Supplementary Material (ESI) for Chemical Communications

-Supporting Information-

Removal of amorphous carbon for the efficient sidewall functionalisation of single-walled carbon nanotubes

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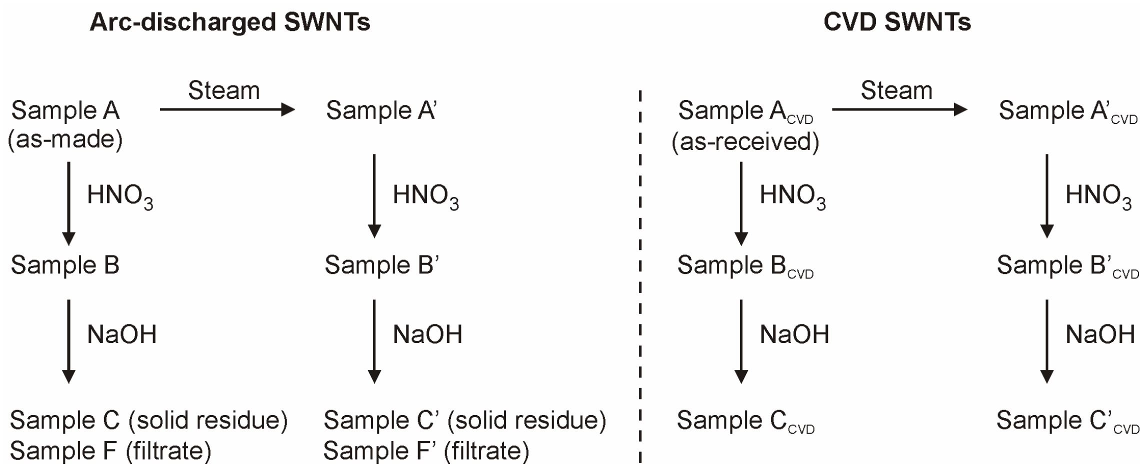
SAMPLE NAMES



Scheme S1. Schematic representation of the treatments done on arc-discharged and CVD SWNTs. For ease comparison between samples, steam treated SWNTs are indicated by the superscript [**’**] and CVD SWNTs by the subscript [$_{\mathbf{CVD}}$]. All the treatments are followed by washing with distilled water.

AFM DATA ON SAMPLES A’, C’ & C

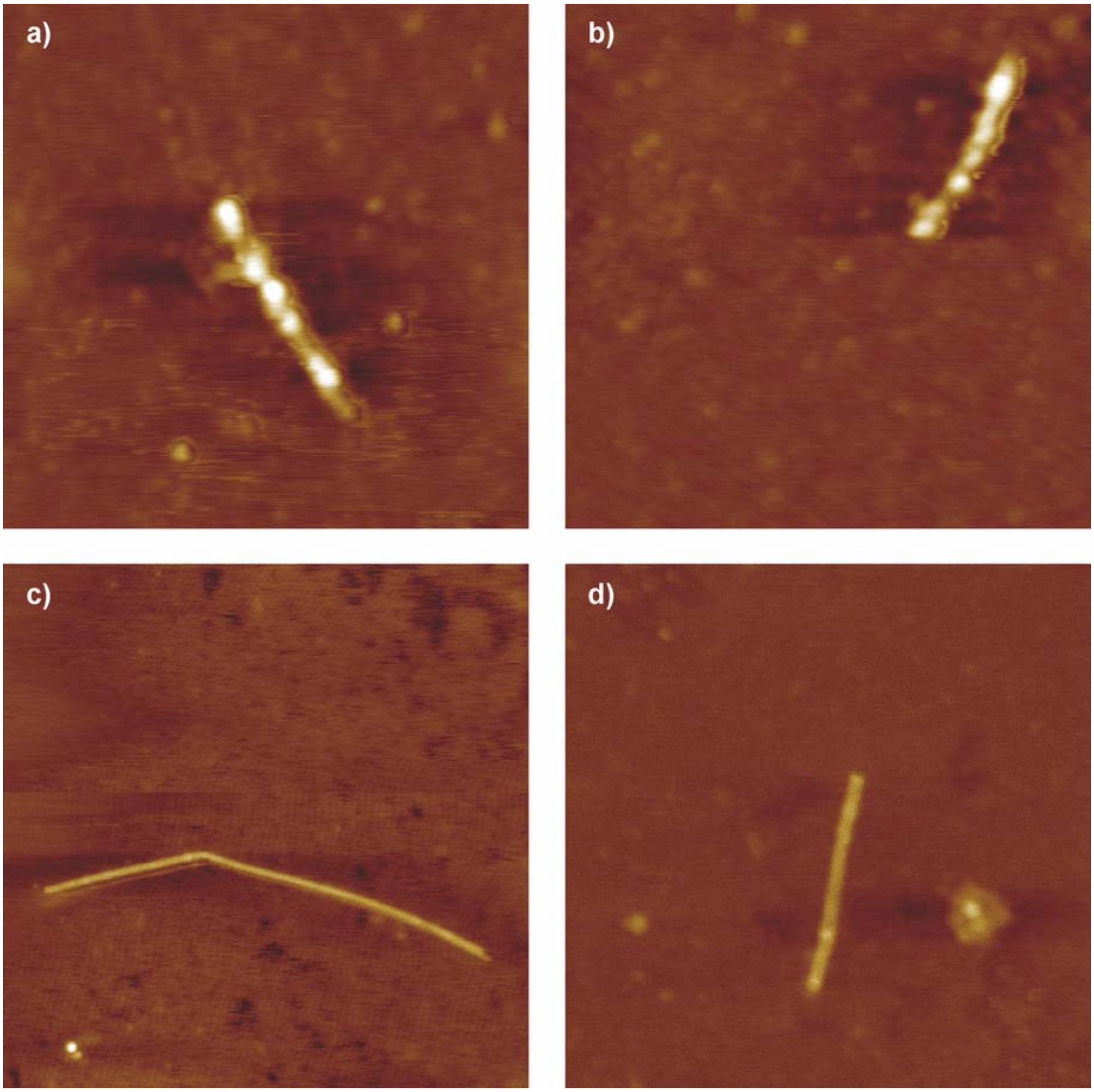


Figure S1. AFM of samples treated with thionyl chloride and cysteamine after exposure of gold colloids (a, b) sample C’, 400x400 nm; (c) blank experiment conducted on sample A’, 750x750 nm; (d) blank experiment conducted on sample C, 400x400 nm. In all images *z* scale is 0-5 nm. Gold nanoparticles (large bright dots) can clearly be seen along SWNT walls in sample C’ (a&b). In contrast, no gold nanoparticles are present along the SWNT walls in the blank experiments (c&d).

CHARACTERIZATION OF CVD SWNTs

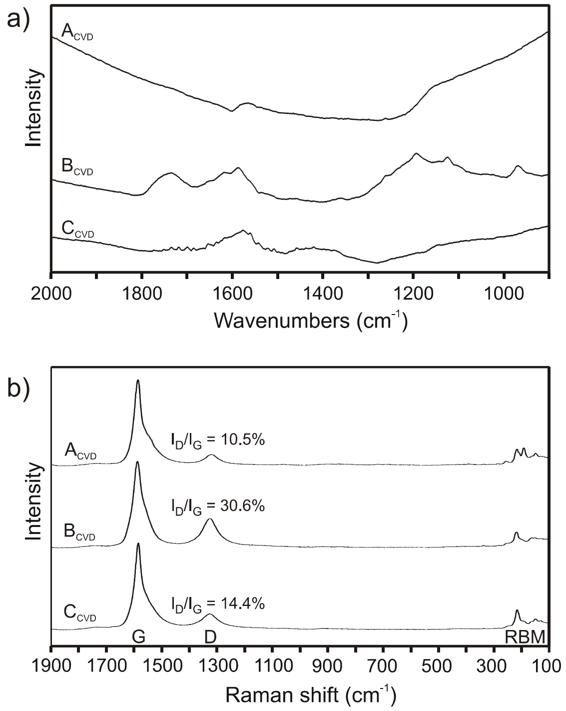


Figure S2. a) FTIR and b) Raman spectra of as-received CVD SWNTs (sample A_{CVD}), after acid treatment (sample B_{CVD}) and base wash (sample C_{CVD}).

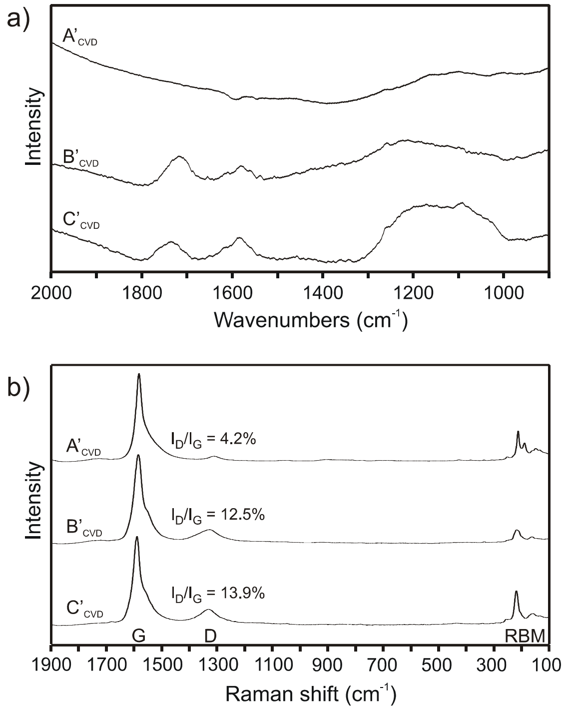


Figure S3. a) FTIR and b) Raman spectra of steam purified CVD SWNTs (sample A'$_{CVD}$), after acid treatment (sample B'$_{CVD}$) and base wash (sample C'$_{CVD}$).

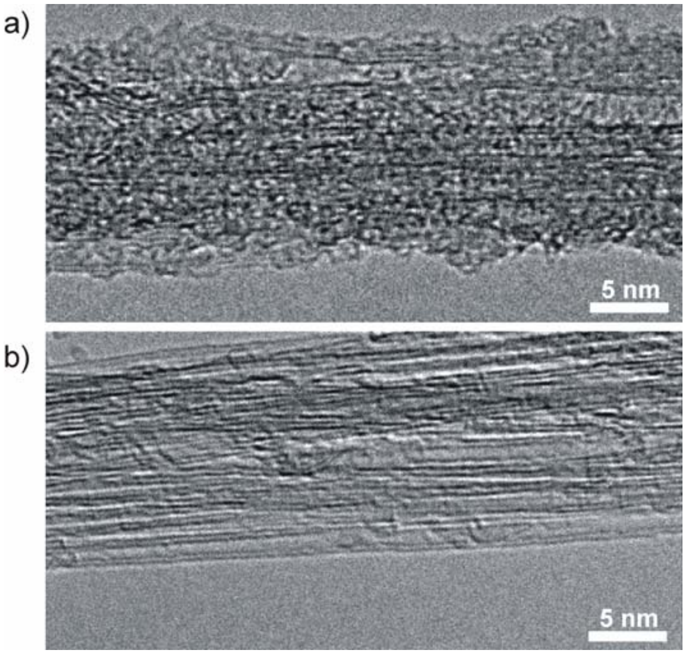


Figure S4. HRTEM image of a) as-received CVD SWNTs after nitric acid treatment (sample B_{CVD}) and b) steam purified CVD SWNTs after nitric acid treatment (sample B'_{CVD}). A much larger degree of amorphous coating (oxidation debris) can be seen in image (a) compared to (b).

EXPERIMENTAL DETAILS

The following procedure was carried out for arc-discharged and CVD SWNTs before (samples A&A_{CVD}) and after the steam purification (samples A'&A'_{CVD}):

SWNTs (50 mg) were refluxed in 3M HNO_3 (50 mL) for 24h. The solution was diluted with 50 mL of distilled water and filtered with a 0.2 µm polycarbonate membrane (Whatman). In order to remove the oxidation debris (CCFs) from the acid treated SWNTs, the sample was then ultrasonicated (Heat Systems – Ultrasonics. Inc. Model W-375) for 5 min in 4M NaOH (50 mL) and filtered (it was found that longer treatment with NaOH was not necessary to remove the oxidation debris). The remaining solid was then ultrasonicated for 1 min in distilled water (50 mL) and filtered. This washing step with water was repeated several times until the filtrate was colorless, neutral and the Raman and IR spectra of the remaining solid presented no change with extra rinsing with water.

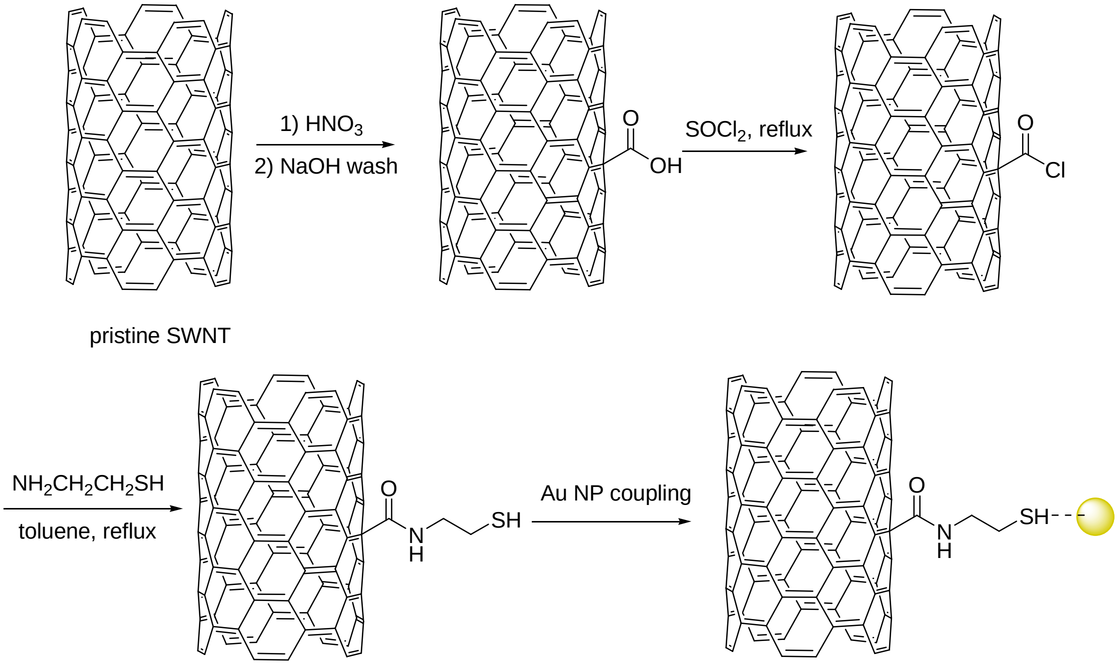
Steam purification of SWNTs

Steam purification of SWNTs was carried out at 900 ^oC as previously reported.[1] Briefly, 400 mg of as-received CVD SWNTs were placed into a silica tube (2.5 cm diameter) and sonicated with 10 mL of water for 15 min. The dispersion was then frozen in liquid nitrogen and attached to a vacuum line through a condenser. After pumping and filling the whole system three times with argon, the sample was kept under argon and allowed to warm to room temperature. The furnace was then heated to 900 °C for 4h.

As-made arc-discharged SWNTs were placed into a silica tube (9 mm diameter) and immobilized with silica wool at both sides. The furnace was heated to 900 °C for 2h whilst steam was introduced by bubbling argon (190 mL/min) through hot water (98 °C). The use of both steam purification systems have been previously reported.[1]

Chemical modification of carboxylic acid groups on sample C' for the detection of functionality by Atomic Force Microscopy (AFM)

Sample C' (2 mg) was refluxed at 65-70 °C in thionyl chloride (5 mL) for 24 hours. The reaction mixture was then cooled to room temperature and concentrated *in vacuo*. The remaining solid was dried at room temperature under vacuum. It was then treated with cysteamine (3 mg) in anhydrous toluene (5 mL) and stirred at 70 °C under an argon atmosphere. After 24 hours, the solution was evaporated *in vacuo* and the reaction mixture was suspended in MeOH (10 mL) by ultrasonic treatment. This sample was subsequently filtered over a polycarbonate film (Whatman, pore size: 0.2 µm) and washed with methanol extensively. A small fraction of the remaining solid was dispersed in methanol and immobilized on a mica substrate by spin coating. The SWNTs on the substrate were checked by AFM (Fig. 4a –main text–) and then exposed to preformed gold colloids (Sigma Aldrich) for 15 min and was subsequently washed with 3 x 5 mL of methanol and dried (Fig. 4b –main text–). The same procedure done on sample C' was followed on samples A' and C for the blank experiments. See figure S1 for AFM data.



Scheme S2. Cysteamine coupling to steam purified, acid treated and base washed SWNTs (Sample C').

CHARACTERIZATION TECHNIQUES

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were recorded in transmission mode on a Nicolet MAGNA-IR 560 spectrometer at 4 cm^{-1} resolution by co-adding 128 scans (MCT/B detector; CsI beam splitter; Happ-Genzel apodization). Thin films of the carbon nanotube samples were prepared on ZnSe disks (2 mm thickness) by dropping 2-propanol dispersions onto the preheated substrates (70 °C).[2] Film thicknesses were increased until the absorbance of the background was ~1. Spectra were then scaled so that the lowest point of the background equals 1. Background corrections were performed by subtracting straight lines in the displayed spectral ranges.

Raman Spectroscopy

Raman spectra were recorded on a Jobin Yvon spectrometer (Labram 1B) equipped with a microscope, through a 50-fold magnification objective (Olympus Co.), by adding four sets of spectra together. A 20 mWHe–Ne laser (632 nm) was used. The 1800 L/mm grating provides a resolution starting from 1.0 cm^{-1} at 200 cm^{-1} up to 0.5 cm^{-1} at 3600 cm^{-1}. The abscissa was calibrated with a silicon standard, and the sharp Raman shifts are accurate to ±2 cm^{-1}. Raman spectra were directly taken from the thin films prepared for IR spectroscopy. To ensure homogeneity of the samples, three spectra were recorded from different spots on the sample (laser spot diameter ~ 1 μm). Raman spectra were then normalized for the intensity of the G-band.

Atomic Force Microscopy (AFM)

A Nanoscope IIIa Digital Instruments (DI) Multimode^{TM} scanning probe microscope running on software v. 5.12 (2001) was used for acquisition of AFM data. All images were captured at 512 pixel lateral resolution with scan rates of 1-2 Hz. An “E” scanner with up to 12.5 μm laterally (*x* and *y* axes) and 3.5 μm vertically (*z* axis) was used. Processing of all the images involved flattening and adjustment of contrast and scales, and was performed with the DI software.

High resolution transmission electron microscopy (HRTEM)

Samples were dispersed in ethanol by sonication and placed dropwise onto a holey carbon support grid for HRTEM observation. They were then examined in a JEOL JEM-4000EX HREM operated at 100kV. At this voltage no beam damage was observed to occur on the SWNT samples.

X-ray Photoelectron Spectroscopy (XPS)

Samples supported on stubs were introduced into the instrument via a turbo molecular pumped entry lock. The entry lock was pumped for about 15 minutes before the sample was introduced into the analysis chamber. XPS was performed in an ion pumped UHV chamber equipped with a VG nine channel CLAM4 electron energy analyser (base pressure 5 x 10^{-10} torr). 300 Watt unmonochromated Mg X-ray excitation was used. The CLAM 4 has variable slits for small area analysis. The largest slit (5mm) was used in this case with no apertures selected. The analyser was operated at constant pass energy of 100 eV for wide scans and 20eV for detailed scans setting the C1s peak to BE 285 eV.[3] Data was obtained using VGX900-W operating system. Peak intensities were measured after background subtraction following methods of Shirley.[4]

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