SUPPLEMENTARY INFORMATION

Cross-Linked Single-Walled Carbon Nanotube Aerogel Electrodes via Reductive Coupling Chemistry

Martina De Marco, Foivos Markoulidis, Robert Menzel, Salem M. Bawaked, Mohamed Mokhtar, Shaeel A. Al-Thabaiti, Sulaiman N. Basahel, and Milo S. P. Shaffer*

Materials and equipment

TGA with evolved gas analysis was carried out on a METTLER TGA/DSC 1 machine (Mettler-Toledo International, Beaumont Leys Leicester, UK) coupled with a Nicolet FT-IR Spectrometer (Thermo Fisher Scientific, Loughborough, UK) and a HPR-20 QIC R&D mass spectrometer (Hiden Analytical Ltd., Warrington, UK). Typically, 2 mg samples were first dried at 100 °C under N₂ for 60 minutes and then heated from 100 °C to 850 °C at 10 °C min⁻¹ in 20 mL of N₂. Raman spectra of powder samples were obtained with a LabRAM Infinity instrument (Horiba Jobin-Yvon Ltd) with a 633 nm He-Ne laser (1.96 eV). Samples were measured in raw powder form and at least five consistent spectra were measured for each sample at different locations to reduce the effect of sample heterogeneity. Scanning electron microscopy (SEM) images were collected using Gemini 1525 FEGSEM, fitted with an Oxford Instruments INCA energy dispersive X-ray spectrometer (EDS). XPS spectra of compacted aerogel samples were recorded using a Thermo Scientific K-Alpha instrument using focused (400 µm spot) monochromatic Al-Kα radiation at a pass energy of 40 eV. The binding energies were referenced to the sp² C1s peak of graphite at 284 eV. Specific surface areas were measured with a Micromeritics Tristar 3000 and calculated according to the Brunauer, Emmett and Teller (BET) equation from the adsorption isotherm. The pore-size distribution of the samples was calculated from desorption branch using the Barrett, Joyner, and Halenda method.

Electrical conductivity through the monolith volume was measured using a custom-made, electrically contactable sample holder consisting of two, large circular, movable aluminium electrodes connected to an Iso-Tech digital multimeter IDM67. Tests at 10% of compression showed that ensuring good thermal and electrical contact between the electrode and the aerogel is crucial to obtain reliable and repeatable resistance measurements. Following other literature reports on nanocarbon aerogels, silver paste was used to reduce contact resistance, and did not permeate the samples.^[1] A control measure was also performed after a mild annealing step at 150°C for 12 hours, in order to test the effects of any moisture on the conductivity. The conductivity of the annealed aerogel (10% of compression) presented no significant differences from the as-synthesised sample, ruling out contribution of adsorbed species. Electrochemical measurements were performed using a multipotentiostat/galvanostat system (Gamry Reference 600): potentiostatic electrochemical impedance spectroscopy (EIS), in the 1 MHz to 10 mHz range; cyclic voltammetry (CV) at various scan rates (0.01, 0.1, 0.5, 1 V s⁻¹); galvanostatic charge-discharge (GCD) at various current densities (0.2, 0.6,

1.2, 2, 6, 12, 23, 58 A g⁻¹). Cyclic stability tests (1 - 10⁵ cycles) were also completed, encompassing successive GCD runs at constant current density (58 A g⁻¹). Symmetric binder-less EDLC cells with 1 cm² active electrode area were fabricated featuring the SWNT cryogel as active electrodes and aluminium carbide-modified aluminium foil as the current collector (Toyo Aluminium K.K.) and cellulose paper (TF4060, Nippon Kodoshi Corp.) as separator. The cryogel was fully soaked into the organic electrolyte (1M TEABF₄/PC, Sigma Aldrich) for one week before testing and connected directly to the collector without employing Ag paint.

Synthesis procedure

Purified small diameter SWCNT HiPco were purchased from NanoIntegris (batch P2-772). The HiPco SWCNT powder is supplied in ethanol to reduce the bulk volume, therefore the material was submitted to prolonged drying under vacuum prior to use and characterisation (4 days, 100 °C, $\sim 10^{-2}$ mbar). In order to remove any further adsorbed moisture immediately before the reaction, the nanotubes were dried with heating gun at 250 °C under vacuum ($\sim 10^{-2}$ mbar) for 3 h, and kept under vacuum for further 12 h before transferring in the glove box. All the reactions were carried out in an mBraun glove box (nitrogen atmosphere, < 0.1 ppm water, < 0.1 ppm oxygen).

Reductive dissolution and cross-linking: In a typical experiment, 25 mg of SWCNT (2.08 mmol) were reduced with Na/naphthalene solution (1 mg mL⁻¹) in N,N-dimethylacetamide, following a procedure reported elsewhere.^[2]

The nanotubide concentration was adjusted to 0.15 M with DMAc and *p*-diiodobenzene (Sigma Aldrich) (*p*-DIB) was added drop-wise to promote the cross-linking reaction (1 eq of *p*-DIB to sodium). The gel-resulting material (Fig. S1b) was then quenched under dry O_2 for the removal of any remaining charges. A control experiment was performed using monofunctional iodobenzene as electrophile (1 eq to sodium). Differently from the *p*-DIB case, the functionalised material appeared as a liquid solution (Fig. S1c). The stability of the solutions before *p*-DIB addition and following monoiodobenze addition rules out gelation by simple precipitation.



Fig. S1 (a) Thermograms of functionalised SWCNTs obtained using different Na concentrations. Grafting ratios (wt%, weight percentage of the grafted specie to the nanotube framework, Fig. S2) were determined by weight loss difference between the grafted SWCNTs and the treated SWCNTs control after the decomposition temperature (580 °C) of the grafted compounds. The 1st derivative peak was used to determine the starting and ending temperature point of each weight loss step. (b) SWCNT cross-linked with *p*-DIB (organogel) and (c) SWCNT-IB control (liquid solution).



Sample (% Wt)	[Na] mM	I _D /I _G ratio
As received SWCNT	1	0.05
Treated SWCNT	1	0.06
6	4	0.16
7	7	0.15
10	9	0.17
15	11	0.20
17	15	0.20
16	19	0.18
14	22	0.17

Fig. S2 (a) Representative Raman spectra of functionalised SWCNT (10 wt %) and treated SWCNT (average of five consistent spectra measured at different locations to minimise sample heterogeneity). (b) Table of calculated I_D/I_G ratio for all the samples. The increase in D band observed here is small compared to other functionalisation methods that provide similar extent of grafting.^[3]

Solvent exchange and freeze-dry: Following oxygen quenching, the SWCNTs organogels were freeze-dried, in order to preserve the 3D network structure by avoiding capillary collapse driven by solvent evaporation. A sequence of solvent exchanges (DMAc-THF-water) was applied in order to convert the organogel to a hydrogel. For each solvent, the washing was repeated several times over seven days and the proceeding of the replacement was monitored via NMR spectroscopy of the supernatant. The THF step was found to accelerate the solvent exchange dynamics considerably, while also allowing removal of unreacted naphthalene and the side product sodium iodide (NaI). Freeze-drying produced highly porous SWCNT cryogels with defined, cylindrical shapes, not significantly distorted from the mould dimensions.



Fig. S3 (a) Scheme of the solvent exchange procedure; (b) representative image of freeze-dried cryogel; NMR spectra monitoring the subsequent solvent exchanges (c) DMAc-THF and (d) THF-water.



Fig. S4 Representative X-Ray Photoelectron spectra of (a) SWCNT-*p*-DIB (17 wt%) (B) SWCNTiodobenzene control. (c) Summary table of iodine content (at %) for all samples and ratio of Cross-Linked/mono reacted functional groups. The ratio was estimated by calculating the mass percentage (wt %) of phenyl iodide in each sample from the iodine XPS data (wt% mono). Subtracting this value to the TGA mass loss returned the mass percentage of cross linked phenyl groups (wt% CL). The molar ratio is then derived from converting the respective weight ratio to molar ratios:

 GR_{TGA} (wt %) – mono (wt%) = CL (wt%)

 $CL:mono = \frac{CL (wt\%)/MW_{C6H4}}{mono (wt\%)/MW_{C6H4I}}$



Fig. S5 (a,d) TEM and SEM images of pristine SWCNTs, showing the typical bundle state of as received material, (c,d) TEM and SEM of cross-linked SWCNT-*p*-DIB cryogels, evidencing effective debundling and formation of a porous network.

[Na] mM	GR (wt%)	Density (mg cm ⁻³)	SSA (m² g⁻¹)	Conductivity at 10 % of compression (S m ⁻¹)
9	10	2.3	695.8 ± 2.3	5.4
11	15	2.3	702.6 ± 2.2	7.2
15	17	2.5	766.1 ± 3.5	9.4
19	16	2.5	762.6 ± 3.6	8.6
22	14	2.7	715.3 ± 2.6	7.1

Table S6. Measured properties of the cryogels. The cryogels porosity was around 99.8 %, obtained by dividing the envelope density by SWNTs density of 1.6 g cm⁻³.^[4]



Fig. S7 Pore size distribution of SWCNTs cryogels. The average pore diameter of the cross-linked cryogels matches closely the cross-linking trend. As shown in the main manuscript, a sodium concentration of 15 mM provides the highest extent of individualisation (and grafting ratio), which is reflected here by a reduced pore size compared to the other samples. Increased pore size (*e.g.* 19 and 22 mM samples) can be attributed to more bundled/salted out SWCNTs that form coarser networks.



Fig. S8 Electrochemical performance of the EDLC with SWCNT cryogel electrodes in 1 M TEABF₄/PC solution: (a) cyclic voltammograms of specific capacitance at various scan rates over a 2.7 V potential window. As expected for well-defined SWCNTs electrodes, the CV curves recorded are deformed rectangular shapes, referred as the "butterfly" shapes commonly recorded for this type of material, and whose origin has been extensively discussed in many papers.^[5] In addition, at low scan rates (and consistently with GCD curves at lower currents, Fig. S8b), additional capacitance is

observed, most likely associated with a slow, voltage-induced, diffusion-limited ion intercalation of the smaller fraction of SWNTs that remain bundled, or other regions of the cryogels where access is limited. (b) Galvanostatic charge-discharge curves at applied currents of 0.2, 0.5, 1, 2, 5, 10, 10, 20, 50 mA. The curves show promising symmetric responses at high rates; at very low rates, an additional capacitive contribution appears, associated with a marked IR-drop. Most likely this feature is related to internal resistance caused by the electrolyte diffusion limit in the smallest pores, and might be exploited more efficiently in future with an alternative drying process. (c) plot of energy density (Wh kg⁻¹) and power density (kW kg⁻¹) over 10⁵ cycles of charge discharge at 50 mA.(c) Ragone plot of CNT-based electrochemical energy storage devices including batteries and supercapacitors, (adapted from ref [6h]).^[6]



Fig. S9 Nyquist plots of the fabricated EDLC devices with SWCNT cryogel electrodes and Al foil or "nanowhisker" Al foil at (a) frequency range between 100 mHz and 1 MHz and (b) inset of the generated Nyquist plots, focusing on the resistive semi-circle Warburg elements (1 Hz to 1 MHz). The nanowhisker collector reduces the resistance at the current collectors.

[1] A. Pénicaud, F. Dragin, G. Pécastaings, M. He and E. Anglaret, Carbon 2014, 67, 360-367.

[2] A. Clancy, M. S. P. Shaffer and J. Melbourne, Journal of Materials Chemistry A 2015.

[3] J. L. Bahr and J. M. Tour, Chemistry of Materials 2001, 13, 3823-3824.

[4] Provided by manufacturer, I. NanoIntegris Technologies, c. o. R. Industries, L. Verendrye and Q. Boisbriand, Canada J7H 1R8 in *Vol.*

[5] a) O. Kimizuka, O. Tanaike, J. Yamashita, T. Hiraoka, D. N. Futaba, K. Hata, K. Machida, S. Suematsu, K. Tamamitsu, S. Saeki, Y. Yamada and H. Hatori, *Carbon* **2008**, *46*, 1999-2001; b) Y. Yamada, O. Kimizuka, O. Tanaike, K. Machida, S. Suematsu, K. Tamamitsu, S. Saeki, Y. Yamada and H. Hatori, *Electrochemical and Solid-State Letters* **2009**, *12*, K14-K16; c) T. Hiraoka, A. Izadi-Najafabadi, T. Yamada, D. N. Futaba, S. Yasuda, O. Tanaike, H. Hatori, M. Yumura, S. Iijima and K. Hata, *Advanced Functional Materials* **2010**, *20*, 422-428.

[6] a) K. H. An, W. S. Kim, Y. S. Park, J. M. Moon, D. J. Bae, S. C. Lim, Y. S. Lee and Y. H. Lee, Advanced Functional Materials 2001, 11, 387-392; b) M. Kaempgen, C. K. Chan, J. Ma, Y. Cui and G. Gruner, Nano Letters 2009, 9, 1872-1876; c) Y. Honda, T. Haramoto, M. Takeshige, H. Shiozaki, T. Kitamura and M. Ishikawa, Electrochemical and Solid-State Letters 2007, 10, A106-A110; d) Y. J. Lee, H. Yi, W.-J. Kim, K. Kang, D. S. Yun, M. S. Strano, G. Ceder and A. M. Belcher, Science 2009, 324, 1051-1055; e) C. Masarapu, V. Subramanian, H. Zhu and B. Wei, Advanced Functional Materials 2009, 19, 1008-1014; f) A. L. M. Reddy, M. M. Shaijumon, S. R. Gowda and P. M. Ajayan, Nano Letters 2009, 9, 1002-1006; g) V. L. Pushparaj, M. M. Shaijumon, A. Kumar, S. Murugesan, L. Ci, R. Vajtai, R. J. Linhardt, O. Nalamasu and P. M. Ajayan, Proceedings of the National Academy of Sciences 2007, 104, 13574-13577; h) K. L. Van Aken, C. R. Pérez, Y. Oh, M. Beidaghi, Y. Joo Jeong, M. F.

Islam and Y. Gogotsi, Nano Energy 2015, 15, 662-669; i) X. Jia, X. Zhu, Y. Cheng, Z. Chen, G. Ning, Y. Lu and F. Wei, Small 2015, 11, 3135-3142.