Electronic Supplementary Information

Surface-engineered tape casting fabrication technique toward the commercialisation of freestanding carbon nanotube sheets

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Experimental

MWCNT samples

Multi-walled carbon nanotube (MWCNT) flakes with the product code of ANS-ECF-01-000-PEG01 were obtained from Applied NanoStructured Solutions, LLC (USA), a spin-off company of the Lockheed Martin Corporation.[1], [2] The MWCNT flakes comprised >93% MWCNTs, <10% fibreglass and <6 wt% polyethylene glycol (PEG), according to the datasheet. The fibreglass serves as the substrate medium during carbon nanotube (CNT) growth, and the PEG as a wetting and dispersant agent. The MWCNT comes in flake shape instead of powder, for easy processing and for safety (because it reduces the likelihood of inhaling hazardous CNT and fibreglass dusts).

Surface-engineered tape-casting procedures

Unless otherwise stated, the MWCNT-$LiFePO_4$ buckypaper refer to a sheet with 1:2 MWCNT to $LiFePO_4$ mass ratio. Deionized water was produced using a Purite Select Fusion Deionised Water Purification System. MWCNT buckypaper was prepared by mixing 400 mg of MWCNT flakes (and 800 mg $LiFePO_4$ for MWCNT-$LiFePO_4$ 1:2 buckypaper or 400 mg $LiFePO_4$ for MWCNT-$LiFePO_4$ 1:1 buckypaper) with 10 ml ethanol and 10 ml de-ionized water; the mixture was then lightly ground using a mortar and pestle for 2 minutes. Next, 90 ml de-ionized water and 90 ml ethanol were added to the slurry while transferring it to a 250 ml capacity beaker. Sonication using a VCX 750 Ultrasonic Processor (Sonic, USA) and magnetic stirring using advanced hotplate stirrers (VWR, USA) were simultaneously performed at room temperature. An amplitude of 40% was set for 10 minutes, with mixing at 1000 rpm for the first 2 minutes and 1600 rpm for the remaining 8 minutes. The sonication process typically has 30-33 Watts power and >18000 Joule energy transferred. Magnetic stirring needs to be maintained during the sonication (otherwise, at the fixed amplitude of 40%, the power goes down to <30 Watts and the energy transferred to <18000 Joule). The dispersed slurry was then degassed using a vacuum oven. Casting was performed manually at room temperature using a micrometer adjustable film applicator (EQ-Se-KTQ-150, MTI Corporation, USA) with a doctor-blade gap of 5 mm unless otherwise stated. The matt-side of the copper foil (EQ-bccf-9u, MTI Corporation, USA) was used as the supporting substrate unless otherwise stated. The copper foil was placed on top of a glass plate (EQ-Tglass, MTI Corporation, USA) with the matt side of the copper foil uppermost. The casted film was then put inside an oven (Binder Forced Convection Oven FD 53) at 120 °C for 1 hour.

Densification of MWCNT sheet

Densification of SETC-made buckypaper was performed using a Carver Auto CH-NE Pressing Machine. SETC-made buckypaper was sandwiched between the shiny side of copper foils (EQ-bccf-9u, MTI Corporation,

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USA), which were further sandwiched using polytetrafluoroethylene (PTFE) sheets. After densification, the SETC-made buckypapers were cut according to specifications: ASTM D638 type V for mechanical testing, 2 cm x 2 cm for electrical testing, and 16 mm diameter for density calculation. The density was calculated by measuring the mass of the 16 mm diameter SETC-made buckypaper using a Mettler Toledo MS105DU, and measuring the thickness of the SETC-made buckypaper using a cross-section scanning electron microscopy (SEM) of Nova NanoSEM, and calculation using the following formula: $\text{Density} = \frac{\text{mass}}{\text{volume}} = \frac{\text{mass}}{(\pi)\left(\frac{diameter}{2}\right)^2 (\text{thickness})}$.

The skeletal density (true density) of SETC-made buckypaper was obtained from uncompressed samples. The SETC-made buckypaper was kept in a vacuum chamber at 50 °C for 3 hours to remove adsorbed moisture. A Mettler Toledo MS105DU analytical balance with readability of 0.01 mg was used to measure the mass of the SETC-made buckypaper. SETC-made buckypaper with a mass of 2.7045 g was placed inside a 10 cm^{-3} chamber insert of an AccuPyc 1340TC Automatic Gas Pycnometer. The measurement used helium gas, with a 0.0050 psig min^{-1} equilibration rate and chamber pre-purging for 10 cycles. Skeletal density was measured 10 times. The average and standard deviation of the SETC-made buckypaper skeletal density were reported.

Physical characterisations

SEM of Nova NanoSEM was used to determine the morphology of MWCNT flakes before and after tape-casting. The samples were put on top of copper double-sided tape on an aluminium stub. The samples were not coated with a palladium/gold layer. Transmission electron microscopy (TEM) of Tecnai TEM 200 kV was performed to determine the size of a single strand of CNT before tape-casting. Samples were prepared by dropping a small volume of MWCNTs dispersed in an alcohol-based solution onto the carbon-coated copper mesh (TedPella, USA). AFM was performed using a Witec Alpha 300RAS with a non-contact mode and 42 Nm^{-1} tip resonance frequency. The sample was prepared by dropping a small volume of MWCNTs dispersed in an alcohol-based solution onto a silicon wafer. Raman spectroscopy was performed using a Witec Alpha 300RAS with 532 nm excitation wavelength. UV-visible-NIR spectrophotometry was done using a Perkin-Elmer Lambda 1050 with 150 mm InGaAs integrating sphere module, photomultiplier (PMT) detector (gain= automatic, time= 0.40 s) and InGaAs detector (gain= 9, time= 0.40 s), scanning from 2400 nm to 200 nm at 2 nm resolution, using 100% transmission and 0% transmission correction, with USRS-99-020 Spectralon standard. X-ray diffraction was performed using XRD Empyrean from PANalytical using a powder method, with copper kα_1 of 1.540598 Å, 45 kV voltage, 40 mA current, scan speed of 0.069630 °s^{-1} and 2θ range from 10 ° to 90 °. Specific surface area measurements were conducted using a Quantachrome NOVA 2000e system. The sample was first degassed at 200 °C for 5 hours, followed by a N_2 adsorption/desorption experiment. The surface area was then calculated by averaging the values acquired from the adsorption and desorption curves using a multi-point technique over the 0-0.35 P/P_o linear points range based on the Brunauer-Emmett-Teller (BET) method. Thermal gravimetric analysis was performed using a TGA 4000 / Pyris 6 from temperature of 30 °C to 990 °C at 5 °C min^{-1} using pure oxygen.

Mechanical characterisations

Tensile testing experiments were performed using an Instron 5982 with 5 kN load and 5 mm min^{-1} speed. SETC-made buckypaper samples were cut according to ASTM D638 type V standard using Ray-Ran test equipment LTD RR/HCP cutter. The tensile strength was measured from the highest point before breaking. Young's modulus was calculated as the slope of the linear region of the stress-strain curve.

Electrical and optical characterisations

In-plane sheet resistance was measured using a Keysight 34465A digital multimeter and four probe configurations with Kelvin clips at room temperature. The SETC-made buckypapers were cut to 2 cm x 2 cm. The thickness of SETC-made buckypaper was measured using cross-section SEM of Nova NanoSEM. The electrical conductivity was calculated according to: $R = \rho \frac{L}{A} = \frac{1}{\sigma} \frac{L}{Lt}$; where R is the measured resistance, ρ is the electrical resistivity, L is the length, A is the cross section area, t is the thickness and σ is the electrical conductivity: $\sigma = \frac{1}{Rt}$.

For optical measurements, we measured the transmittance and reflectance. The absorbance was calculated using the following formula: $\%\text{Absorbance} = 100 - (\%\text{Transmittance} + \%\text{Reflectance})$. Optical bandgaps were determined using the Planck's equation.

Electrochemical characterisations

SETC-made MWCNT-$LiFePO_4$ buckypaper was cut using a punch with a diameter of 16 mm. The mass loading (unless otherwise stated; 5.2 mg cm^{-2}) was taken using a precision balance (Mettler Toledo MS105DU Semi-Micro Analytical Balance) with a readability of 0.01 mg. Conventional $LiFePO_4$ on aluminium foil samples were obtained from two different commercial vendors and then cut as 12 mm disk with a typical mass loading of 19.1 mg cm^{-2} (vendor A) and 22.64 mg cm^{-2} (Vendor B). The cut samples were heated at 80 °C for at least 12 hours in a mini vacuum oven attached to the glovebox (MBraun MB-Labstar 1450/780 Glove Box) to remove residual moisture before cell assembly. Coin cells of 2032-type were assembled using a crimping machine (MSK-110 Coin Cell Crimping Machine) inside the glovebox. The liquid electrolyte used was 1 M $LiPF_6$ in EC:EMC (1:1 vol%) with 2 wt% FEC. A half-cell configuration was used in which a lithium metal foil serves as the anode. For cyclic voltammetry, the SETC-made MWCNT-$LiFePO_4$ buckypaper was cut using punch with a relatively small diameter of 6 mm. This is to ensure that the Li counter electrode has higher surface area than the working electrode.

Coin cells were tested using a battery tester (Maccor Battery Test System Series 4000) inside an environmental chamber (CSZ Model MC-3 Chamber) at a constant temperature of 25 °C. Battery testing was performed at various rates with a potential window of 2.5 – 3.75 V vs. Li/Li^+. The charging procedure was constant-current charging at C-rate followed by constant-voltage charging at 3.75 V until the current decreased to 0.05 C or 15-minute timeout.

Unless otherwise stated, the specific capacities were calculated by considering the mass of the whole electrodes: mass of MWCNTs+$LiFePO_4$ for the SETC-made MWCNT-$LiFePO_4$ cathode; mass of aluminium_current_collector+$LiFePO_4$+carbon_conductor+binder for conventional $LiFePO_4$ cathode. When the specific capacities of SETC-made MWCNT-$LiFePO_4$ cathode were calculated by considering the mass of $LiFePO_4$, the capacity contribution of MWCNT (~10 $mAhg^{-1}_{MWCNT}$) was subtracted prior to normalizing with the mass of $LiFePO_4$.

Cyclic voltammetry was performed at 0.1 mV s^{-1} scan rate from 2.5 – 4.0 V vs. Li/Li^+, using a multi-channel potentiostat/galvanostat (Princeton Applied Research PMC-1000) without iR compensation. Electrochemical impedance spectroscopy (EIS) measurement were performed using an Autolab PGSTAT302N; the acquisition of the impedance spectra was done at open-circuit potential with frequencies between 10^6 Hz to 10^{-1} Hz and at an amplitude of 50 mV RMS.

Dispersion stability

Dispersion stability of MWCNT solutions

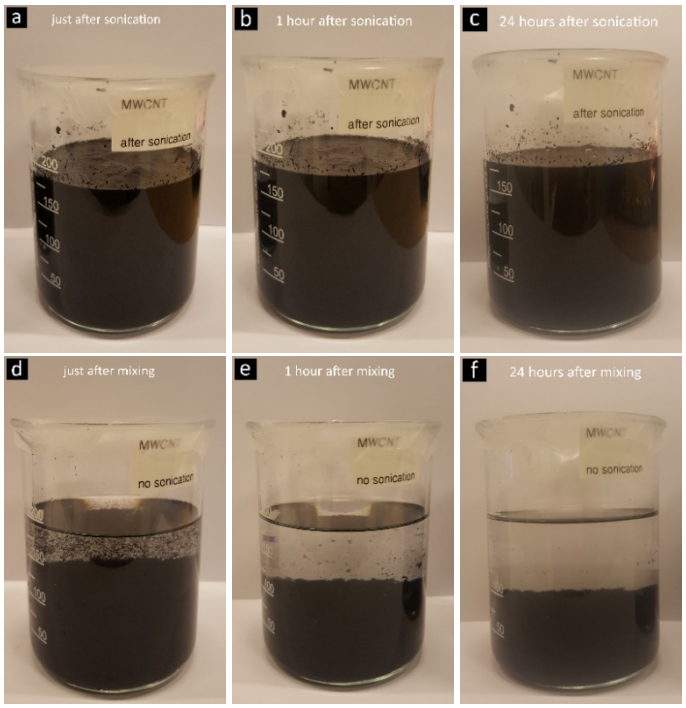


Figure S1 (a-c) The MWCNT solution was well dispersed, evidenced by stability at (a) just after sonication, (b) after 1 hour idle and (c) after 24 hour idle. (d-f) Control sample shows the MWCNT easily settled down when no sonication was performed.

Dispersion stability of MWCNT-$LiFePO_4$ solutions

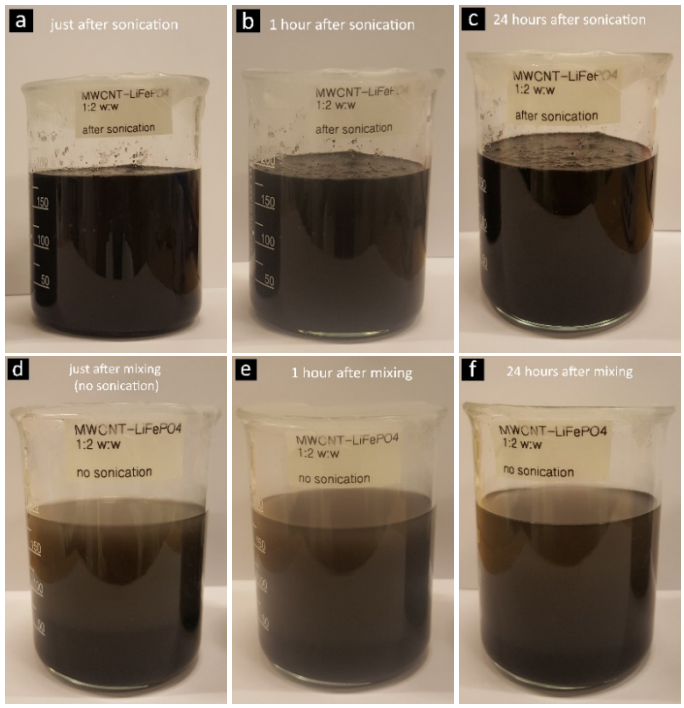
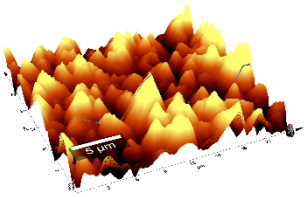


Figure S2 (a-c) The MWCNT-$LiFePO_4$ solution was well dispersed and stable (a) just after sonication, (b) after 1 hour idle and (c) after 24 hour idle. (d-f) Control samples shows the MWCNT settled down while the $LiFePO_4$ powder stayed as a suspension.

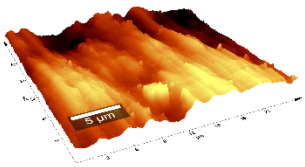
Selection of supporting substrate

Table S1 Selection of supporting substrate

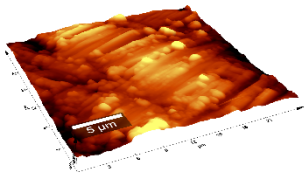
#	Supporting substrate	Flexibility of supporting substrate	Wetting of MWCNT solution on supporting substrate	Separation between dried MWCNT buckypaper and supporting substrate
1	Copper (micro-pyramidal structure)	Flexible	Excellent	Excellent
2	Copper (smooth)	Flexible	Excellent	Cannot be separated
3	Copper (randomly rough)	Flexible	Excellent	Cannot be separated
4	Silicon (micro-pyramidal structure)	Not flexible	Excellent	Excellent
5	Silicon (smooth)	Not flexible	Excellent	Cannot be separated
6	Silicon (randomly rough)	Not flexible	Excellent	Cannot be separated
7	Aluminum (smooth)	Flexible	Excellent	Cannot be separated
8	Aluminum (randomly rough)	Flexible	Excellent	Cannot be separated
9	PTFE (randomly rough)	Flexible	No wetting	Good (has residues)



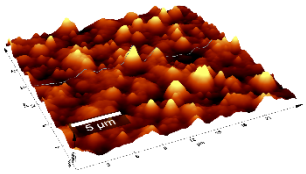
Copper (micro-pyramidal structure)
RMS = 448.2 nm



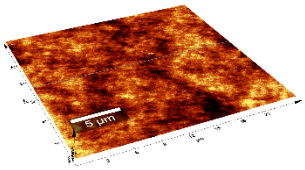
Copper (smooth)
RMS = 324.6 nm



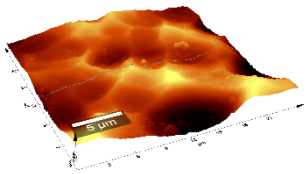
Copper (randomly rough)
RMS = 621.5 nm



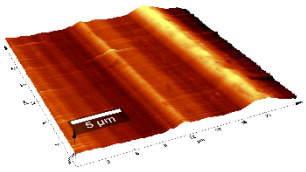
Silicon (micro-pyramidal structure)
RMS = 151.3 nm



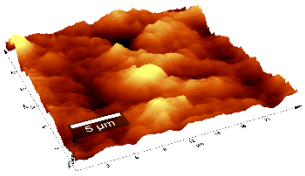
Silicon (smooth)
RMS = 137.1 nm



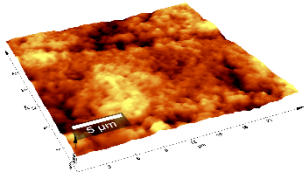
Silicon (randomly rough)
RMS = 294.5 nm



Aluminum (smooth)
RMS = 245 nm



Aluminum (randomly rough)
RMS = 331.4 nm



PTFE (randomly rough)
RMS = 669.4 nm

Figure S3 The Atomic Force Microscopy (AFM) of different supporting substrates

Alignment of MWCNT flakes

The pre-alignment of MWCNT flakes

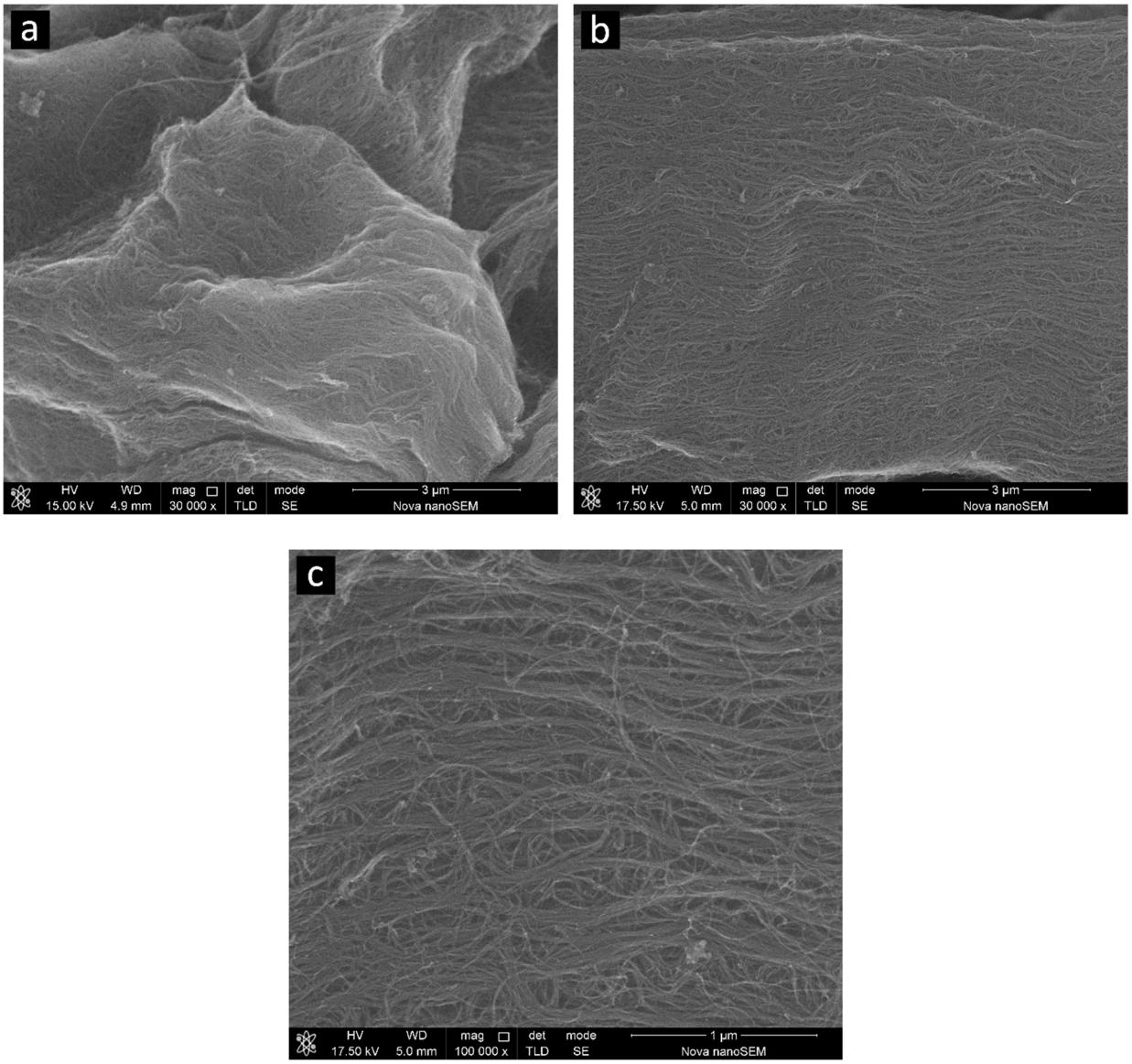


Figure S4 (a,b,c) High magnification scanning electron microscopy (SEM) images of MWCNT flakes before casting.

Random orientation MWCNT buckypaper using filtration method

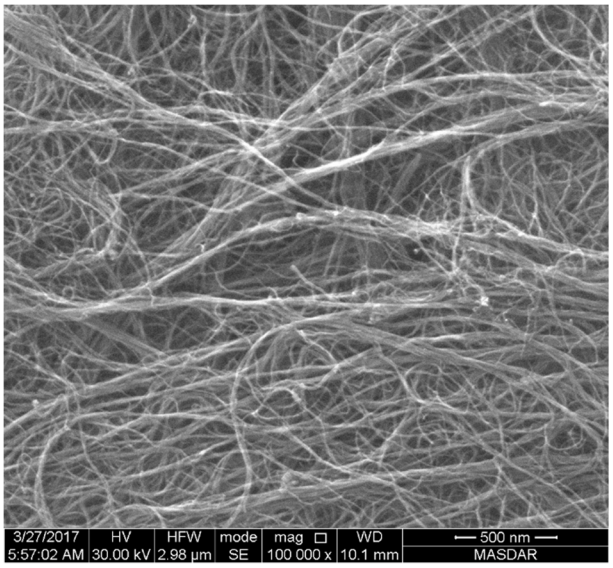


Figure S5 SEM image of MWCNT buckypaper made with filtration using the same MWCNTs batch.

Mechanical and optical properties of SETC-made MWCNT buckypaper

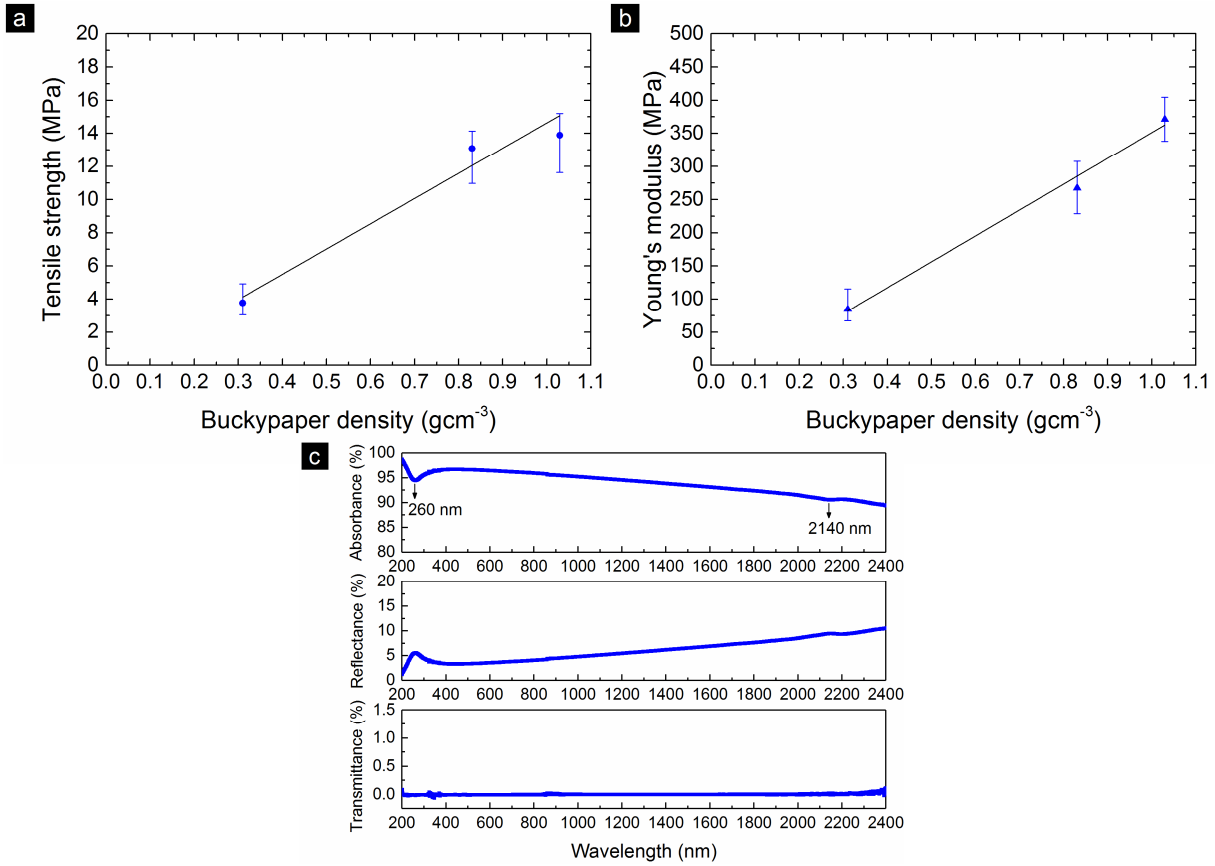


Figure S6 (a) Tensile strength, (b) Young's modulus and (c) UV-VIS-NIR spectroscopy of SETC-made buckypaper.

Figure S6a shows that our SETC-made buckypaper had a tensile strength of 3.77, 13.09 and 13.90 MPa for a density of 0.31, 0.83 and 1.03 gcm^{-3}, respectively. The tensile strength (13.90 MPa) is higher than that of buckypaper made using the filtration technique (~4 MPa) but lower than that of high-density filtered buckypaper (45.6 MPa)[3]. Figure S6b shows a similar trend for the Young's modulus, at 84.78, 267.13 and 371.38 MPa for a SETC-made buckypaper density of 0.31, 0.83 and 1.03 gcm^{-3}, respectively. The Young's modulus of 371.38 MPa is higher than filtered buckypaper (~167 MPa) but lower than that of high-density filtered buckypaper of ~1150 MPa [3]. These findings show that buckypaper made using tape-casting is of comparable quality to buckypaper made using membrane filtration, and that higher density leads to better tensile strength and Young's modulus. The density of SETC-made buckypaper was limited by the maximum load of our pressing equipment. Theoretically, it could be increased through better mechanical pressing up to MWCNT buckypaper's true density (skeletal density) of 1.9398 ± 0.0028 g cm^{-3}. This value of true density of the MWCNT buckypaper was determined using helium pycnometer and precision balance. It is worth noting that our SETC-made buckypaper contained the electrically insulating impurity of glass fibre. Bandgap energy was calculated from the UV-Vis-NIR spectrum. Figure S6c shows that the transmittance of the SETC-made buckypaper was almost zero, the reflectance was below 11% and the absorbance was more than 89% from the wavelength range of 200 to 2400 nm. Two transition points were determined at 2140 and 260 nm, which corresponded to an optical bandgap energy of 0.58 and 4.77 eV; these were attributed to MWCNTs and glass fibre, respectively.

Warburg coefficient

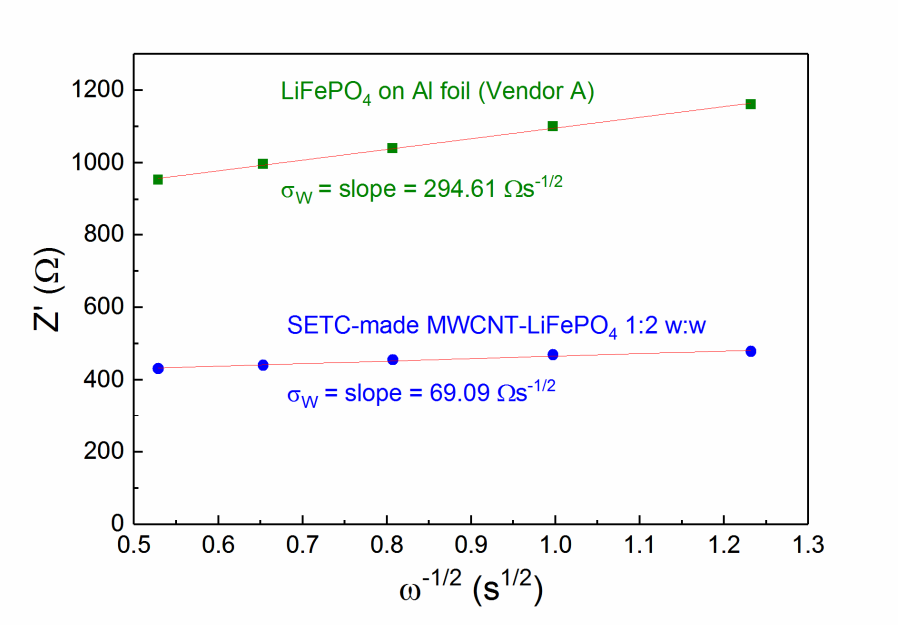


Figure S7 The plot of Z' vs. $\omega^{-1/2}$ of SETC-made MWCNT-$LiFePO_4$ 1:2 w:w and $LiFePO_4$ on Al foil (Vendor A).

First cycle's Coulombic efficiency after formation

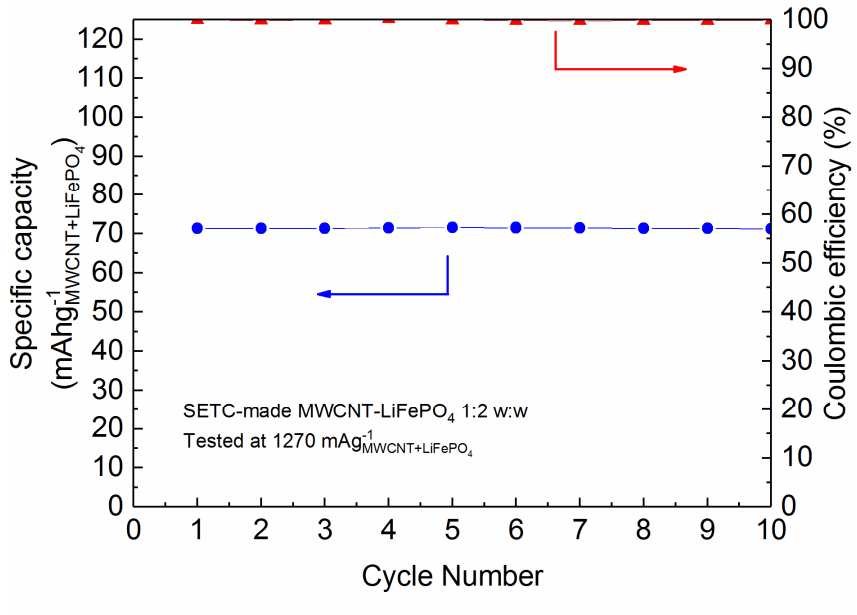


Figure S8 Constant-current charge-discharge (CCCD) of MWCNT—$LiFePO_4$ sheet after formation process.

References

[1] B. K. Malet and T. K. Shah, “Glass substrates having carbon nanotubes grown thereon and methods for production thereof.” Google Patents, 22-Jul-2014.

[2] T. K. Shah, H. Liu, J. M. Goldfinger, and J. J. Morber, “Carbon nanostructure-coated fibers of low areal weight and methods for producing the same.” Google Patents, 11-Aug-2015.

[3] H. Younes, R. A. Al-Rub, M. Mahfuzur Rahman, A. Dalaq, A. Al Ghaferi, and T. Shah, “Processing and property investigation of high-density carbon nanostructured papers with superior conductive and mechanical properties,” *Diam. Relat. Mater.*, vol. 68, no. July, pp. 109–117, 2016.