200 cm^{-1} on a LabRam Infinity Raman spectrometer, using a 532 nm laser. The I_G/I_D ratio was determined from the ratio of surface areas under the Raman bands at around 1580 cm^{-1} (G-band) and at around 1350 cm^{-1}(D-band). A large I_G/I_D ratio indicates pronounced graphitic crystallinity and implies a small defect concentration.[2]

Inverse gas chromatography (IGC) allows the determination of the dispersive surface energy ($\square^{d}$), reflecting CNT surface properties purely due to London forces, and the calculation of acceptor and donor numbers (K_A and K_D), quantifying the ability of the CNT surface to undergo electron accepting and donating interactions.[3] IGC measurements were carried out in a gas chromatograph (Surface Measurement Systems Ltd., UK), at constant conditions which were chosen to obtain reliable and comparable results.[3] The CNT samples were preconditioned in the IGC column at 120ºC for 2 h before each measurement to eliminate any physiosorbed surface contaminants. IGC tests employed a column temperature of 100ºC, a flow rate of 10 mL/min and an injection volume of 1.125 mL. All measurements were performed using helium as carrier gas and methane as inert reference (both gases purchased from BOC, UK). Adsorbate vapors were generated from the organic liquid (HPLC grade, purchased from Sigma-Aldrich); n-hexane, n-heptane and n-octane were used for the quantification of the dispersive surface energy, and ethanol, butanone, ethyl acetate and 1,4-dioxane were employed for the determination of the acceptor and donor numbers. IGC results presented are average values of three measurements. For the dispersion experiments, 5 mg CNTs were sonicated in 5 mL solvent for 30 min and then centrifuged at 10000 rpm for 15 min in order to sediment non-dispersed CNTs. The absorbance of the supernatant was measured on a Lambda 950 spectrometer (Perkin, UK) at 800 nm, and the CNT concentration was determined using Lambert-Beer's Law employing an extinction coefficient[4] of 35.10 mg mL^{-1} cm^{-1}. Dispersion and IGC experiments were also performed on CNTs that were heat-activated under the conditions outlined above , and subsequently exposed to air (instead of organic reactant) for more than 12 h; this control sample is referred to as 'air-exposed' CNTs in this paper.

For Böhm's titration, 2.5 mL of 0.05 M aqueous sodium hydroxide solution were added to 50 mg CNTs in a polypropylene vial. The CNT suspension was sonicated for 2 hours and further mechanically agitated on an orbital shaker for 4 days. The mixture was then filtered through a polypropylene membrane filter (0.2 mm pore size) and back titrated against 0.01 M aqueous hydrochloric acid solution under nitrogen to restrict any CO_2 absorption.

X-band (9 GHz) continuous-wave Electron paramagnetic resonance (cw-EPR) spectra were recorded with a Bruker ESP300 spectrometer equipped with a high sensitivity resonator (SHQEW0401). Temperatures were adjusted between room temperature and 4 K by a helium cryostat (Oxford ESR 910). Conditions used were as follows: Microwave frequency 9.39 GHz; microwave power, 20mW;

modulation frequency, 100 kHz; modulation amplitude, 0.2mT.

For the radical quenching experiment, 4.8 mg of galvinoxyl were dissolved in 100 mL dry toluene, and 10 mL of the solution were added to 10 mg of thermally-activated and untreated commercial CNTs, respectively, under vacuum in the liquid-phase experimental setup, and left to react for 1 h. 200 μl of reacted solution were diluted by 2 mL of dry toluene and the UV-Vis spectra were recorded on a Perkin Elmer 950 UV-Vis spectrometer between 350 and 550 nm. Tagging of the grafted in-house CNTs with gold particles was carried out by sonicating around 0.5 mg CNTs in 2 mL methanol for 10 min, followed by addition of 1 mL of aqueous dispersion of 20 nm gold colloids (used as purchased from Sigma-Aldrich) and further sonication for 10 min. A few drops of the resulting dispersion were deposited on an aluminum stub. After drying in air overnight, the CNTs deposit was repeatedly rinsed with water to remove excess gold particles.

Characterisation data

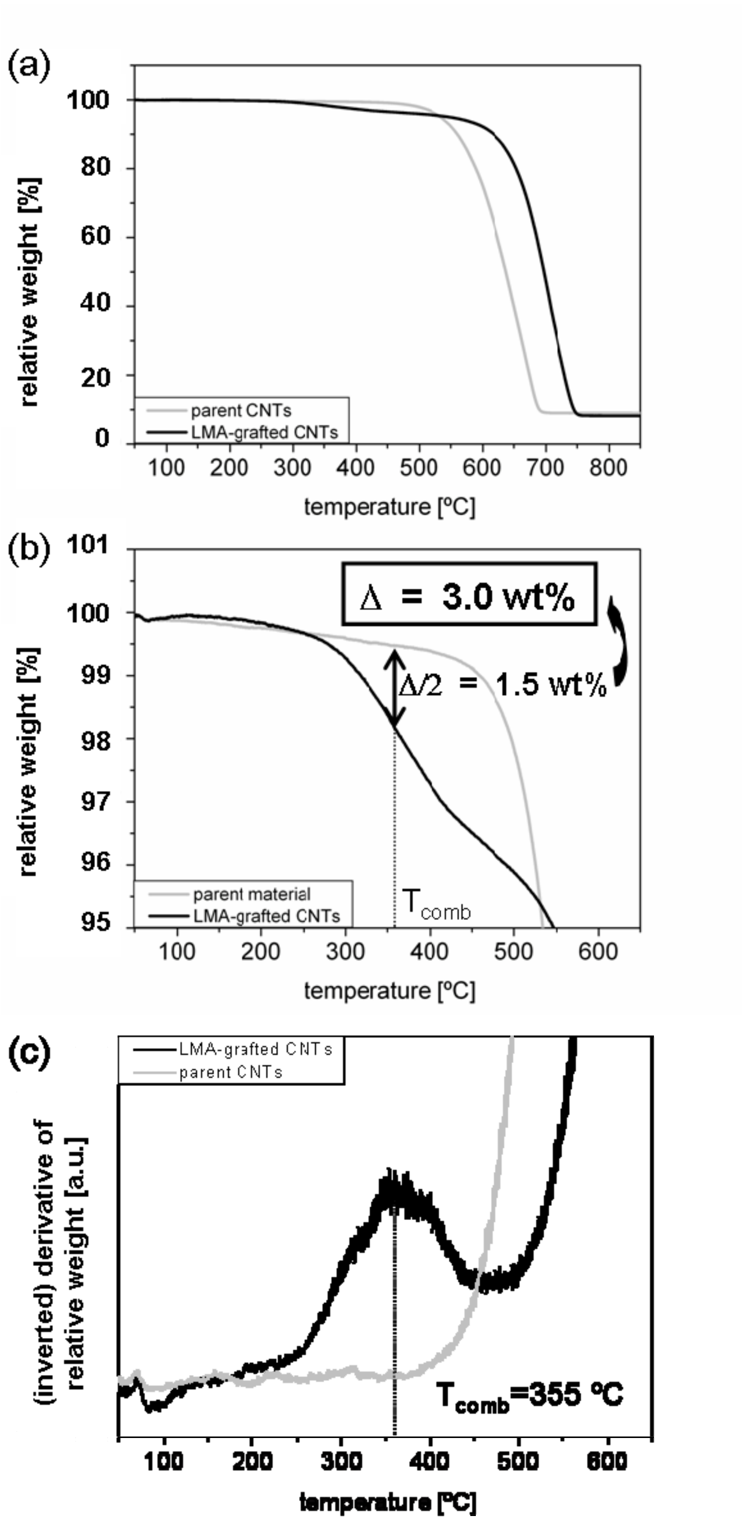


Figure S1: TGA analysis of LMA-grafted CNTs illustrating the determination of the combustion temperature of the grafted organic matter, T_{comb}, and the grafting ratio, Δ : (a) complete weight loss profiles in the temperature range of 50-850ºC; (b) magnification of (a) in the temperature range of 50-650 ºC; (c) derivatives of weight-loss profiles in (b).

In the first derivative of the TGA weight loss profile, the two peaks corresponding to the combustion of the grafted organic matter and the CNTs, respectively, were usually not entirely separated, indicating that the oxidation of the grafted oligomers was not completed at the onset of the CNT combustion. Therefore, the grafting ratio Δ could not directly be determined from the height of the corresponding TGA step feature, but was estimated as double of the weight loss at the combustion temperature, T_{comb}, of the grafted organic matter (Figure S1(b)). T_{comb} was determined at the peak maximum of the corresponding peak in the first derivative of the TGA trace (Figure S1(c)).

Note that LMA-grafting improves the combustion resistance of the CNTs significantly (see shift of the complete TGA trace to higher temperatures in Figure S1(a), due to protection of pre-existing defect sites.

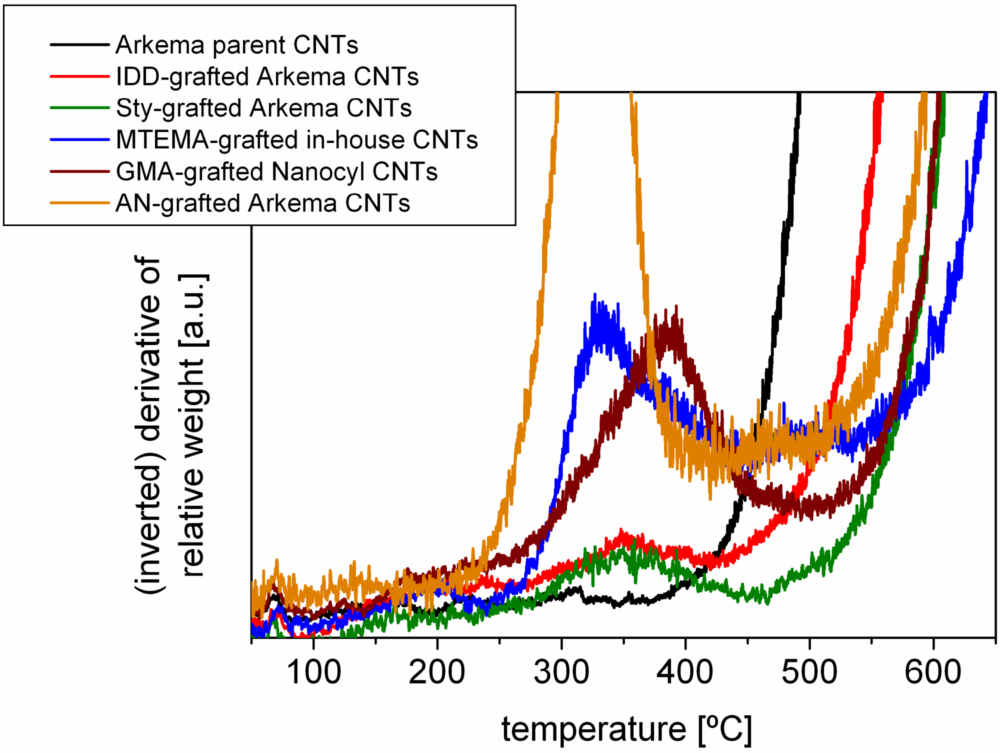


Figure S2: Derivatives of the TGA-profiles in Figure 5 of the main text.

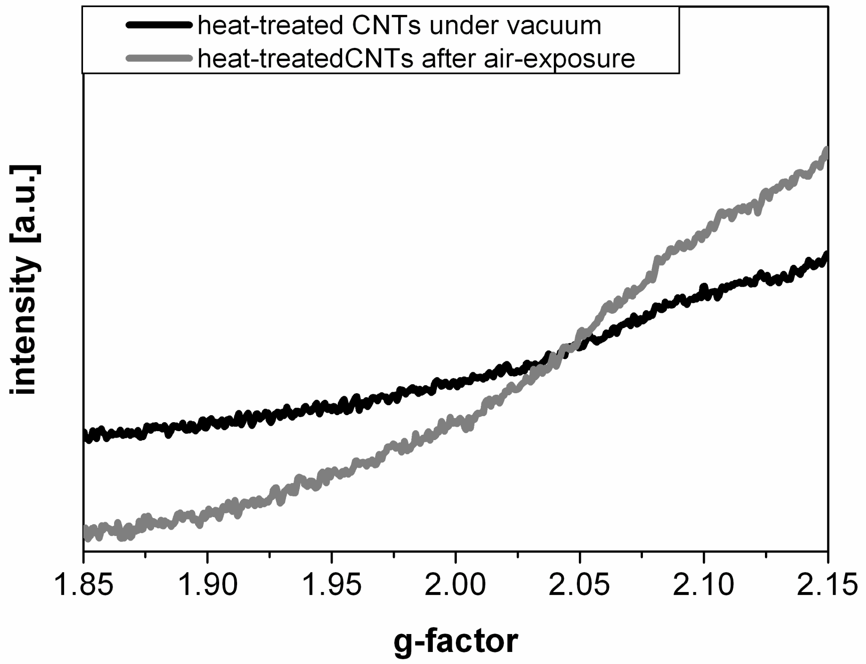


Figure S3: EPR spectra of heat-treated Arkema CNTs before and after air exposure, recorded at room temperature.

The exchange coupling model[5] states that the spin resonance of localised spins starts to dominate the EPR spectrum of materials with conduction electrons, such as CNTs, only at very low temperatures. Therefore, radicals on the CNTs are not expected to be detectable at room temperature, particularly at the low concentrations relevant to the current study. A broad EPR signal at g~2 has been observed in the room temperature EPR spectra of carbon nanotubes in some cases. This signal is usually attributed to the spin resonance of the delocalised conduction electrons (CESR) of the CNTs.[6] For our heat-treated samples, we do not detect such a signal at g~2 at room temperature (see Figure S3); a similar absence of the CESR signal has been previously reported for (catalyst-containing) MWCNTs[7] and heat-treated SWCNTs[8] and has been attributed to interference by metal impurities in the samples and/or defectiveness of the carbon framework.

grafted monomer	**setup**	**K_D**	**K_A**	**I_G/I_D**
parent	n/a	0.53	0.23	0.85
air-exposed	n/a	0.59	0.25	0.86
Sty	LP	0.52	0.21	0.82
IDD	LP	0.51	0.19	0.80
MMA	LP	0.58	0.19	0.81
MMA	GP	0.57	0.19	0.84
LMA	LP	0.58	0.19	0.78
GMA	LP	0.51	0.20	0.81
DMAEMA	LP	0.63	0.22	0.84
AN	GP	0.63	0.24	0.84
AN	LP	0.63	0.26	0.86
AA	LP	0.41	0.22	0.83

Table S2: Electron acceptor and donor numbers, K_A and K_D, from IGC measurements, and I_G/I_D ratio from Raman spectroscopy for commercial CNTs grafted with various functional organic compounds.

sample	**concentration of dispersed CNTs [mg/L]**						
	hexane	**toluene**	**butyl acetate**	**DMF**	**ethanol**	**water**	**Water (pH4)**
parent	0.5±04	0.51±0.08	3.2±0.1	31±2	14±1	0.12±0.02	0.14±0.09
air-exposed	0.4±0.3	0.5±0.2	1.2±0.1	11±1	2.4±0.9	0.11±0.05	0.12±0.06
LMA	1.2±0.1	0.68±0.09	35.6±0.3	34±2	2.6±0.2	0.2±0.1	0.2±0.1
MMA	0.2±0.1	0.58±0.09	30.7±0.7	30±2	1.6±0.1	0.18±0.09	0.2±0.1
DMEMA	0.12±0.09	0.22±0.05	2.1±0.1	5.4±0.1	5.3±0.7	0.6±0.2	8.7±0.4
AN	0.2±0.1	0.8±0.1	42±1	52±3	21±2	1.0±0.5	0.11±0.06

Table S3: Dispersion in different solvents for commercial CNTs grafted with various functional compounds. ‘air-exposed’ refers to heat-activated CNTs that have been exposed to air instead of organic reactant.

References

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