The limitation of electrode shape on the operational speed of a carbon nanotube based micro-supercapacitor

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Supplementary information

Experimental details To present the experimental systematic study we fabricated micro-SCs electrodes in a monolithic process flow using a homogenous nanocarbon material reported in methods of a reference[21]. All cells possess the same electrodes area and similar thickness, hence volume, but different electrode shapes. Thanks to the procedures we could achieve the set of various electrodes with the same amount of active material and its quality characterized by the same structure, electrical properties, surface chemistry. Finally, all different micro-SCs were measured using the same techniques and tools.

Electrodes design We studied four different cell designs differed by the electrode AR (Fig.1a and Fig S1). All having the same area of Au MC pathways (272 x 10^3 μm^2), Au electrical metallic paths, and electrode (width x Length, *w x L*). The latter, in combination with similar electrodes thickness, resulted in similar electrodes volumes, with the same inter-electrode separation (50 µm).

Electrodes material The mesh film consists of Super Growth (SG-) SWCNTs[31] was used as the electrode material. The dispersion of SG-SWCNTs and cells patterning were conducted according to the process flow described in methods of a reference[21]. This time the CNT mesh film was made of 0.5 wt.-% paste dispersed in *N-Methyl-2-pyrrolidone (NMP).* There were no clues of a structural alignment regardless of the plane direction. Because the sets of various electrodes were made in one process flow, we could assume the influence of any physical damage subjected to the CNT film or formation of functional groups at CNTs had the same effect on all designs, the CNT film was characterized by the same mesh homogeneity, conductivity, and contact resistance to the MC pathways. In addition the micro-SC electrodes were selected to possess the same CNT film thickness in range of (18+/-1.8) µm (Fig. S2c).

Characterization The cells were filled with a liquid electrolyte (100-200 nL) using a micro-inkjet and epoxy cell barriers, described in a reference[21], so as to confine exactly only the CNT mesh electrodes (Fig. S1). The reason was to avoid an excess electrolyte that could influence the conductivity and provide additive migration of electro-active species. As the reference to show there was no dead electrolyte volume, we used the MC pathways surrounded by the cell barriers and filled with the liquid electrolyte, without CNTs (Fig S3). We applied a constant operational voltage of 1 V to the active CNT electrodes and we conducted measurements using electrochemical techniques (Cyclic Voltammetry, CV, and potentiostatic Electrochemical Impedance Spectroscopy, EIS) under the same conditions. Next, the data were analyzed and summarized. The complex capacitance was derived based on the complex permittivity definition[32,33]. It consists of the real and imaginary capacitance *(ImagC*) and the latter comprises all dielectric losses of the capacitor, ie. present in the CNTs electrodes and in the electrolyte. Meanwhile, the amplitudes of *ImagC* were similar meaning the dielectric losses were the same in magnitude but, upon the electrode shape, differed with the dynamics in time.

Table S1. The dimensions of different designs according to the electrode aspect ratio, electrode AR.

Electrode AR (L/w)	Length, *L* /µm	Width, *w* /µm
0,2	200	1360
1	340	800
2	544	500
7	1360	200

Resistance calculation – MCC and CNT electrodes

$R_{MCC} = 2*L/(\sigma*t_{Au}*w)$ (Eq.S1),

$R_{CNT} = 2*t_{CNT}/(\sigma*L*w)$ (Eq. S2),

where t_{Au} and t_{CNT} are the thickness of Au MCC paths (300 nm) and CNT electrode (ave. 18 µm), respectively, while *w* and *L* are the electrode width and length, respectively.

The values of conductivity σ are: $4.1*10^7$ Sm^{-1} (Au) and 0.54 Sm^{-1} (CNT)[34].

Ionic Conductivity calculation – based on EIS

$K = 1/R_{el.} = \kappa * A/l \rightarrow \kappa = (1/R_{el.})*l/A$ (Eq. S3),

where κ is the ionic conductivity of the electrolyte, K and $R_{el.}$ are conductance and the electrolyte resistance estimated from the EIS, $A=L*t_{CNT}$ is a cross section area perpendicular to the electric field, l – length along the action of the E field, here equals to (1/2)*50 µm[35].

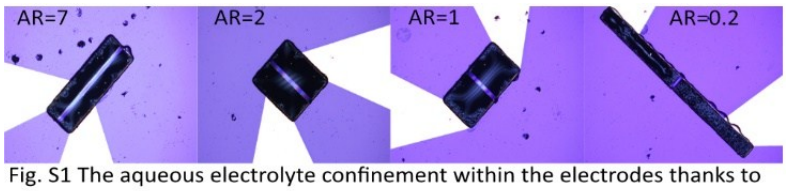

Fig. S1 The aqueous electrolyte confinement within the electrodes thanks to the cell barrier.

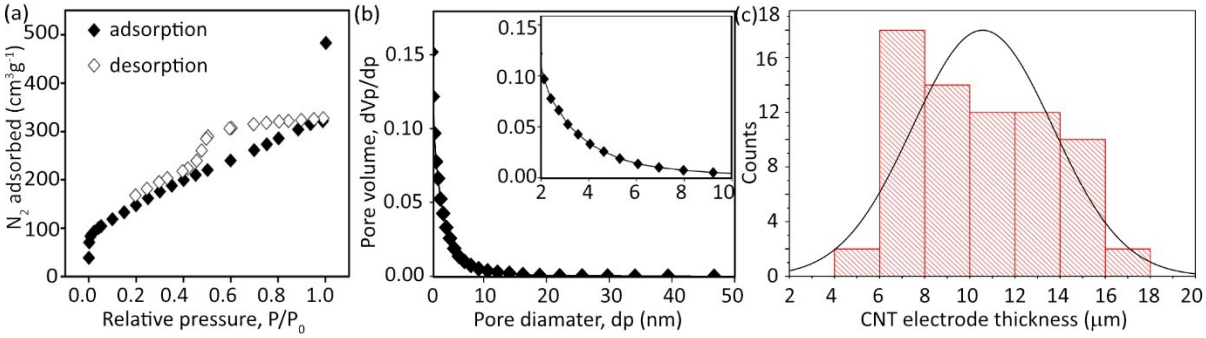

Fig.S2 CNT electrodes properties - the graphs: (a) adsorption/desorption isotherms, relative pressure P/P_0 versus N_2 adsorped/desorped volume; (b) BJH plot, pore volume $dVp/d(dp)$ vs. pore diameter dp; (c) the histogram - CNT electrodes thickness.

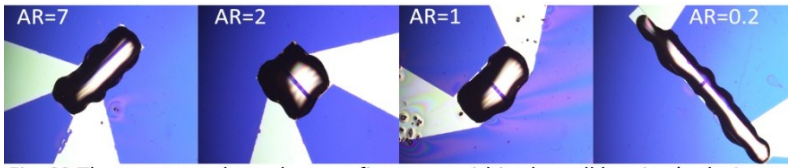

Fig. S3 The aqueous electrolyte confinement within the cell barrier (only Au MCC paths w/o CNT electrodes).