Ultra-stiff large-area carpets of carbon nanotubes

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Supplementary information

The alignment and the overall microstructure of the samples were studied using JEOL JSM-840F and JSM-6500F scanning electron microscopes at 5-10 kV acceleration voltage. The structure of individual tubes was observed by high-resolution transmission electron microscopy and analysed by selected area electron diffraction using JEM-2200MCO and JEOL JEM-3000F field emission gun transmission electron microscopes operating at 200 kV and 300 kV respectively. A JY Horiba Labram Aramis imaging confocal Raman microscope with a 532 nm green laser was used to compare the defect density and level of graphitisation of samples. Using a Perkin Elmer Pyris thermogravimetric analyser the oxidation behaviour and the residual iron concentration of the samples was investigated at a heating rate of 10 °C/min in air up to 1000 °C. X-Ray diffraction was carried out on a Bruker D5000 machine using copper radiation. Scans were performed from 10-80 2-theta using a step size of 0.05 2-theta and count

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time per step of 15 seconds. The samples were spun during data collection. Analysis was performed using the Bruker 'EVA' software package along with the International Centre for Diffraction Data database. X-ray photoelectron spectroscopy was used to analyse the surface of plasma-treated carpets using a Thermo Scientific K-ALPHA machine equipped with a monochromated Al X-rays at 12 kV. Wide scans were performed at a pass energy of 200 eV and analysis performed using the Thermo scientific 'Avantage Data System' software package.

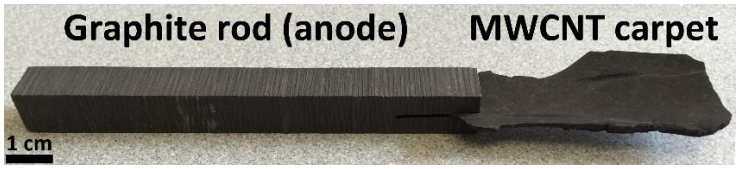

Figure SI1. Carpet of vertically aligned multi-wall carbon nanotubes (VA-MWCNTs) suspended from a slit in graphite rod, prepared for plasma treatment (direct exposure to arc discharge).

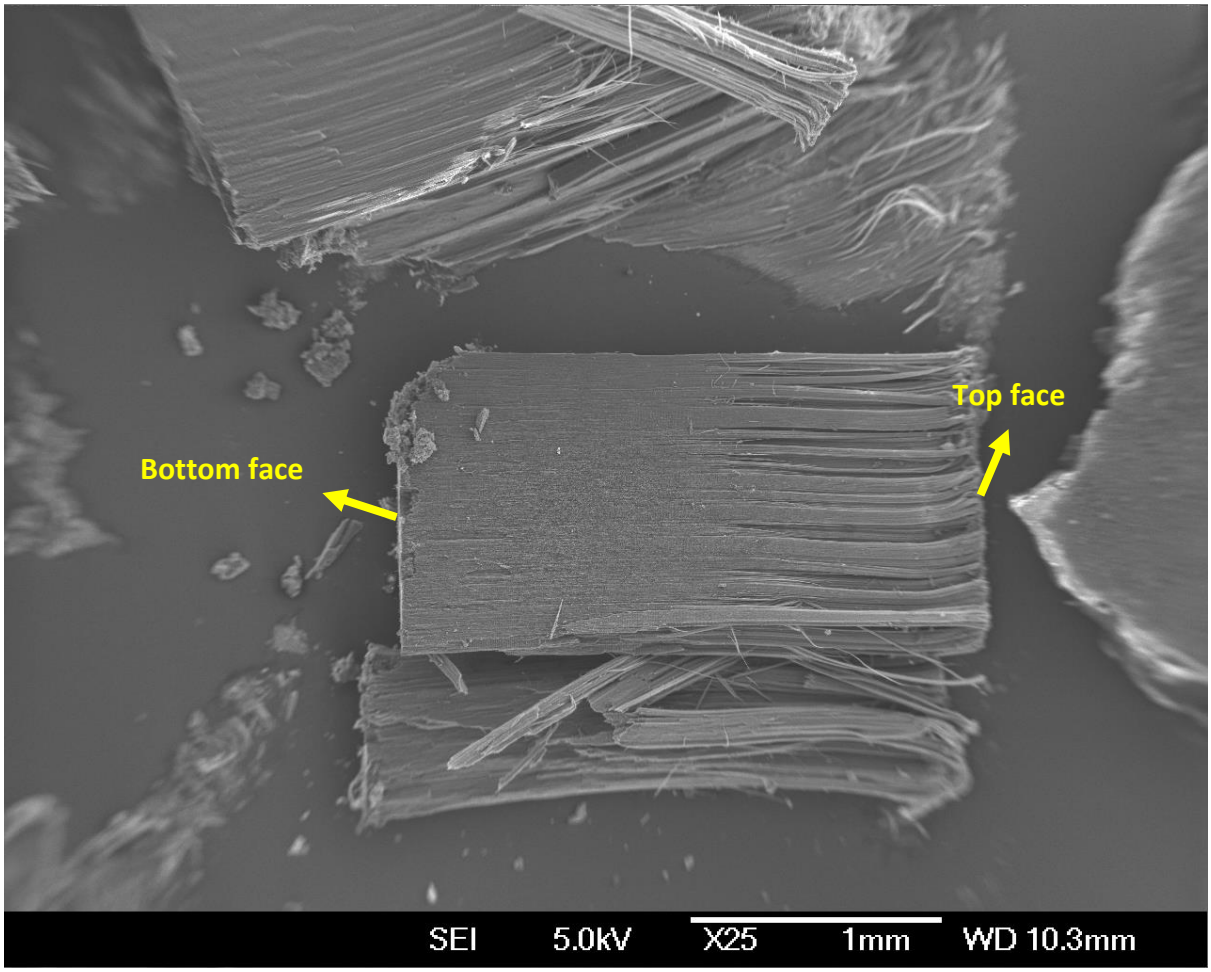

Figure SI2. Representative scanning electron micrograph of a VA-MWCNT carpet showing the difference between the compactness of the ensemble of MWCNTs at the bottom and top of the carpets.

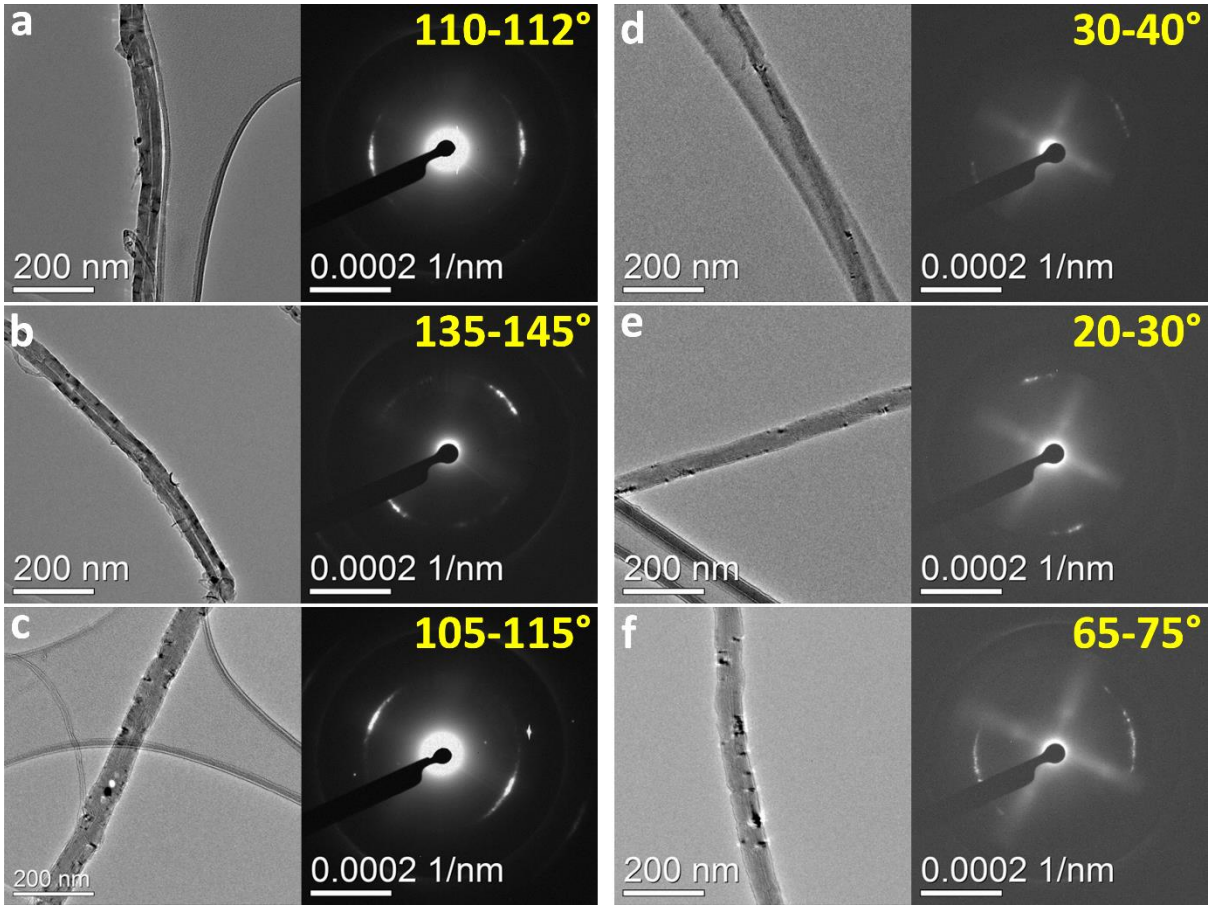

*Figure SI3. Representative transmission electron micrographs and corresponding electron diffraction patterns of individual pristine (**a, b and c**) and heat treated (**d, e, and f**) MWCNTs with similar outer diameter and straightness.*

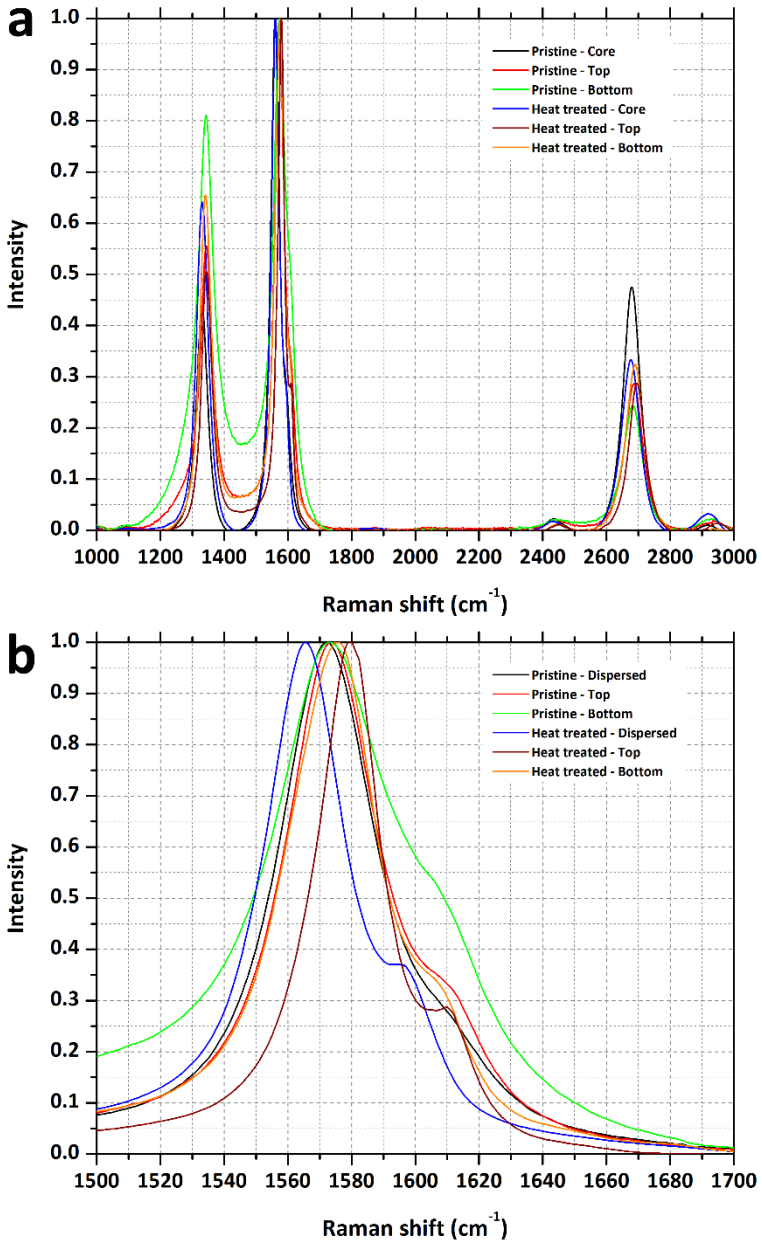

*Figure SI4. Full range Raman spectrum (**a**) and Raman G-band range (**b**) of the core, top and bottom of the pristine and heat treated carpets of VA-MWCNTs.*

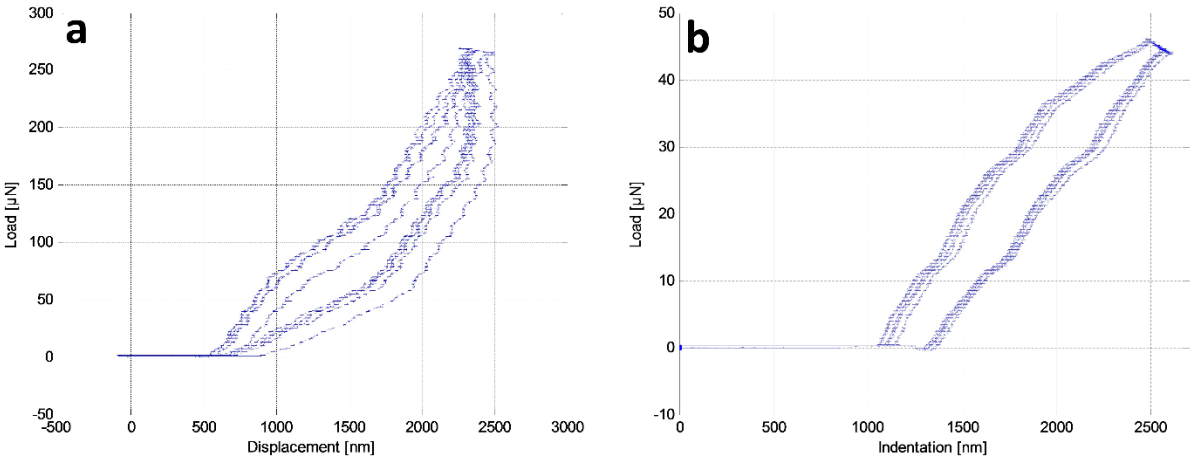

*Figure SI5. Representative load-indentation graphs of the (**a**) bottom and (**b**) top surface of a typical pristine VA-MWCNT carpet.*

Plasma treatment of large-area carpets of ultra-long MWCNTs

As can be seen from scanning electron micrographs in figure SI6, the carpets treated with plasma transformed into a composite consisting of graphite, CVD MWCNTs and arc-discharge-like CNTs [1]. The formation mechanism of the graphite matrix is rather indeterminate but seems to be due to the evaporation, ion flow and deposition of graphite from the electrodes, instead of graphene layers folding as proposed in top down mechanisms for the formation of fullerenes and CNTs [2]. The arc-discharge-like CNTs were significantly thinner, straighter and hence easily distinguishable from CVD MWCNTs. Moreover, they mostly seem to have grown from the tip of the CVD MWCNTs. Again, the formation mechanism is not fully understood but XPS revealed (figure SI6) no traces of residual CVD iron-containing particles on the surface of carpets after the plasma treatment. Therefore, it is unlikely that the formation of arc-discharge-like CNTs is catalysed by reactivated residual CVD iron-containing particles because such particles probably evaporated during the arc discharge. The parts of the carpet exhibiting this type of composite structure changed colour from black to silver. The transformation under the plasma was non-uniform as there were some areas fully covered with graphitic particles while other areas remained unchanged. This composite could potentially

exhibit interesting mechanical properties as the microstructure resembles that of carbon-carbon composites [3]. Due to the high integrity of the structure, isolation of individual arc-discharge-like CNTs for further characterisation was not possible. We were unable to observe any arc-discharge-like CNTs under TEM, even after 30 minutes of intensive sonication of sample in acetone. The Raman spectra taken from the whole structure was exactly identical to pure synthetic graphite with no sign of Raman Radial Breathing Mode (RBM) resonance suggesting the absence (or extremely low abundance) of single-wall CNTs.

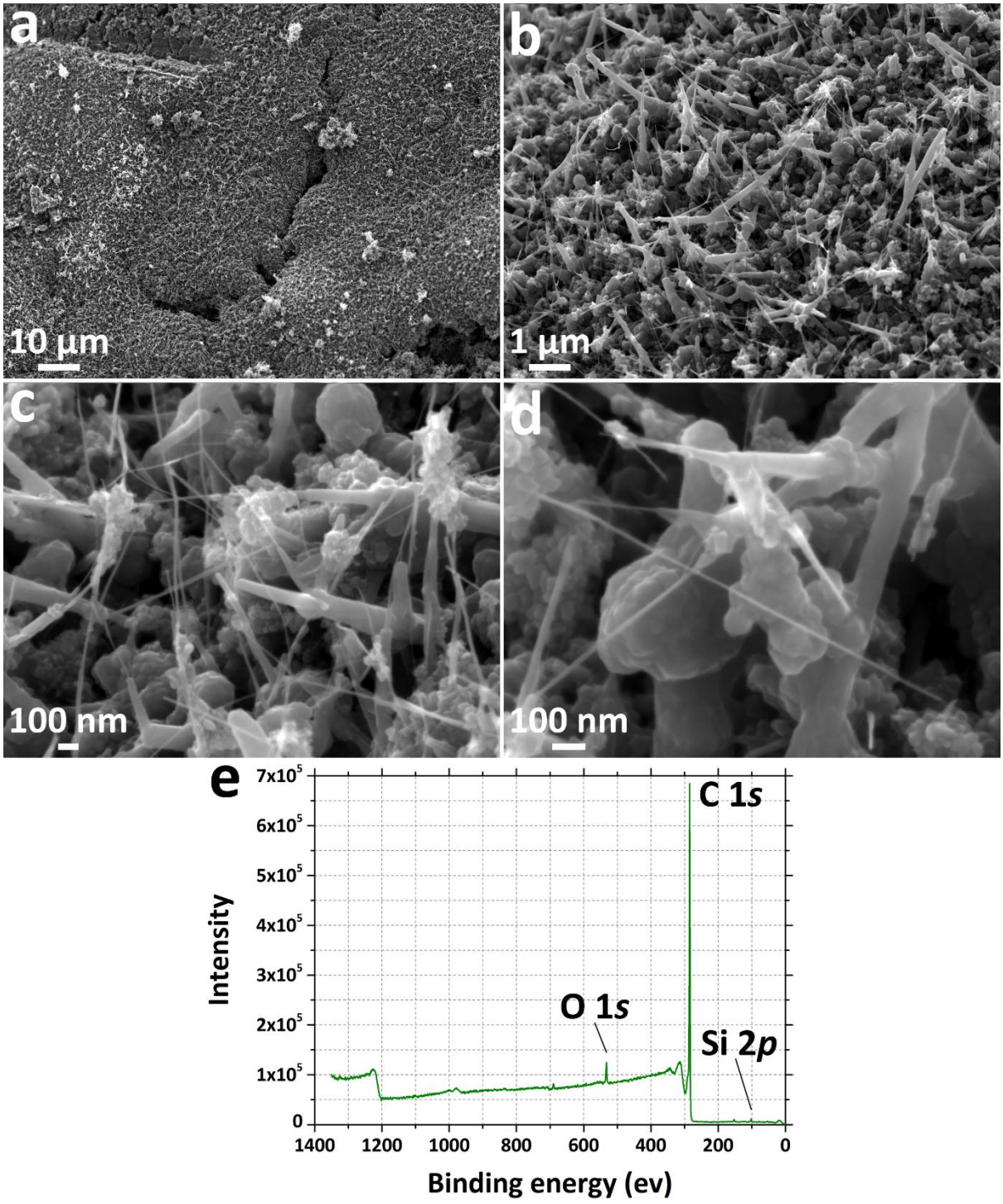

*Figure SI6. Scanning electron micrographs (**a**-**d**) and X-ray photoelectron spectrum (**e**) of the surface of the plasma treated carpets of VA-MWCNTs composed of CVD and arc-discharge-like MWCNTs embedded in a graphite matrix.*

References

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