Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

ESI. Pore structure and electrochemical properties of CNT-based electrodes studied by in-situ small/wide angle X-ray scattering

Cleis Santos,[a] Evgeny Senokos,[a;b;c] Juan Carlos Fernández-Toribio,[a;b] Álvaro Ridruejo,[b] Rebeca Marcilla[c] and Juan José Vilatela [a*]

[a] IMDEA Materials Institute, Eric Kandel 2, Madrid 28906, Spain. ; E-mail: juanjose.vilatela@imdea.org

[b] E. T. S. de Ingenieros de Caminos, Universidad Politécnica de Madrid, 28040 Madrid, Spain

[c] IMDEA Energy Institute, Avda. Ramón de la Sagra 3, Madrid 28935, Spain

Electrochemical impedance spectroscopy data

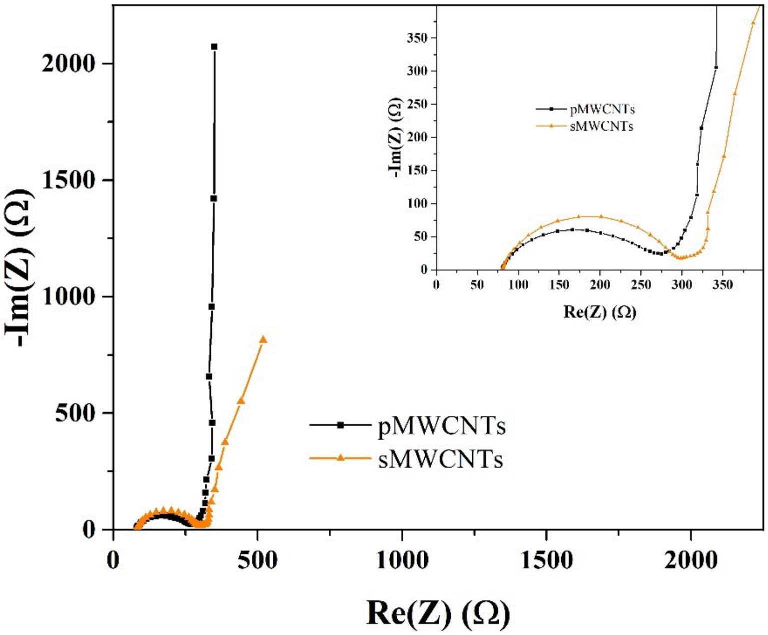

Fig. S1. Nyquist plot for the pristine MWCNTs (pMWCNTs) and swollen (sMWCNTs) fibre electrodes.

In spite of the large increase in surface area, swelling does not significantly affect either equivalent series resistance (ESR, obtained by EIS analysis) or coulombic efficiency (determined by CVs), as summarized in Table S1. This is due to the long length of the constituent CNTs enabling the coexistence of large domains where the CNTs are packed in crystalline bundles, thus suitable for charge transfer, with a large area exposed to the electrolyte.

Table S1. Equivalent Series Resistance (ESR) and Coulombic Efficiency of pristine and swollen MWCNTs fibre electrodes.

Electrode	ESR @ EIS (Ohm)	Coulombic Efficiency @ CVs (%)
PMWCNTs	265.40 ± 45.77	100 ± 1
sMWCNTs @ 500s	256.27 ± 6.75	100 ± 1
sMWCNTs @ 1500s	266.47 ± 12.46	99 ± 1
sMWCNTs @ 3600s	277.10 ± 21.68	98 ± 3

Swelling of Single-Walled CNT fibres (SWCNTs)

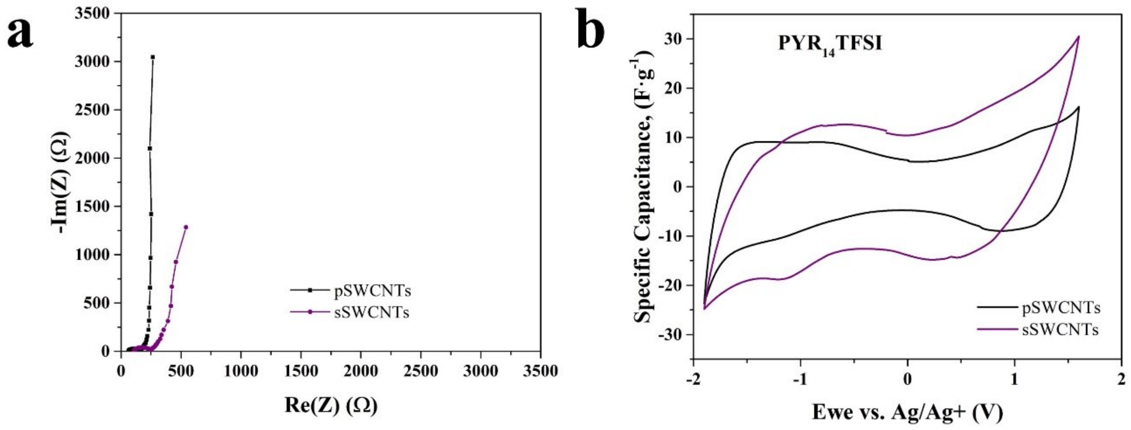

Fig S2. (a) Nyquist plot for the pSWCNTs and sSWCNTs fibre electrodes. (b) CVs of the pSWCNTs and sSWCNTs in $PYR_{14}TFSI$ at 20 mVs^{-1} and 3.5 V operating window.

Cycling test of Swollen CNT fibre.

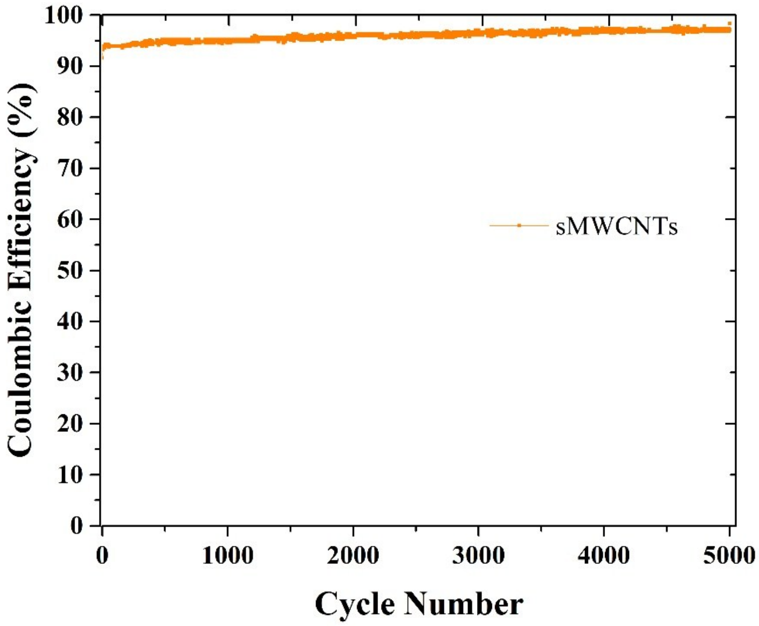

Fig. S3. Swollen CNT fibre (full swelling time) coulombic efficiency (from charge-discharge tests at 20 mA/cm^2) vs. cycle number in $PYR_{14}TFSI$.

Coulombic efficiency of the swollen CNT fibre (MWCNTf) in all cycles is higher than 95 %, confirming the effective energy storage processes in supercapacitor cycling tests.[1]

Plot of theoretical quantum capacitance and Density-of-States (DOS) for single-walled CNT.

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[1] A. Burke, *Journal of Power Sources*, 2000, **91**, 37-50.

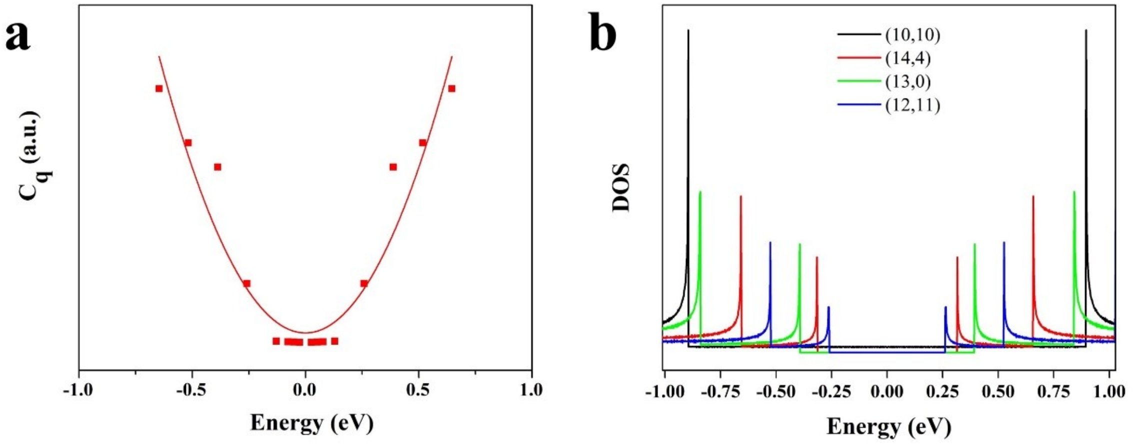

Fig. S4. (a) Theoretical Cq of a superposition of individual single-walled CNT. (b) Superposition of DOS of individual single-walled CNTs (10,10), (14,4), (13,0) and (12,11).

Surface Area by N_2 physisorption isotherm

The characterization of hierarchical pore structures (e.g. CNT fibre-based materials) in terms of the specific surface area (SSA) and porosity requires caution not only to stablish adequate measurement conditions, but also to allow a comprehensive porous network assessment. The mass of sample needed, which depends upon materials density and expected SSA, is set in 100 mg ± 13. Time and temperature degassing conditions are established as 20 hrs. and 150 ºC, respectively.

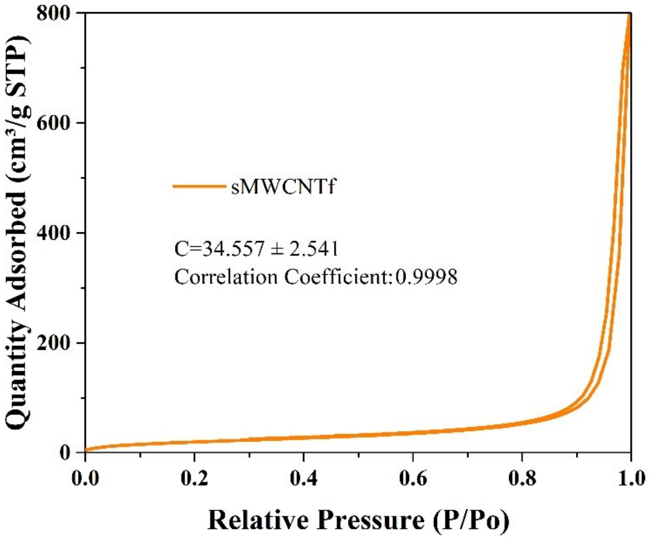

Fig S5. N_2 Isotherm for the swollen (sMWCNTf) electrodes.

We conducted several BET gas-adsorption measurements on electrochemically swollen CNT fibres and found that such samples are consistently unsuitable for BET analysis, as indicated by the lineshape of the isotherm (see Figure S5). This is due to the presence of strongly adsorbed ionic liquid which cannot be removed without recourse to treatments that would induce undesired structural/chemical changes in the electrode, such as sonication or high temperature annealing. Additionally, as it is claimed in the 2015

IUPAC's technical report,[2] in materials of high porosity (i.e. swollen CNT fibres, P_{SAXS}= 0.72-0.87) an elastic deformation of the adsorbent occurs with a significant influence on the sorption isotherm. The C value between 20-50 obtained in several BET analysis of swollen CNT fibres (for comparison, in pristine CNT fibres, P_{SAXS}= 0.66, C=118 ± 32) is an evidence of the simultaneous formation of mono- and multilayer, thus the BET area is not reliable for the swollen CNT fibres. This difficulty in using BET for structural characterisation in fact highlights the importance of having an additional, independent characterisation tool (i.e. SAXS).

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[2] Thommes, M., Kaneko, K., Neimark, A., et al. (2015). Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). Pure and Applied Chemistry, 87(9-10), pp. 1051-1069. Retrieved 24 Jan. 2019, from doi:10.1515/pac-2014-1117