Supporting Information

High-resolution on-chip supercapacitors with ultra-high scan rate ability

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Experimental details

<u>Process developments</u>: A 500 nm SiO₂ was first thermally grown at 1100°C on a 4-inch silicon wafer in order to provide a good electrical insulation. Current collectors were then deposited using the evaporation of a 100 nm Ti / 400 nm Au layer, annealed at 250°C for 20 min, and patterned with a conventional lift-off process. The current collectors were then protected by an insulating SU8 masking layer (800 nm thick) via a second photolithography step. To improve the resolution of the micro-device, a 2.5 μ m N-LOF photoresist was deposited in the gap between the electrodes via a third photolithography step. A thin layer of 50 nm of Au was afterwards deposited on the whole wafer, followed by the electrodeposition of the active material. Both Au and active layers on the unwanted areas were finally lift-off to obtain the final devices.

<u>Electrophoretic deposition</u>: Commercial MWCNTs (Nanostructured & Amorphous Materials, Inc.) were oxidized in 15.5 mol L⁻¹ HNO₃ stirring solution for 8h at 120 °C. The powder was then successively washed with distilled water, rinsed with ethanol and dried at 80 °C. A stable suspension of 50 mg of oxidized MWCNTs in 100 ml distilled water were prepared by ultrasonication dispersion for 1 h (-35.7 mV zeta potential for an average particle size of 131.5 nm). The active material was then deposited by electrophoretic deposition by applying an electric field of 100 V cm^{-1} for 30 s before the second lift-off step. The deposit was finally annealed at $100 \text{ }^{\circ}\text{C}$ for 1 h to remove the remaining water.

<u>Electrolytic deposition</u>: Hydrous ruthenium oxide was carried out from an aqueous chloride solution composed of 10 mM RuCl₃.*x*H₂O in 10^{-1} M KCl / 10^{-2} M HCl, and adjusted to pH 2 with a 2M KOH aqueous solution. Cyclic voltammetry between -300 and +950 mV *vs*. Ag/AgCl at 50 mV s⁻¹, and performed at 50 °C for 100 cycles under stirring conditions, was used to induce the growth of the RuO₂ deposits. The samples were then annealed in air at 150°C for 1 h.

<u>Characterizations</u>: Micro-devices were soaked in de-aerated 0.5 M H_2SO_4 electrolyte and electrochemical characterizations were performed using a SP-240 potentiostat from BioLogic equipped with a linear scan generator for high scan rates. Electrochemical Impedance Spectroscopy measurements were carried out at open circuit potential and frequencies ranging from 100 kHz to 10 mHz. Scanning Electron Microscopy (SEM) was performed using a Hitachi S-4800 field-emission electron microcope. The chemical composition of the films was estimated *via* X-ray Photoelectron Spectroscopy (XPS) using a Thermo Scientific spectrometer operating with a monochromatic AlK_a X-ray source (1486.6 eV).

Simulations

Theoretical determination of the electrolyte resistance R_e

The resistance of an ionic solution R_e (Ω) depends on its resistivity ρ_e (Ω cm) and the geometric constants of the cell K (cm⁻¹) according to the following equation:

$$R_e = \rho_e \times K \tag{S1}$$

In the case of planar interdigitated electrodes, the analytical expression of the cell constant K developed by W. Olthuis *et al.*²² is described by the following equation:

$$K = \frac{1}{(N-1) \times L} \times \frac{2 \times K(k)}{K\left(\sqrt{(1-k^2)}\right)}$$
(S2)

with K(k) the complete elliptic integral of the first kind:

$$K(k) = \int_{t=0}^{1} \frac{dt}{\left[(1-t^2)(1-k^2t^2)\right]^{\frac{1}{2}}}$$
(S3)

and

$$k = \frac{i}{i+w} \text{ for } N = 2 \tag{S4}$$

$$k = \cos\left(\frac{\pi}{2}\frac{w}{i+w}\right) \text{ for } N > 2 \tag{S5}$$

with *i* the interspace, *w* the width, *L* the length and *N* the number of interdigitated fingers.

Theoretical determination of the time constant τ

We have defined the time constant τ (µs) as:

$$\tau = R \times C \tag{S6}$$

with $R(\Omega)$ and C(F) the total resistance and capacitance of the cell, respectively.

R can also be defined as:

$$R = ESR + EDR \tag{S7}$$

with ESR the "Equivalent Series Resistance" and EDR the "Equivalent Distributed Resistance" related to the distributed resistance/capacitance of the porous electrode. The main contributions of the ESR are the current collector, R_{cc} , and the electrolyte resistance, R_e , while the EDR depends on the properties of the active material.

Taking into account Equations (S1), (S6) and (S7), we can write:

$$\tau = (Rcc + K \times \rho_e) C \tag{S8}$$

Simulations of CVs curves

The simulations of CV curves have been based on the equations developed by B.E. Conway.²³ Neglecting the leakage current, the anodic I_a and cathodic I_c current can be written:

$$I_a = sC - \left(\frac{2sC}{1 + exp\left(-\frac{\Delta V}{sRC}\right)}\right) exp\left(-\frac{V}{sRC}\right)$$
(S9)

$$I_{c} = -sC + \left(\frac{2sC}{1 + exp\left(-\frac{\Delta V}{sRC}\right)}\right) exp\left(\frac{V-1}{sRC}\right)$$
(S10)

with *s* the scan rate (V s⁻¹), ΔV (V) the potential window and *V* (V) the applied potential. Taking into account Equation (S6), Equations (S9) and (S10) can be written:

$$\frac{I_a}{sc} = 1 - \left(\frac{2}{1 + \exp\left(-\frac{\Delta V}{s\tau}\right)}\right) exp\left(-\frac{V}{s\tau}\right)$$
(S11)

$$\frac{I_c}{sc} = -1 + \left(\frac{2}{1 + \exp\left(-\frac{\Delta V}{s\tau}\right)}\right) exp\left(\frac{V-1}{s\tau}\right)$$
(S12)

Resolution



Fig. S1 Optical image of calibration patterns (with different interspaces) down to 1 μ m.

XPS analysis



Fig. S2 Scanning electron microscope (SEM) observations of the morphology of the electrodeposited (a) MWCNTs and (b) hRuO₂ layers. (c) X-ray photoelectron spectroscopy (XPS) analysis of MWCNTs and oxidized O-MWCNTs showing carboxyl groups. (d) Ru3d spectra showing a stoichiometric close to the RuO₂.nH₂O structure.²⁷

CVs characterizations



Fig. S3 Cyclic voltammetry charaterizations (CV) of $hRuO_2$ -based micro-supercapacitor. (a) CVs obtained at different scan rates in de-aerated 0.5M H_2SO_4 electrolyte. (b) Evolution of the discharge current versus scan rate.



Nyquist and Bode plots

Fig. S4 (a) Nyquist and (b) Bode plots obtained from a $hRuO_2$ -based micro-supercapacitor in 0.5M H_2SO_4 .

Life cycle



Fig. S5 Evolution of the relative capacitance as a function of the number of electrochemical cycles at 1 V s^{-1} for a hRuO₂-based micro-supercapacitor.

Supplementary Reference

28 D. Rochefort, P. Dabo, D. Guay and P.M.A. Sherwood, *Electrochim. Acta*, 2003, **48**, 4245-4252.