Electronic Supplementary Material (ESI) for Nanoscale.

DOI: 10.1039/ x0xx00000x
Article type: Communication

Dry shear aligning: A simple and versatile method to smooth and align the surfaces of carbon nanotubes thin films

D. D. Tune,[a,b] B. W. Stolz,[a] M. Pfohl,[a] and B. S. Flavel[a]

[a] Institute of Nanotechnology, Karlsruhe Institute of Technology, 76021 Karlsruhe, Germany
[b] Centre for Nanoscale Science and Technology, Flinders University, Adelaide 5042, Australia

Corresponding author email: daniel.tune@kit.edu, ben.flavel@kit.edu

Experimental details

Various kinds of nanotubes were used in this study: commercially obtained small diameter single walled (Raw and SuperPure HiPco, NanoIntegris, USA) as well as material sorted in our labs by gel permeation chromatography from the raw HiPco source, large diameter single walled (P2-SWNT, Carbon Solution Inc, USA), double walled nanotubes (D4L1-5, NanoLab Inc, USA) and small diameter multiwalled nanotubes (NC3100, Nanocyl, Belgium). Further data is provided in Table S1 and the specific type used in each experiment is indicated along with the relevant data. The nanotube films shown in this report were produced by either vacuum filtration from aqueous suspension or by slide-casting from solutions of nanotubes dissolved in sodium polyelectrolyte (PE) inks or chlorosulphonic acid (CSA) (hazardous – read and understand MSDS and handle with care). In the case of vacuum filtration, nanotubes were added to 1 % aqueous TritonX-100 at 0.1 mg mL^{-1} then bath sonicated for 1 h. After centrifugation at 20 000 g for 20 mins, VF films were captured from the supernatant onto mixed cellulose ester (MCE) membranes (0.45 µm, HAWP, Merck Millipore) and rinsed thoroughly with copious DI water. Films were deposited by placing them nanotube side down on the desired substrate; they were then wet with a drop of water, compressed with Teflon and baked at 110 °C for 15 min. To remove the MCE from the films, the cooled substrates were placed in an acetone (EMSURE, Merck) bath for 30 min then transferred to two fresh acetone baths for a further 30 min each then baked for 10 min at 60 °C in air. Single and double walled nanotubes were dissolved in PE inks by adding freshly cleaved sodium (50 mmol) (ACS reagent, Sigma) to a solution of oven dried (150 °C, 3 h) nanotubes in anhydrous DMA (3 mg mL^{-1}) (99.8 %, Alfa-Aesar) in an argon glovebox and stirring vigorously for three days, over which time the solutions evolved from discreet black particles in clear liquid to homogeneously dark bronze inks. Nanotubes were dissolved in CSA by simple addition of the oven-dried powder to the acid (97 %, Merck), followed by stirring for 3 days. It was not possible to dissolve the multiwalled nanotubes used in this study in either CSA or the PE solutions at the concentrations needed. Both CSA and PE films were produced in inert atmosphere by solution shearing a.k.a slide casting a.k.a shear casting. This involves placing a small drop (3-5 µL) in between two glass slides, applying a compressive force of between 40 - 80 N (corresponding to an applied pressure of 27 - 43 kPa on the 7.5 x 2.5 cm^2 glass slides used) and then rapidly drawing the slides apart at a shear velocity of ~0.01 m s^{-1}. After evaporation of the solvent, the films are exposed to atmosphere then redeposited onto fresh glass slides by aqueous transfer. This involves floating the films onto water by slowly immersing the glass slides at a near horizontal orientation, allowing the surface tension of the water to peel the film from the glass surface. The floating film can be exposed to various aqueous and water-miscible reagents or immediately transferred to a new substrate by simply lifting the target substrate up from underneath the floating film. Residual water remaining after this process is removed by heating to 110 °C in air for 15 min.

For DSA on nanotube films attached to filtration membranes, a cylindrical 8 x 30 mm PTFE stirrer bar was used as the aligner. The membranes were placed on a flat glass surface, nanotube side up, and held in place while the stirrer bar was very firmly (~ 60 N) sheared across the film surface at around 2 - 3 mm s^{-1}. The nanotube films changed in appearance from matt grey/black to become visibly smoother and more reflective, with the direction of shear faintly discernible to the eye. For DSA on bare nanotube films on glass, silicon, etc, latex (glove) was lightly (5 – 10 N) sheared across the film at around 5 mm s^{-1}. A similar change in appearance of the film occurred as for the films on the filtration membranes.

Table S1 Properties of the nanotubes used in this study.

Type	Supplier	Product	Diameter (nm)	Length (μm)	Carbon purity (%)	Nanotube purity[#]
Single	NanoIntegris	Raw HiPco	0.8 - 1.2	0.1 - 1	> 65	high
Single	NanoIntegris	SuperPure HiPco	0.8 - 1.2	0.1 - 1	> 95	very high
Single	*gel sorted (6,5) from raw HiPco		0.75 - 0.85	0.1 - 1	> 95	very high
Single	Carbon Solutions	P2-SWNT	1.4	0.5 - 3	> 90	high
Double	NanoLab	D4L1-5	3 - 5	1 - 5	> 95	low
Multi	Nanocyl	NC3100	9.5	1.5	> 95	very high

[#] qualitative estimate from SEM images

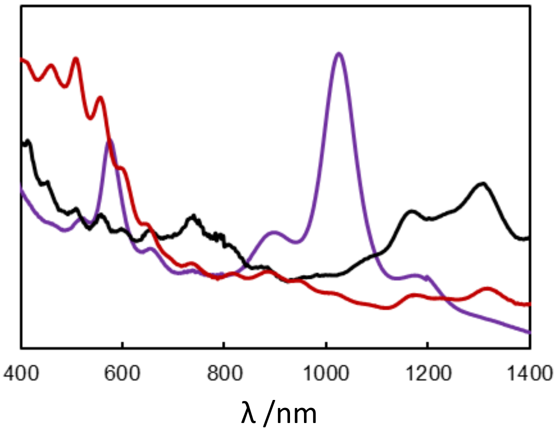

Figure S1 Absorption spectra of small diameter single walled nanotubes (Raw HiPco, NanoIntegris, USA) (black) as well as the 'metallic' fraction (red) and (6,5) chirality (purple) sorted from the raw material via gel chromatography.

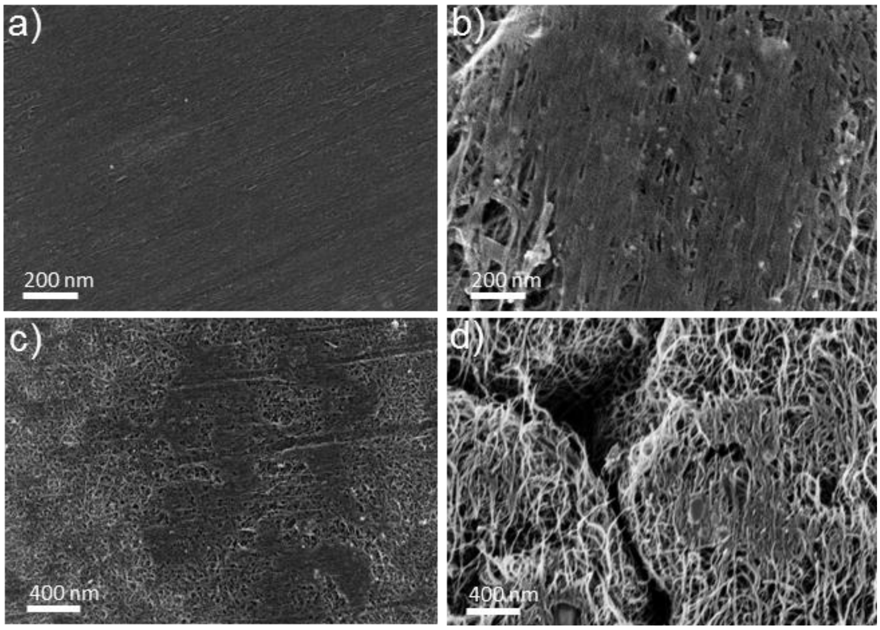

Figure S2 SEM images of films showing dependence of the extent of rearrangement of the films on the nanotube diameter where the images show nanotube films, vacuum filtered from surfactant solutions, where DSA has been applied directly on the membrane using a Teflon aligner, a) small diameter single walled nanotubes flattened and highly aligned, b) large diameter single walled nanotubes flattened and aligned in patches, c) double walled nanotubes flattened and aligned in patches and d) multiwalled nanotubes flattened and marginally aligned in patches. All films were identically prepared using the same surfactant and were of similar thickness. The images were obtained from the films whilst still bound to the filtration membrane.

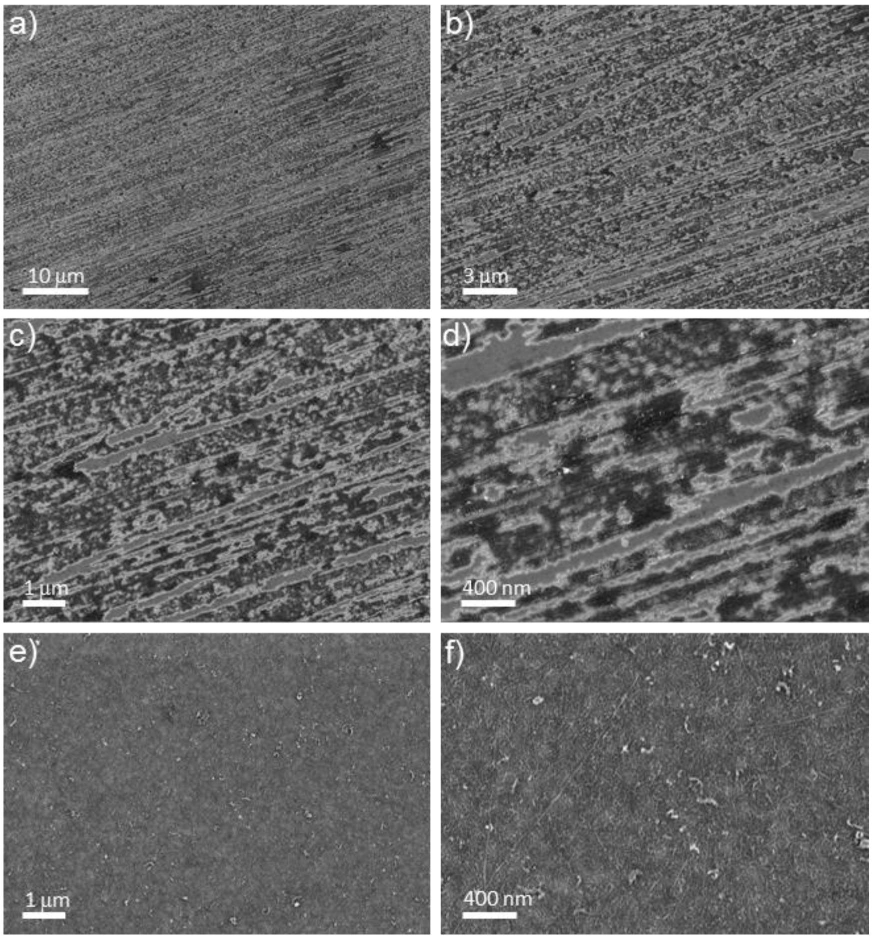

Figure S3 (a-d) SEM images at various magnifications showing tearing of films during DSA due to impurities and particulates leading to poor adhesion and uneven distribution of pressure. Films were formed from DW nanotubes (D4L1-5, NanoLab Inc, USA) slide cast from CSA then transferred to glass. The sheet resistance increased from ~70 kΩ for the freshly transferred films on glass, to >100 MΩ after DSA due to the severe disruption of the films by the tearing of the material from the substrate, (e-f) shows the same films before DSA.

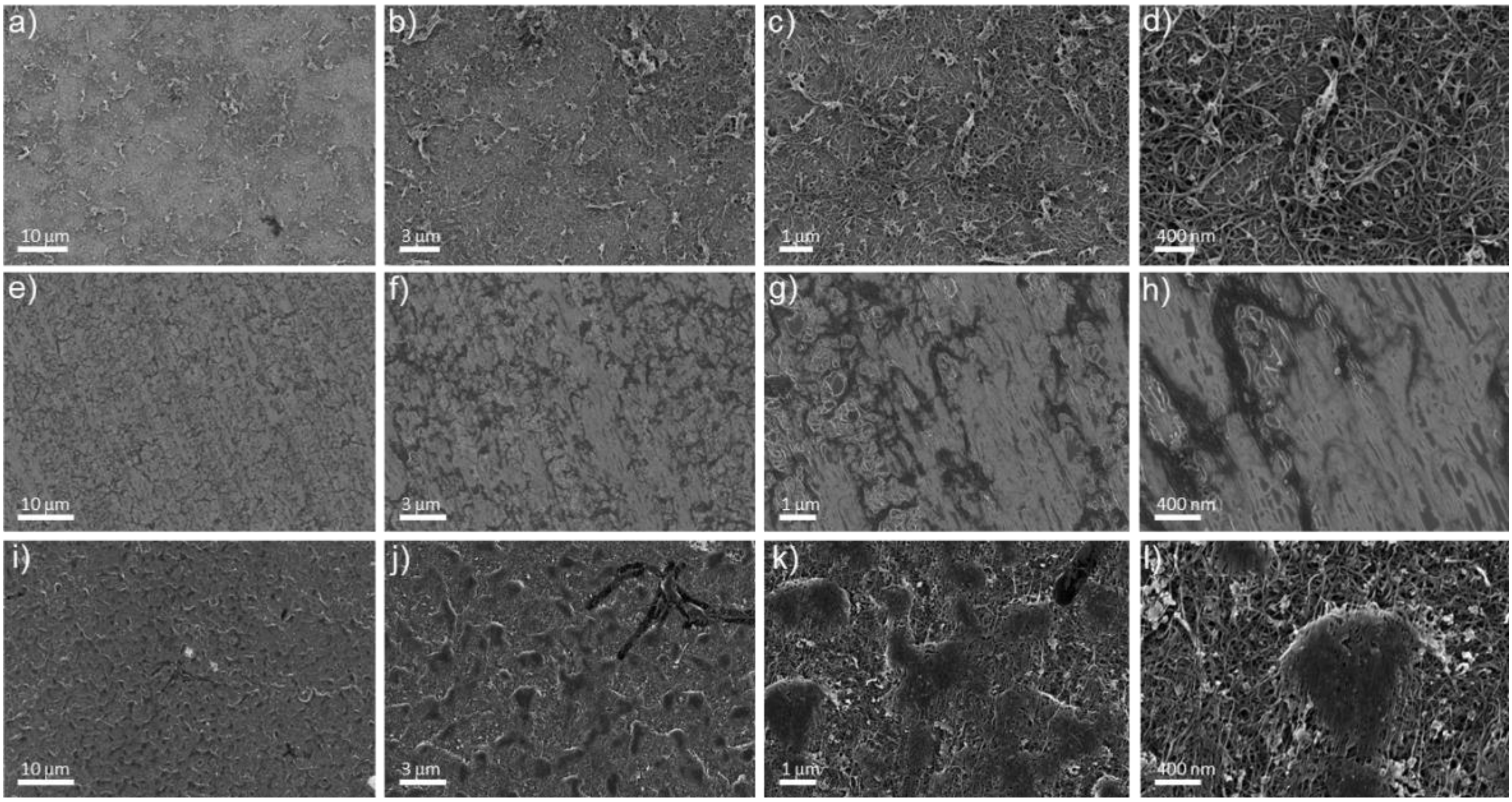

Figure S4 Large diameter single walled nanotube films, vacuum filtered from surfactant solutions, at different magnifications, (a-d) bare film, (e-h) DSA applied to film after transfer onto glass, (i-l) DSA applied directly on membrane. The nanotubes (P2-SWNT, Carbon Solutions Inc, USA) were filtered from 1 % aqueous TritonX-100 suspension formed by 1 h bath sonication onto 0.45 µm mixed cellulose ester membranes (Merck Millipore, Germany).

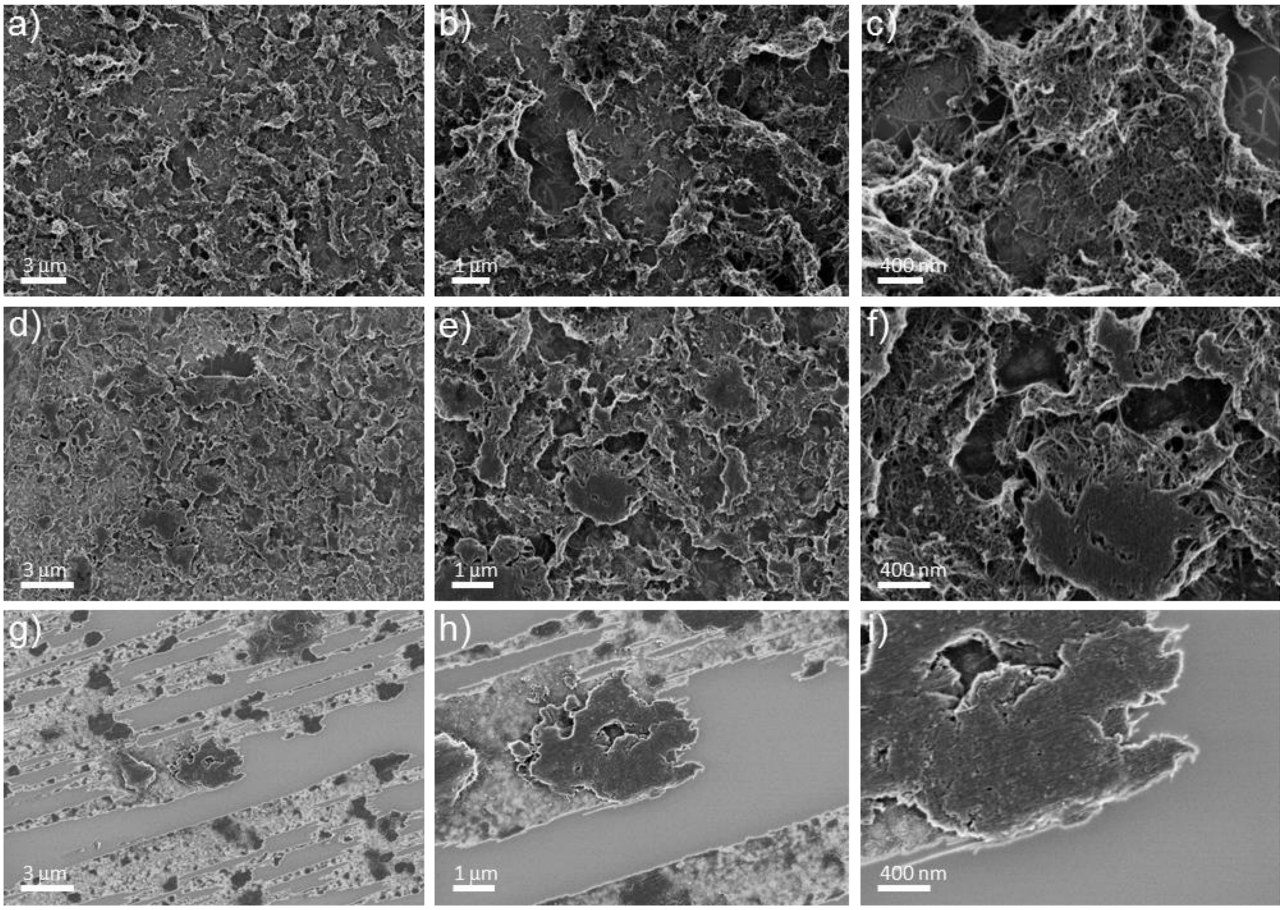

Figure S5 Double walled nanotube films, vacuum filtered from surfactant solutions, at different magnifications showing, (a-c) bare films and, (d-f) DSA applied directly on membrane. As shown in (g-i), it was not possible to perform DSA on films after transfer to glass due to tearing of the film caused by high level of impurities and particulates. The nanotubes (D4L1-5, NanoLab Inc, USA) were filtered from 1 % aqueous TritonX-100 suspension onto 0.45 µm mixed cellulose ester membranes (Merck Millipore, Germany).

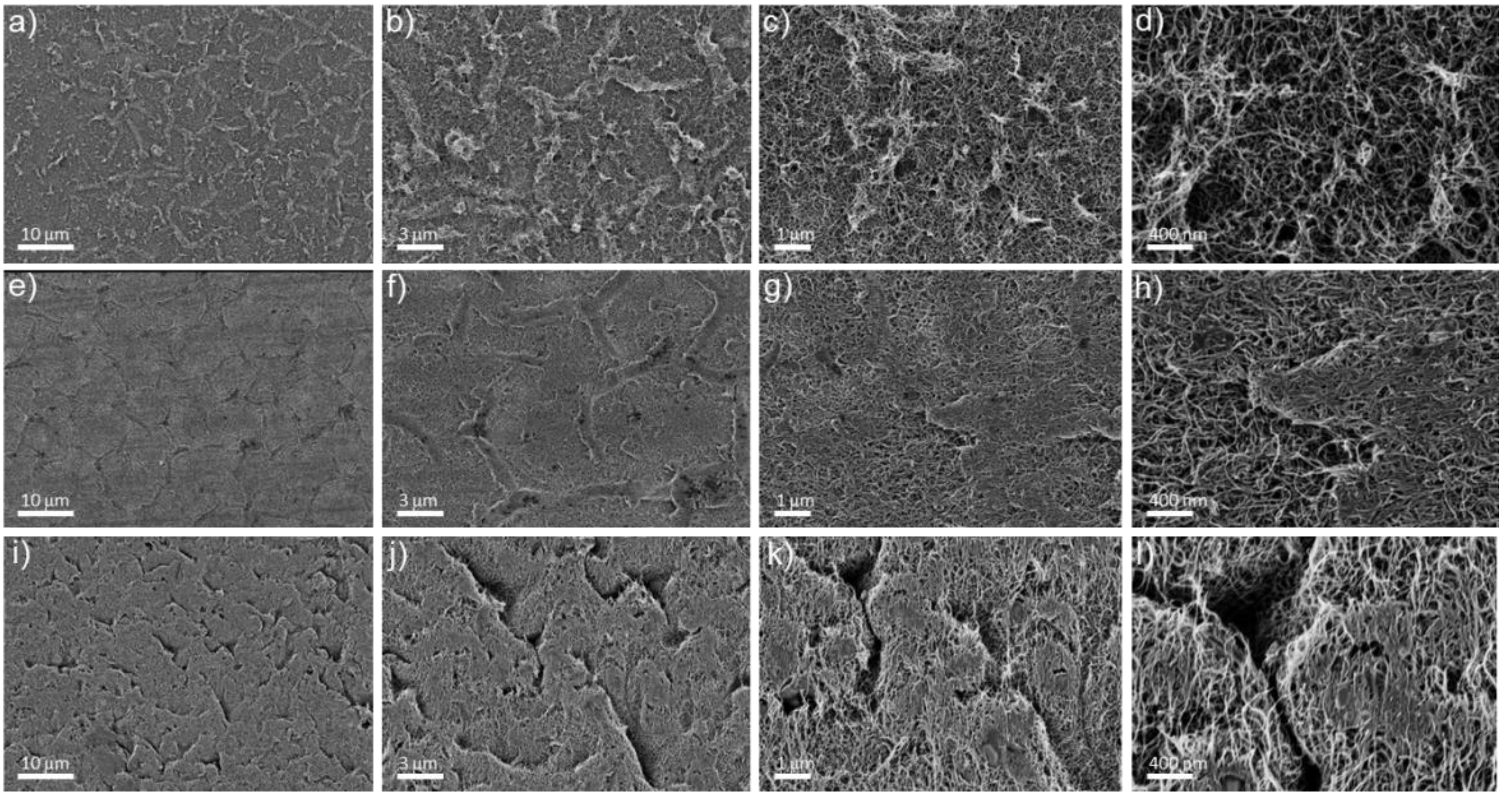

Figure S6 Multiwalled nanotube films, vacuum filtered from surfactant solutions, at different magnifications, (a-d) bare films, (e-h) DSA applied to film after transfer onto glass, (i-l) DSA applied directly on membrane. The nanotubes (NC3100, Nanocyl, Belgium) were filtered from 1 % aqueous TritonX-100 suspension onto 0.45 μm mixed cellulose ester membranes (Merck Millipore, Germany).

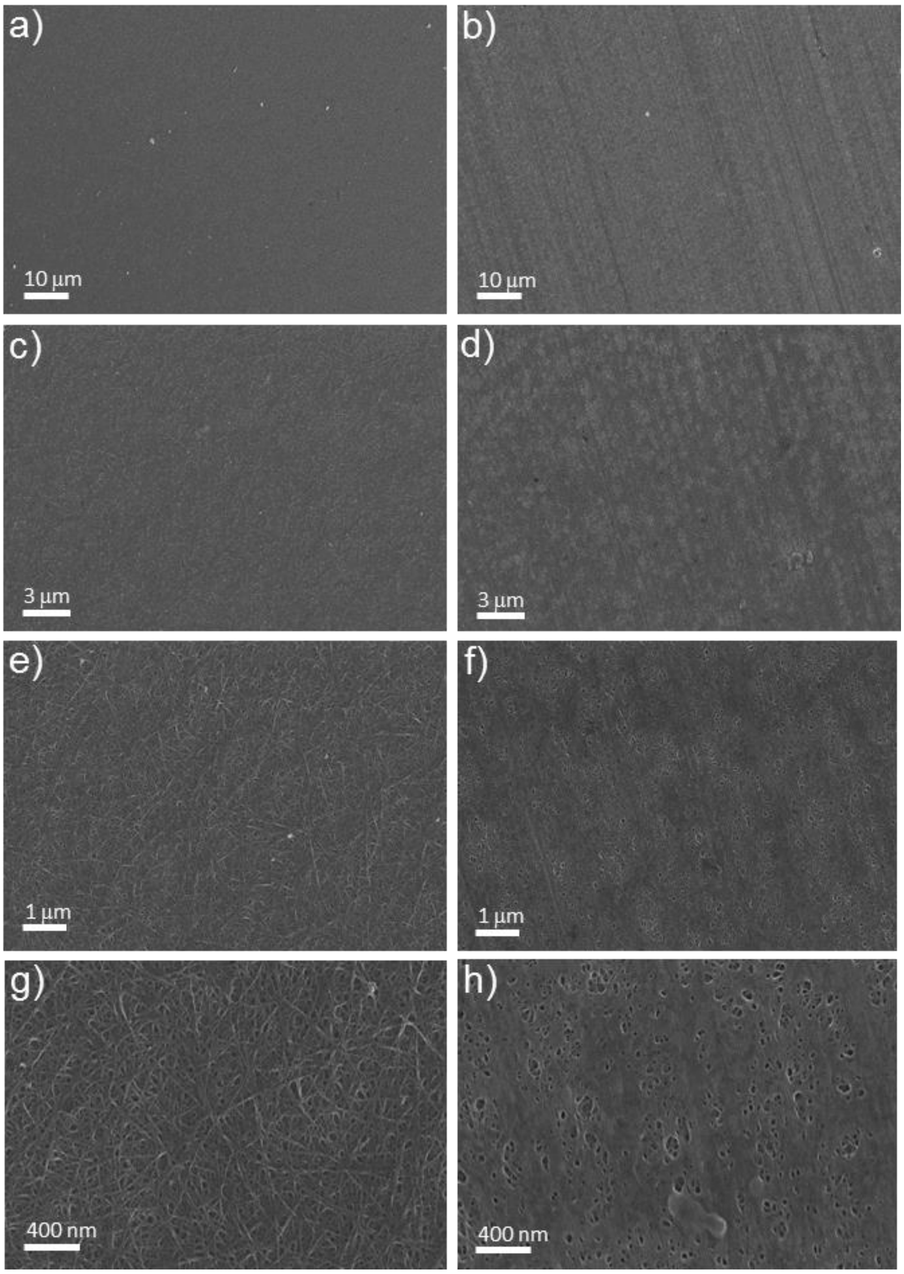

Figure S7 Gel-sorted (6,5) nanotube films formed by slide casting from CSA, (a, c, e, g) as deposited and (b, d, f, h) after transfer to glass and DSA. To prepare the ink for slide casting, the sorted fraction was diluted 1:1 with acetone to aggregate the nanotubes, which were then collected by filtration onto nylon membranes (0.5 µm, Phenomenex, UK) and rinsed with copious DI water and isopropanol. After drying at 130 °C for 4 h the filter cake was fully dissolved in CSA at 3 mg mL^{-1}.

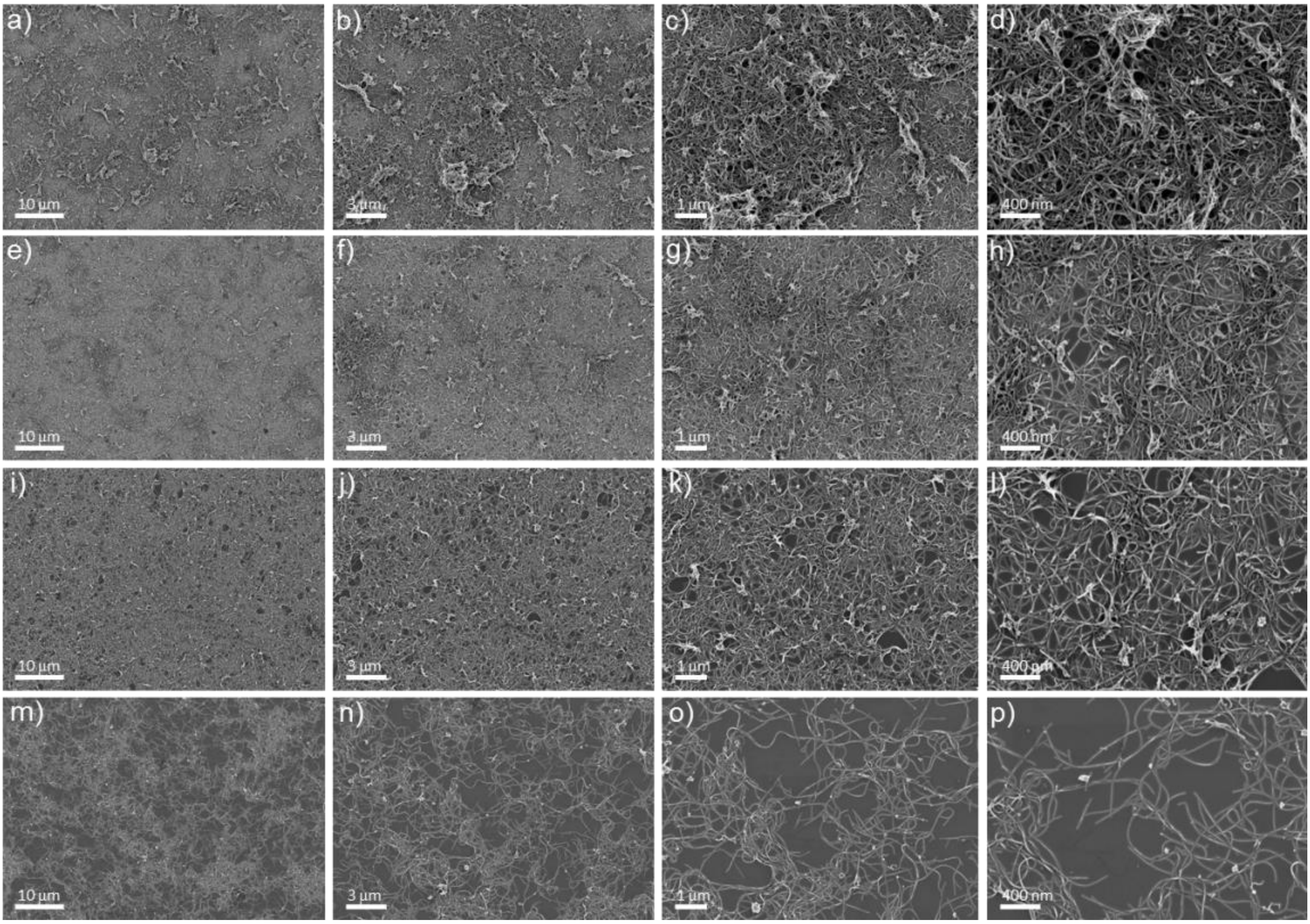

Figure S8 As deposited large diameter single walled nanotube films of varying thickness, vacuum filtered from surfactant solutions, at different magnifications; (a-d) T_{550} = 55 %, (e-h) T_{550} = 79 %, (i-l) T_{550} = 89 %, (m-p) T_{550} = 97 %.

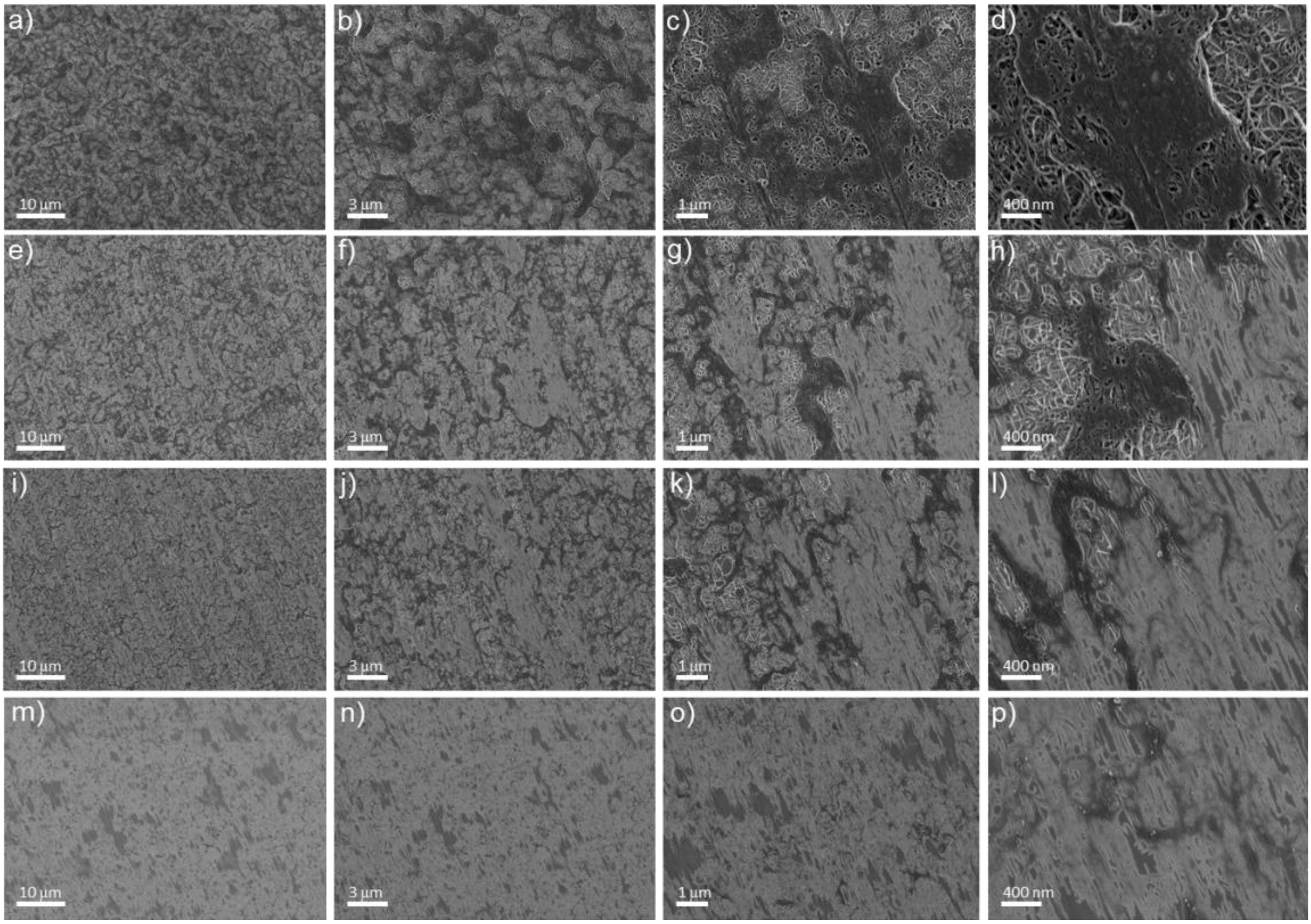

Figure S9 Aligned large diameter single walled nanotube films, vacuum filtered from surfactant solutions, at different magnifications after DSA was applied on top of the films shown in Figure S7; (a-d) T_{550} = 55 %, (e-h) T_{550} = 79 %, (i-l) T_{550} = 89 %, (m-p) T_{550} = 97 %. Note near-monolayer coverage by the thinnest film.

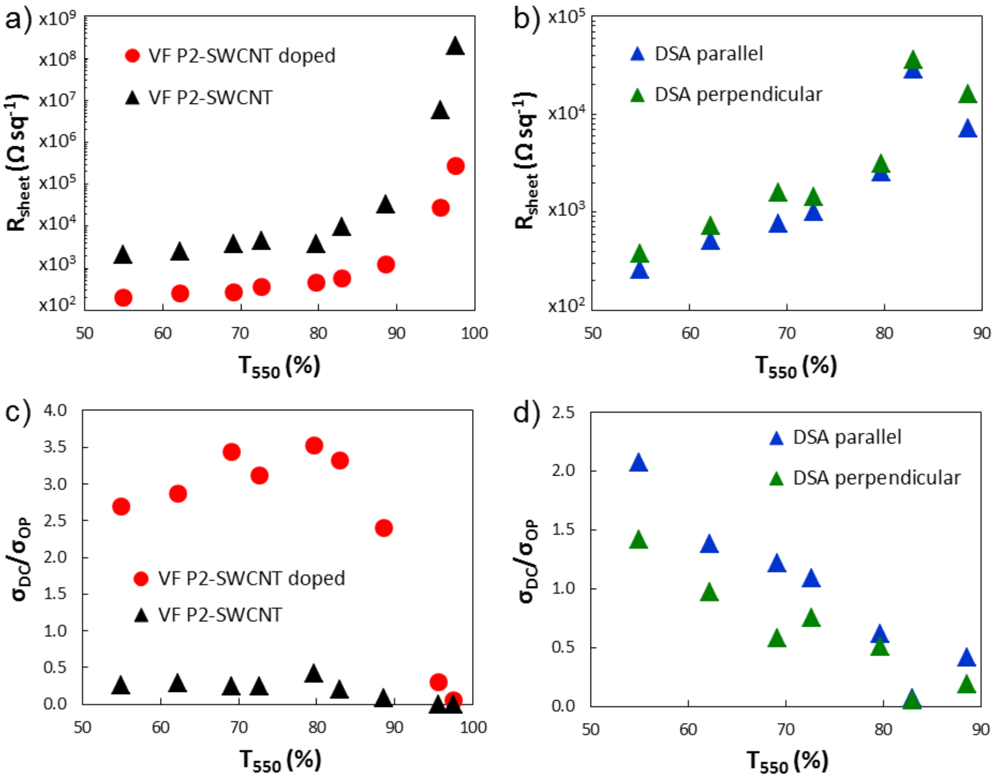

Figure S10 (a) variation in the sheet resistance with film thickness for vacuum filtered films of large diameter single walled nanotubes with and without $SOCl_2$ doping, (b) variation in the sheet resistance with film thickness for vacuum filtered films after DSA taken with the four point probe either parallel or perpendicular to the shear direction, (c) variation in the ratio of DC electrical to optical conductivity with film thickness with and without $SOCl_2$ doping, (d) variation in the ratio of DC electrical to optical conductivity with film thickness, calculated using either the parallel or perpendicular measurements.

The ratio of the electrical to optical conductivity, σ_{DC}/σ_{OP}, was calculated as per Hecht et al.[1] by substituting the measured R_{sheet} and T_{550} values into:

$$T(\lambda) = \left(1 + \frac{1}{2R_S} \cdot \sqrt{\frac{\mu_0}{\varepsilon_0}} \cdot \frac{\sigma_{OP}(\lambda)}{\sigma_{DC}}\right)^{-2}$$

where μ_0 and ε_0 are the free space permeability and permittivity, respectively.

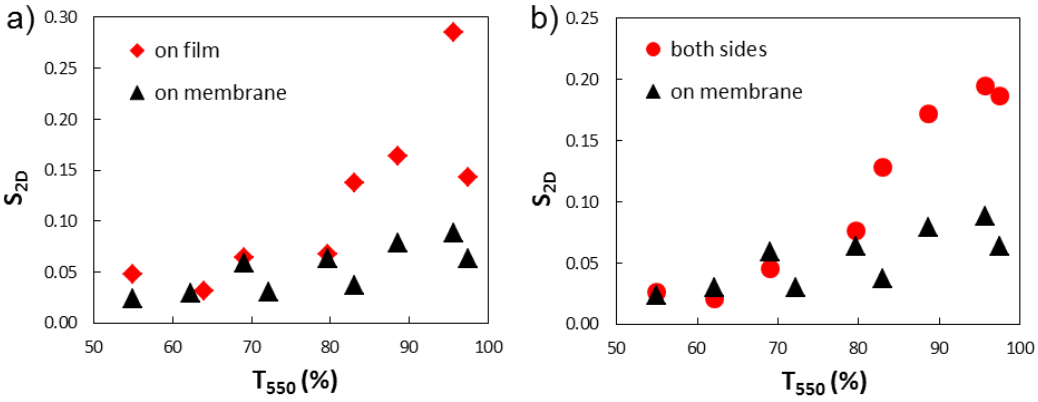

Figure S11 Variation in the 2D order parameter with film thickness where (a) compares DSA performed on the film whilst it is on the filtration membrane i.e., before transfer onto substrate, to DSA performed on the film after transfer onto glass substrate and, (b) compares DSA performed on the film whilst it is on the filtration membrane i.e., before transfer onto substrate, to DSA performed on the same films in the same direction after transfer onto substrate and removal of filtration medium. In both cases the effect of DSA on the film after transfer increases considerably for thinner films with T_{550} > 80 %, compared to the effect of performing DSA on films whilst still on the filtration membrane.

The 2D order parameter was calculated from the polarised optical data via;[2]

$$S_{2D} = (A_{\parallel} - A_{\perp})/(A_{\parallel} + 2A_{\perp})$$

It is possible to quantify surface-only alignment from direct measurement of SEM features using various graphics software packages, yielding much higher values of the order parameter than that stated in the text for the bulk of the film. However, this is a somewhat arbitrary process that depends on the choice of which surface features are considered in the statistics and so we have chosen to rely only on the superior method of polarised optical transmittance measurements, which cannot be affected by observer bias.

References

1. D. S. Hecht, A. M. Heintz, R. Lee, L. Hu, B. Moore, C. Cucksey and S. Risser, *Nanotechnology*, 2011, **22**, 169501.
2. D. L. White and G. N. Taylor, *J. Appl. Phys.*, 1974, **45**, 4718-4723.