

Electronic Supplementary Information (ESI)

Multifunctional Single-Walled Carbon Nanotube-Cellulose Composite Paper

Experimental Section

SWCNT-cellulose solutions

PK-6. Raw NRC-UdS SWCNT were purified through the WCPP method. The purified plasma-grown SWCNT material used in this sample was the part of the seventeenth precipitate fraction (highest SWCNT concentration) from DMF. The DMF was evaporated and the purified SWCNT was dried in an oven before use. 50 g of dry SWCNT powder was ground in a mortar and pestle with a small amount of distilled water. 75 g CMC was dissolved in distilled water and added to the SWCNT. After multiple sonication and shear mixing cycles over 3 day, 9.2 g of precipitate was filtered and collected. The final total amount of SWCNT (including residual impurities) was 40.8 g. The final total weight of the mixture was adjusted to 3.64 kg with distilled water. This produced a final sample with 1.12 wt% p-SWCNT (plus impurities) and 2.06% CMC.

PK-8. This sample was prepared with NRC-UdS SWCNT raw stock without purification. 30 g of r-SWCNT raw was sonicated and mixed in distilled water to form a suspension. To this suspension 30 g of CMC was added gradually. The rest of the sample preparation was the same as PK-6. This produced a final sample with 1.67 wt % r-SWCNT (plus impurities) and 1.67 wt% CMC.

SWCNT-paper sheet manufacture

Typically retention aids are added to pulp suspensions to retain small fibrous elements (fines) and inorganic fillers such as clay. Sizing agents such as rosin are used alter the degree of cellulosic fibers during paper manufacture. The hydrophobic sizing limits water absorption by capillary action and helps keep ink on the surface of the paper rather than in the sheet. Alum is a common paper making additive used for both retention and sizing. Figure S1 shows the mechanism with which alum typically fixes rosin or, in this case, CMC on a cellulose substrate such as Kraft fiber. A 3 % (w/v) stock solution of alum was prepared from aluminum sulfate crystals. The pH of pulp suspensions were between 5.4-5.8 for handsheet formation. To see how alum interacted with the SWCNT, alum and PK-7 were mixed in the absence of fiber. After 1 h incubation, the samples were filtered on a 0.4 μm polycarbonate filter (Millipore) for microscopy.

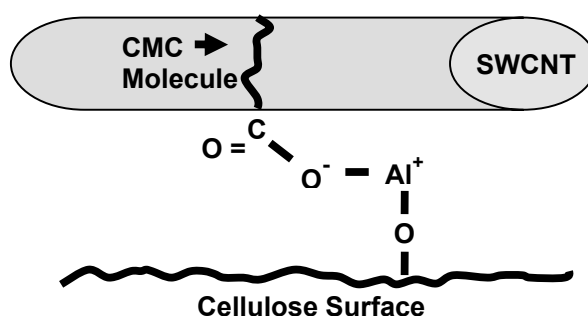


Fig. S1 Schema of interaction between CMC-functionalized SWCNT, alum and cellulose surface of the Kraft fiber. Alum gives a positive charge that attracts the CMC and hence the SWCNT to the negatively-charged fiber surface.

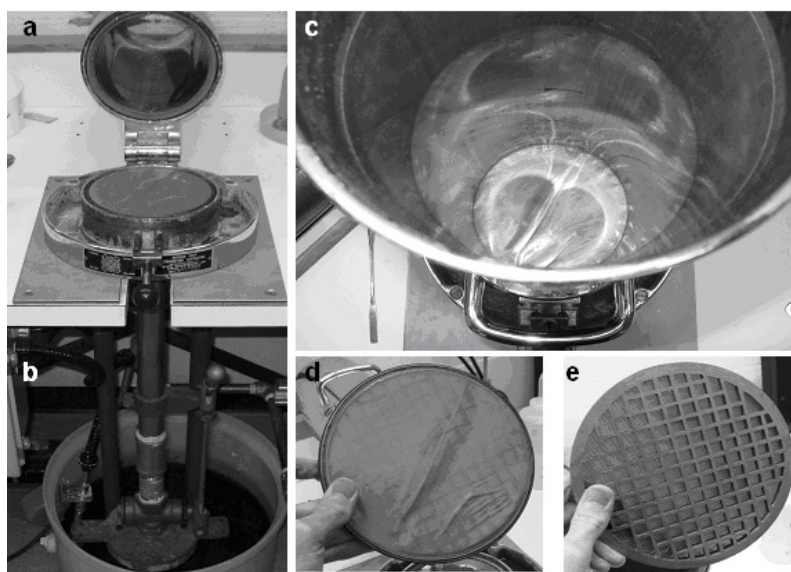


Fig. S2 Photographs of British Handsheet Maker: a) Handsheet maker showing cylinder that contains pulp slurry (deckle) and forming plate, b) drain, c) deckle in closed position, d) top side of sheet forming screen, e) metal backing supporting screen.

SWCNT-Paper Composite Strength Measurements

Breaking Length, km						Mean	STD DEV	% Difference
Control	2.82	2.92	2.72	2.55	2.51	2.70	0.17	
PK-6	2.04	1.99	1.68	1.89	1.89	1.90	0.14	27.7%
PK-8	1.48	1.6	1.58	1.63	1.29	1.52	0.14	47.5%
Stretch, %						Mean	STD DEV	
Control	1.54	1.37	0.94	0.98	1.29	1.22	0.26	
PK-6	1.43	1.45	0.73	1.07	1.11	1.16	0.30	7.1%
PK-8	0.85	0.84	0.79	0.85	0.61	0.79	0.10	44.8%

Table S1

Electrical Measurements

The stability of a SWCNT: Cellulose (25:75% w.t.) composite ($137 \pm 7 \mu\text{m}$) and the reversibility of sheet resistance upon heating is shown in supplementary figure S3. The sheet resistance is monitored continuously at ambient conditions. There is a slow conductivity enhancement (20%) stabilizing 48 hours after preparation. The origin of this relaxation is probably caused by the slow segregation of conductive carbon nanotubes from hydrophilic cellulose units. Heating to 150°C somewhat randomizes the dispersion of nanotubes between the cellulose units, reducing the conduction by $\sim 35\%$. On cooling to back to room temperature, the sheet resistance decays to $\sim 90 \Omega/\text{sq}$. (on a similar timescale), or a conductivity of 0.8 S/cm . The enhancement (degradation) is attributed to the reduction (increase) in solubility of carbon nanotubes in the cellulose matrix. There may be additional contributions from water absorption in the SWCNT and cellulose chains.

The results indicate a small mass fraction of SWCNT incorporated into normally insulating “paper”, causes a large measureable electrical conductivity without compromising mechanical properties.

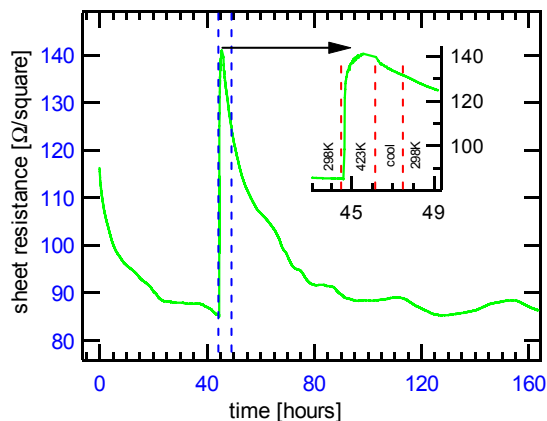
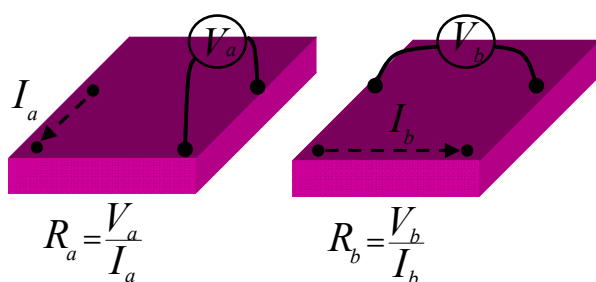


Fig. S3 Sheet resistance vs. time plot showing the stability of the SWCNT:Cellulose composite and the reversibility of sheet resistance upon heating.



sheet resistance R_s is solved from :

$$\exp\left(-\pi \cdot \frac{R_a}{R_s}\right) + \exp\left(-\pi \cdot \frac{R_b}{R_s}\right) = 1$$

Test equipment



Inside probe-station

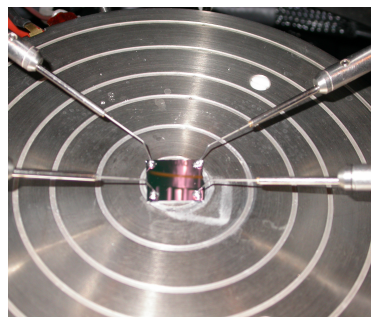


Fig. S4 Experimental set up for electrical measurements using the Van der Pauw Technique (1958). Source constant currents (I_a , I_b) between two contacts and measure voltage drops (V_a , V_b) across opposite contacts. “Pseudoresistances” R_a and R_b can be used to calculate the Sheet Resistance R_s .

Acoustic Measurements

Analysis of the standing wave pattern illustrates how the sample absorbs sound. If there is perfect absorption, then there is no reflected wave in the tube and the magnitude of the sound pressure is constant along the tube. If there is perfect reflection, then there is a reflected wave traveling in the direction to that of the incident sound wave. Along parts of the impedance tube there are constructive addition (giving double the pressure) and at other positions there are destructive cancellation (giving zero pressure). The distance between pressure nulls is a half-wavelength.

For example, a general sample would be partially reflecting and partially absorbing. The standing wave pattern will still consist of alternating maxima and minima of sound pressure, but the minima will not be zero pressure. Letting p_i be the magnitude of the incident pressure wave, and p_r be the magnitude of the reflected pressure wave, the reflection coefficient r will have a magnitude p_r/p_i . This is the measure of the reflection properties of the sample. The energy reflection coefficient is $|r|^2$ and the transmission coefficient is $1 - |r|^2$. For the standing wave pattern, maxima will have a value of $p_i(1+|r|)$ while minima will have a value of $p_i(1-|r|)$. An example of a measured standing wave pattern is shown below (figure S5). The sample is highly reflecting, as evidenced by the deep nulls in the pattern. A numerical curve fit, accounting for the small attenuation of sound waves along the tube, gives the best estimate of the reflection coefficient. In this example, the pressure reflection coefficient has a magnitude of 0.983. There is always a small amount of background noise in the tube, preferentially raising the nulls, so even a perfectly reflecting sample will not show a unity reflection coefficient. The measurement uncertainty is something like ± 0.01 . This value of 0.983 must be interpreted as highly reflecting and poorly absorbing.

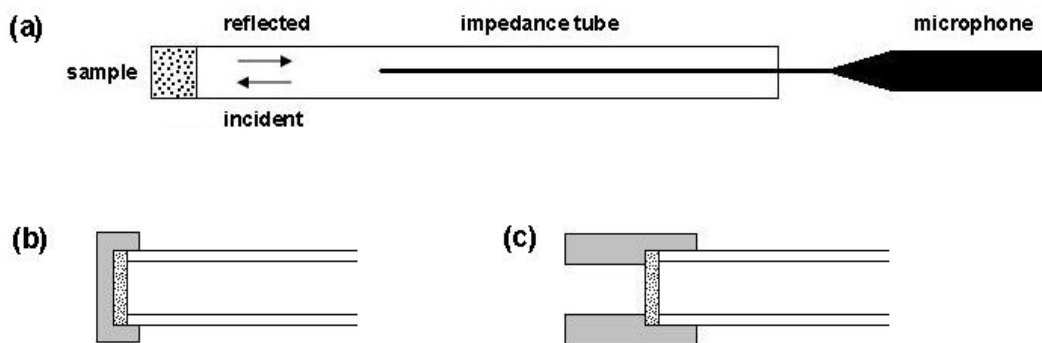


Fig. S5 Sketches of (a) the impedance tube (in cross-section) apparatus used for acoustic measurements, (b) the rigid backed mounting and (c) the open backed mounting.

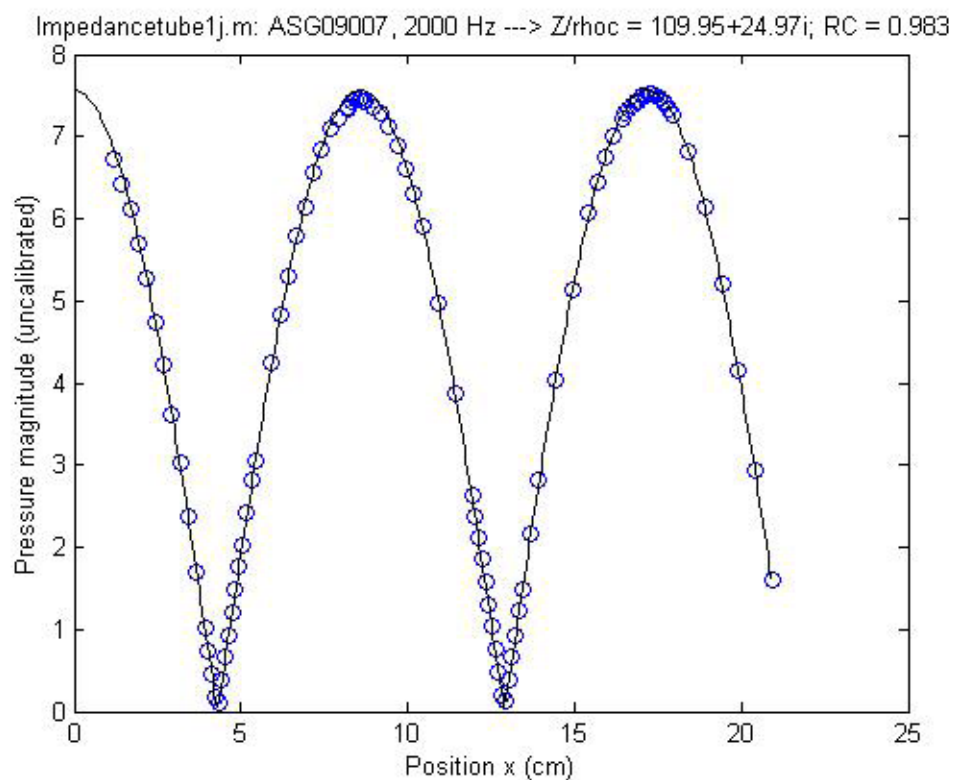


Fig. S6 Example of a measured standing wave pattern from a sample that is highly reflecting and poorly absorbing.

Sample	Frequency (Hz)	Reflection Coefficient	
		rigid backing	open backing
PK-6	500	0.992	0.971
PK-6	1000	0.985	0.950
PK-6	2000	0.983	0.972
PK-8	500	0.989	0.949
PK-8	1000	0.991	0.954
PK-8	2000	0.989	0.979
Blank	500	0.989	0.976
Blank	1000	0.999	0.943
Blank	2000	0.991	0.975

Table S2 Reflection coefficients from acoustic testing. All samples were made from Alum 35%/HWKP 200 g/m² handsheets, "PK-6" having also 35% PK-6, "PK-8" with 35% PK-8, and "blank" without nanotubes.