Electronic Supplementary Information (ESI) -Switchable changes in the conductance of single-walled carbon nanotube networks on exposure to water vapour.

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Supporting Information

The UV-Vis-NIR absorption spectroscopy data for the aqueous HiPco DOC, HiPco SC, HiPco CTAB, HiPco CTAT, HiPco Triton X-100 and HiPco control (surfactant free) solutions at different dilutions is presented in Figure S1. The absorbance at $\lambda \approx 730$ nm was used to calculate the carbon concentration of the diluted solutions using the Beer-Lambert law

$$C = \frac{A_{\lambda}}{\varepsilon_{\lambda} l},\tag{1}$$

where A_{λ} , ε_{λ} and l are absorbance, extinction coefficient and optical path length respectively. The relevant extinction coefficients (ε_{λ}) experimentally determined by Goak *et al*¹ (SWCNTs stabilised with CTAB : $\varepsilon_{\lambda} = 34.5 \text{ mL mg}^{-1} \text{ cm}^{-1}$, SWCNTs stabilised with SC: ε_{λ} = 33.6 mL mg⁻¹ cm⁻¹) were used to approximate the carbon concentration for each of the diluted solutions. The concentration of the concentrated HiPco SWCNT solutions was determined by applying a linear fit to the absorbance data to obtain the predicted absorbance for the concentrated 1 X solution, and calculating the concentration in accordance with the Beer-Lambert law.

The mass filtration method was used to compare and confirm the concentration of the concentrated HiPco DOC SWCNT solutions calculated from the UV-Vis measurements. Three HiPco DOC samples were prepared, with the average carbon concentration calculated as 1.4 ± 0.2 mg mL⁻¹, in good agreement with the concentrations calculated using the UV-Vis data (as displayed in Table 1 in the main article).

Raman spectroscopy was performed on each of the samples. Figure S2, S3 and S4 show the G-bands (1560 cm⁻¹ to 1620 cm⁻¹), D-band (1295 cm⁻¹), G'-band (2600 cm⁻¹) and radial breathing modes (RBMs, 100 cm⁻¹ to 500 cm⁻¹) for the samples under investigation. A Renshaw inVia Raman microscope with laser wavelength $\lambda = 785$ nm and 1 mW power was used on each of the surfactant wrapped HiPco SWCNT thick films after deposition and drying on 3 x 3 mm alumina substrates. Wet measurements were obtained by depositing 1 μ L of deionised water (H₂O, CAS Number: 7732-18-5, HPLC grade) on top of the SWCNTs and re-obtaining the Raman spectra.

The hot-probe method² has been used previously to determine the *n*-type or *p*-type nature of semiconducting films. It has been applied to confirm *p*-type conductivity in SWCNT networks.³ The potential difference across the films was measured using a Keithley 2100/230-240 digital multimeter. A positive probe was heated to a set temperature while in contact with the SWCNT network using a soldering iron tip and the induced change in potential was recorded (see Figure S5). A negative voltage at the heated probe indicates that holes are the majority charge carrier in the semiconducting portion of the network as described previously.² The setup was then adapted so that a portion of the SWCNT network could be exposed to a flow of either dry or wet air (by passing dry air through a Dreschel flask containing deionised H₂O, BOC certified synthetic air, 20% pure oxygen, 80% pure nitrogen, CAS number: 132259-10-0) without contacting or affecting the temperature of the hot-probe. The hot-probe method was then applied whilst additionally modulating a flow of dry or wet air to a partitioned segment of the film. Any additional change in the potential difference (and thus *p*-type nature of the network) across the film due to the presence of water vapour was subsequently recorded (see Figure S6).

An optical microscope was used to obtain the thicknesses of the thick HiPco SWCNT networks deposited on alumina substrates, estimated to be $19 \pm 5 \mu m$. The thicknesses of the thin networks were not obtainable using an optical microscope, and were estimated to be < 1 μ m. A side on view of a thick SWCNT layer on an alumina substrate, as well as optical images of the thick and thin networks deposited on an alumina substrate between gold electrodes are shown in Figure S7.

The current-voltage relationship across the SWCNT network becomes non-linear, as displayed in Figure S8, after wetting for the surfactant containing films. The current-voltage characteristics across the SWCNT network (source to drain) were measured using a Keithley 4200 semiconductor characterisation system when dry and after wetting with 1 μ L of H₂O for the thick control film, the thick SWCNT network containing DOC surfactant (c) and the thick SWCNT network containing CTAB surfactant.

References

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Figure S 1. UV-Vis-NIR absorbance data for (a) HiPco DOC, (b) HiPco CTAB, (c) HiPco Triton X-100, (d) HiPco SC, (e) HiPco CTAT and (f) HiPco control (surfactant free) solutions. The legend indicates the volume of 1 X concentrated HiPco SWCNT solution added to 3.5 ml of deionised water to achieve the dilutions required to measure absorbance over a range of concentrations. A linear fit was applied to the Absorbance vs HiPco SWCNT volume data in accordance with the Beer-Lambert law to calculate the concentration of the concentrated 1 X HiPco SWCNT solutions.



Figure S 2. Raman spectroscopy data for the dry (•) and wet (•) HiPco control (surfactant free) samples. (a) The ratio of the G⁺-bands at 1594 cm⁻¹ to D-band at 1295 cm⁻¹ indicates good sample purity. (b) The radial breathing modes (RBMs) in the range 100 cm⁻¹ to 500 cm⁻¹ suggest that nanotubes of different chirality and thus electronic type are also present in the deposited layer.(c) G'-band feature (2600 cm⁻¹). Laser wavelength $\lambda = 785$ nm at 1 mW power.



Figure S 3. Raman spectroscopy data for the dry (•) and wet (•) HiPco DOC samples. (a) The ratio of the G⁺-bands at 1594 cm⁻¹ to D-band at 1295 cm⁻¹ indicates good sample purity. (b) The radial breathing modes (RBMs) in the range 100 cm⁻¹ to 500 cm⁻¹ suggest that nanotubes of different chirality and thus electronic type are also present in the deposited layer.(c) G'-band feature (2600 cm⁻¹). Laser wavelength $\lambda = 785$ nm at 1 mW power.



Figure S 4. Raman spectroscopy data for the dry (•) and wet (•) HiPco CTAB samples. (a) The ratio of the G⁺-bands at 1594 cm⁻¹ to D-band at 1295 cm⁻¹ indicates good sample purity. (b) The radial breathing modes (RBMs) in the range 100 cm⁻¹ to 500 cm⁻¹ suggest that nanotubes of different chirality and thus electronic type are also present in the deposited layer.(c) G'-band feature (2600 cm⁻¹). Laser wavelength $\lambda = 785$ nm at 1 mW power.



Figure S 5. The potential difference induced by the application and removal of a soldering iron to the positive measurement probe (hot-probe) in contact with the HiPco SWCNT control (surfactant free) network. The progressively larger negative change in potential difference across the SWCNT network between the positive and negative measurement probes upon heating of the positive probe (hot-probe, to 160°C, 200°C and 240°C) suggests that the semiconducting nanotubes in the network are p-type.



Figure S 6. The potential difference across the SWCNT networks induced by the application of the hot-probe method whilst additionally delivering H_2O to the (a) HiPco DOC SWCNT network and (b) HiPco CTAB SWCNT network. At (i) the potential difference across the films is recorded using a Keithley 2100/230-240 digital multimeter in a flow of dry air. At (ii) the soldering iron is applied to the positive probe (hot-probe) in contact with the SWCNT network, inducing *p*-type negative increase in voltage. At (iii) wet air is delivered to a partitioned portion of the film so that the wet air cannot contact the hot-probe, inducing another change in potential difference, the direction of which is dependent on the type of surfactant present in the network. At (iv) the wet air is turned off and dry air flow resumes. The process is repeated with wet air on at (v) and (vii) and wet air off at (vi) and (viii). At (ix) the hot-probe is turned off and the potential difference across the film returns to initial levels in dry air at (x).



Figure S 7. Optical image of (a) a side on view of a thick HiPco DOC SWCNT network deposited on an alumina chip, (b) a thick HiPco DOC SWCNT network deposited on an alumina chip between interdigitated gold electrodes of 175 μ m separation and (c) a thin HiPco DOC SWCNT network deposited on an alumina chip between interdigitated gold electrodes of 175 μ m separation and (c) a thin HiPco DOC SWCNT network deposited on an alumina chip between interdigitated gold electrodes of 175 μ m separation.



Figure S 8. Current-voltage characteristics across the SWCNT network (source to drain) when dry (black \bullet) and after wetting (red \bullet) with 1 μ L of H₂O for the (a) control film (b) the SWCNT network containing DOC surfactant (c) the SWCNT network containing DOC surfactant (d) the SWCNT network containing DOC surfactant at different scale to show non-linearity after wetting and (d) the SWCNT network containing CTAB surfactant.