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Supporting information for:

Adsorption of F127 onto single-walled carbon nanotubes characterised using small-angle neutron scattering

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Supporting Information Available

Transmission electron microscopy

10 μl of the F127/SWCNT/H_2O stock solution was diluted with 3 ml of 1% F127 in H_2O. A drop was pipetted onto a carbon coated copper grid placed on filter paper, with the excess dispersion being wicked away by the filter paper. The grid was left to dry and imaged

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using a JEOL 2010 high-resolution transmission electron microscope operating at 200 kV for magnifications of up to 1 million. The microscope was fitted with a bottom-mounted 11 megapixel Gatan Orius 832 camera for high resolution.
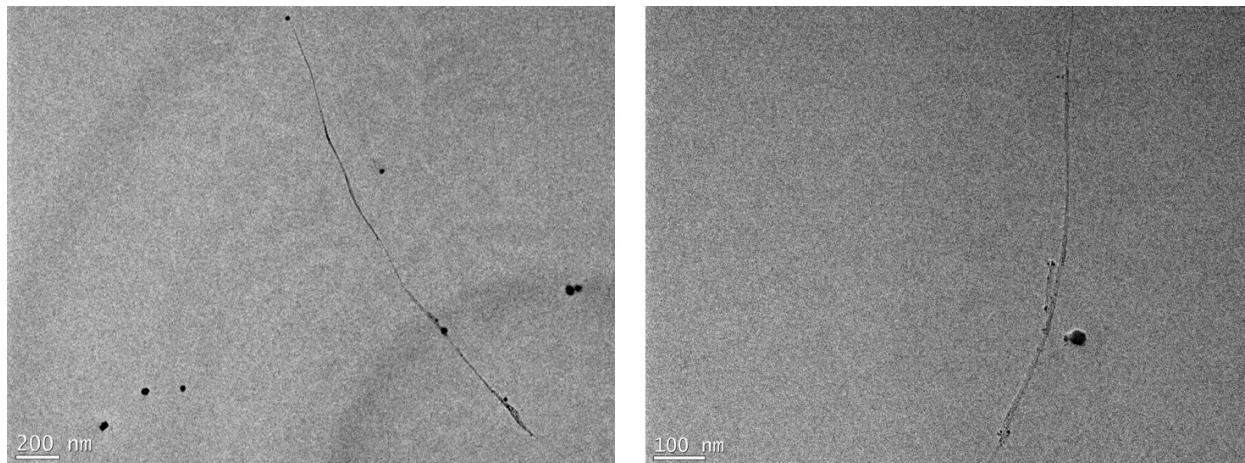

Figure S1: TEM images showing SWCNT/F127 dispersions. Scale bars: left 200 nm, right 100 nm.

TEM images in fig. S1 show that small bundles and individual tubes are present in the dispersion. These are similar in diameter to dimensions obtained from the SANS data fitting, which suggest that the SWCNTs are present as small bundles of 10 Å radius. Residual catalyst particles from the synthesis of the SWCNTs are also seen to be present in TEM images, thought to be iron nanoparticles. From TEM image analysis, it can be estimated that nanoparticles are approximately 1 nm in diameter, and there are approximately 5 nanoparticles per micron length of SWCNTs. This corresponds to a volume fraction of $\sim 10^{-6}$. Thus the volume fraction of nanoparticles is too low to make a significant contribution to the neutron scattering. Bittova et al. reported that the nanoparticles were in the form of Fe_3C, and using this information the estimated contribution of the nanoparticles was calculated. At a volume fraction of $\sim 10^{-6}$, Fe_3C particles would give a scattering of intensity $\sim 10^{-3}$ cm^{-1}, and would thus not affect the scattering pattern of the SWCNTs.

Small-Angle X-ray Scattering

Small-angle X-ray scattering experiments were done using a GANESHA 300 XL (SAXSLAB, Copenhagen, Denmark) SAXS system, with an adjustable sample detector set to 1.041 m. X rays were detected using an in-vacuum Pilatus 300k detector (Dectris, Baden, Switzerland) and were generated using a sealed tube generator with a copper anode (X-ray wavelength 1.54 Å). Fluid samples were loaded into 1.5 mm quartz-glass capillary tubes (Capillary tube supplies, UK), Measurements were performed for 10 minutes. A transmission-normalised surfactant background was subtracted from the data, and a mask was used to remove sections of data not related to sample scattering, such as the beamstop. The data was radially averaged to produce one-dimensional scattering curves, which were fit using SasView fitting software.
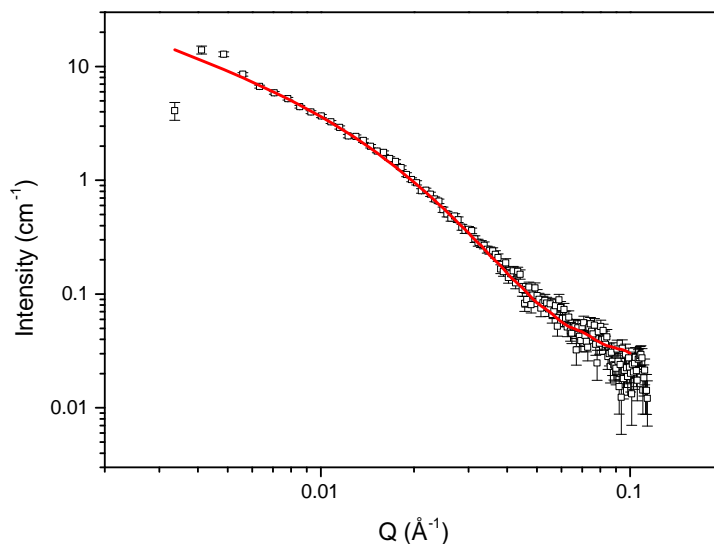
Figure S2: Small-angle X-ray scattering curve of F127/SWCNTs at 100% D_2O studied using SANS. The scattering curve can be fit to a core-shell cylinder model, suggesting that the small catalyst particles present in the sample do not affect the scattering.

A SAXS experiment was performed on the 100% D_2O/F127/SWCNT sample analysed using SANS, in order to determine the effect of the iron nanoparticles on the scattering, reported by Bittova et al. to be in the form of Fe_3C, whose X-ray scattering length density

has been calculated to be $4.2\times 10^{-5}\text{Å}^{-2}$.[S1] Thus the nanoparticles have a higher contrast to the solvent than SWCNTs (ρ_{SWCNT} was calculated to be $1.7\times 10^{-5}\text{Å}^{-2}$). The SAXS data was fit to a core-shell cylinder model with the same parameters that were used to fit the SANS data, although ϕ_{F127} in the adsorbed layer was found to fit to a value of 0.19, rather than 0.06 from the SANS data fitting, thought to be caused by the sample being run at 25 °C rather than 15 °C. It has therefore been assumed that the catalyst particles present do not affect the scattering of the SWCNTs.

Small-Angle Neutron Scattering

F127 data below the CMT were fit to a Debye-Guinier model for flexible polymers in solution with a Gaussian distribution of polymer segments around the centre of mass of the polymer chain.[S2] The parameters required to fit this data to the Debye-Guinier model are:

1. Scattering length density difference between the polymer and solvent

2. Volume fraction of polymer in solution

3. Molecular weight of polymer

4. Radius of gyration of the polymer in solution

5. Background scattering from the sample

6. Density of the bulk polymer

   Parameters 2, 4 and 5 were allowed to float in order to produce fits for the low temperature F127 data, an example of which is shown in fig. S3, for which the radius of gyration was fit to a value of 38 Å. The upturn in the data of F127 is thought to be due to a combination of imperfect background scattering, masking the data and some residual scattering from the particular cell used.
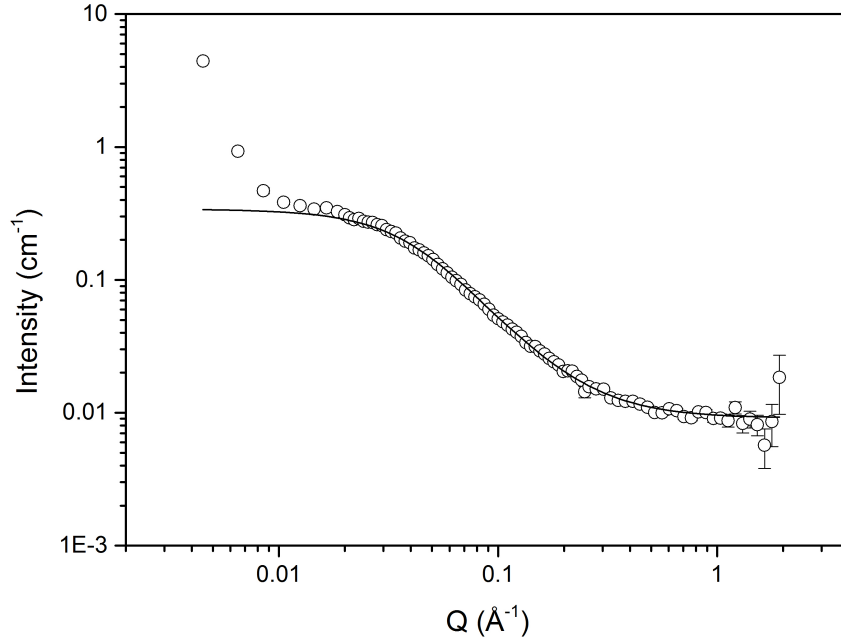
Figure S3: 1% F127 in 100% D$_2$O below the CMT (○), fit to a Debye-Guinier model for free polymers. Parameters used for this fit are given in table S1.

Table S1: Parameters used to fit 1% F127 data below the CMT. Other parameters used were: volume fraction of polymer 0.00496; polymer molecular weight 12.5 kgmol^{-1}; bulk polymer density 1060 kgm^{-3}.

Parameter	100% D$_2$O	80% D$_2$O	70% D$_2$O
$\Delta\rho$ / 10^{-6} Å^{-2}	5.84	4.44	3.75
Background / cm^{-1}	0.00913	0.00565	0.00638

The subtraction of the F127 scattering from the F127/SWCNT scattering therefore consisted of first fitting the F127 data to a Debye-Guinier model for free polymers, then scaling this down by a factor of 0.75 in order to match the F127/SWCNT scattering at high angles. This scaled-down fit was then subtracted from the SWCNT/F127 data in order to obtain the scattering contribution for the decorated SWCNTs. An example of this subtraction can
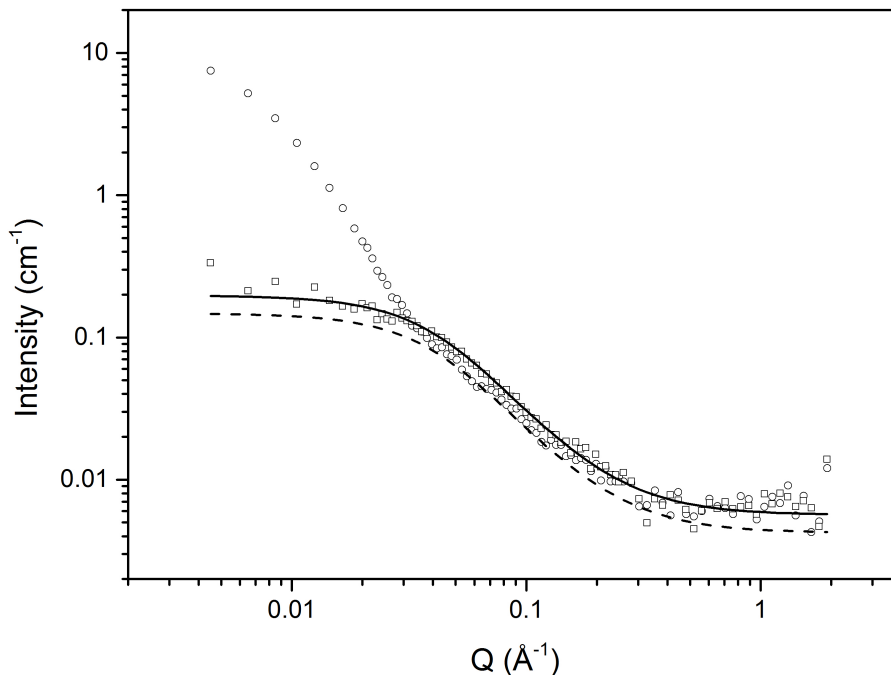
be seen in fig. S4.

Figure S4: Subtraction of the Debye-Guinier fit for F127, shown as a solid line (in this case, the 80% D_2O data has been used to illustrate the process). As the F127 data has a higher intensity than the F127/SWCNT data, the fit had to be multiplied by a factor of 0.75 (dotted line) before being subtracted from the F127/SWCNT data.

The polydispersity function used for thickness is shown in fig. S5.

Confidence in the values for the radius of the core and thickness of the adsorbed layer was estimated by attempting to fit the data with a radius of 5 and 15 Å. Similarly, the thickness was changed to 50 or 70 Å and these changes meant that it was difficult to get good fits with parameters which were consistent across all contrasts studied. However, as the values for the amount of water in the core and shell (the model parameters ρ_{core} and ρ_{shell}) only affect the intensity of the fit, rather than the shape, it is possible to obtain fits to the data equally good as those shown here, by adjusting these values together with the volume fraction of decorated cylinders. However, this would mean that the calculated adsorbed amount from the fit would change, and move further away from the estimated adsorbed amount based on
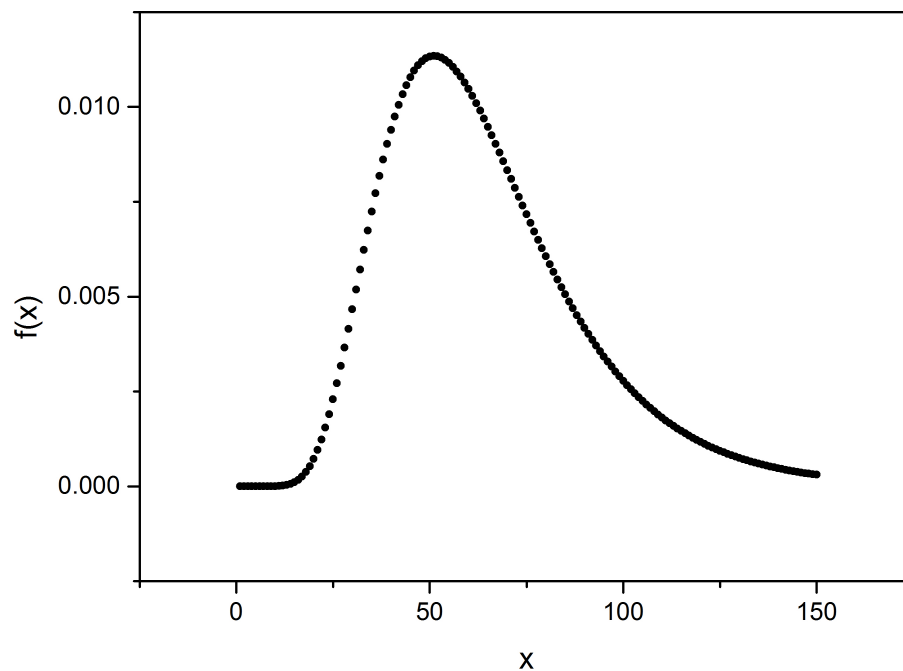
Figure S5: Log-normal polydispersity function used to fit the data to a polydisperse adsorbed layer with a dense carbon core.

the data subtraction.

Surface Area

The surface area of (single-sided) SWCNTs was calculated. The carbon atoms were assumed to have the same C-C bond length as they do in graphene sheets, 0.142 nm.[S3] Each carbon atom is shared between 3 hexagons, therefore the area per carbon atom is half the area of one hexagon. The area of a hexagon is given by the equation $\frac{3}{2}\sqrt{3}a^2$, with a being the C-C bond length. The area per carbon atom in this case is 2.62 Å^2, and taking the mass of one carbon atom as 1.99×10^{-23} g, this gives a surface area of 1316 m^{2}g^{-1}, which agrees with surface area values found in literature.[S4]

SLD calculations for SWCNTs

There are discrepancies between measured SWCNT scattering length density (ρ_{SWCNT}) values in the literature with each other, as well as with theoretical (calculated) values. Table S2 shows a variety of scattering length densities (both measured and calculated) for SWCNTs taken from different papers, which gives an indication of just how different the behaviours of SWCNTs can be. Hough et al. calculated ρ_{SWCNT} to be 4.6×10^{-6} Å^{-2} but measured it as 4.0×10^{-6} Å^{-2},[S5] while Zhou et al. measured ρ_{SWCNT} as 4.9×10^{-6} Å^{-2}, by dispersing the SWCNTs in toluene at a variety of solvent compositions.

Table S2: Scattering length density values for SWCNTs taken from literature.

ρ_{SWCNT} /Å^{-2}	Reference
7.5	Yurekli et al.[S7]
4.9	Zhou et al.[S6]
4.0	Hough et al.[S5]
4.6	Hough et al. (calculated)[S5]

The value of ρ_{SWCNT} can be calculated by using the scattering length of pure carbon-12 (6.65×10^{-5} Å). The area of one carbon atom in graphene was calculated previously to be 2.62 Å^2, and this can then be multiplied by the van der Waals thickness of graphene (3.4 Å)[S8] to obtain the volume of one carbon atom in graphene (8.91 Å^3). The scattering length of carbon is then divided by this volume to obtain a calculated scattering length density of 7.46×10^{-6} Å^{-2}.

The overall scattering length density of the SWCNTs, however, will depend on whether they are solvent-filled or empty. Cambré and Wenseleers reported that HiPCO nanotubes, the majority of which are thought to have a hemispherical 'cap' around each end,[S10] can remain end-capped with careful sonication involving stirring or mild sonication in a bile salt solution, however commonly used methods involving ultrasonication will open the ends of

the tubes.[S9] Therefore, our tubes are likely to be open-ended and thus water-filled.
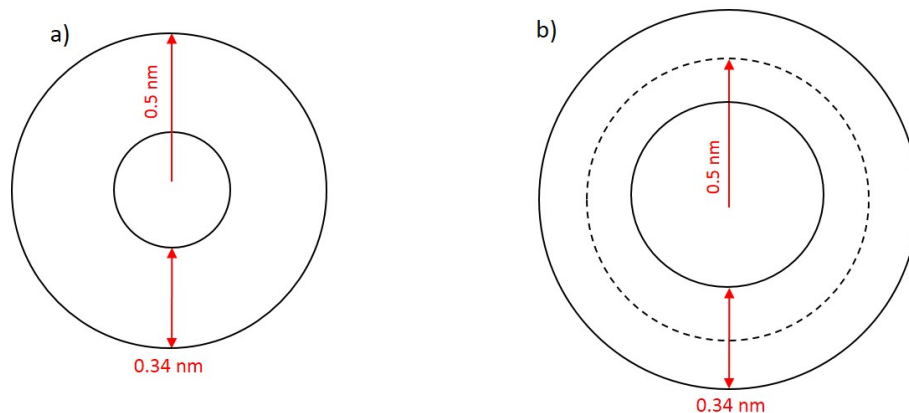

Figure S6: Diagram showing the methods used to calculate the carbon:water ratio of the SWCNTs, and thus to calculate their scattering length density.

The two ways used to calculate the SWCNTs scattering length density are shown in fig. S6. If we assume that the SWCNTs' radius is 0.5 nm, which extends to the centre of the carbon layer, then the total radius will be 0.67 nm and the inner radius will be 0.33 nm. This gives a volume ratio of hollow core:outer carbon shell is 0.24:0.76.

If the HiPCO SWCNTs are assumed to have a total radius (including the nanotube wall) of 0.5 nm (shown in part (b) of fig. S6) and the carbon wall is assumed to be 0.34 nm (using the van der Waals thickness of graphene),[S8] then the volume ratio (inner hollow centre:outer carbon shell) is 0.10:0.90.

If the inner core is assumed to be filled with D_2O, then the SLD of the filled nanotubes can be calculated to be between 7.15 and 7.30×10^{-6} Å^{-2}, whereas if they are empty, (with the inside of the tube having an SLD of 0) the SLD of the whole cylinder would drop to between 5.62 and 6.66×10^{-6} Å^{-2}. To model the scattering of the SWCNT cylinders, we have assumed that 20% of the core consists of solvent, with the remaining 80% consisting of carbon.

This material is available free of charge via the Internet at `http://pubs.acs.org/`.

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