Issues and Challenges facing Micro-Supercapacitors

David Pech

LAAS-CNRS

Context: Self Powered Applications

Embedded systems with a complete autonomy of energy

Energy scavenging and harvesting → **Energy storage and management** → **Application**

photovoltaïc, thermoelectric, piezoelectric, electromagnetic

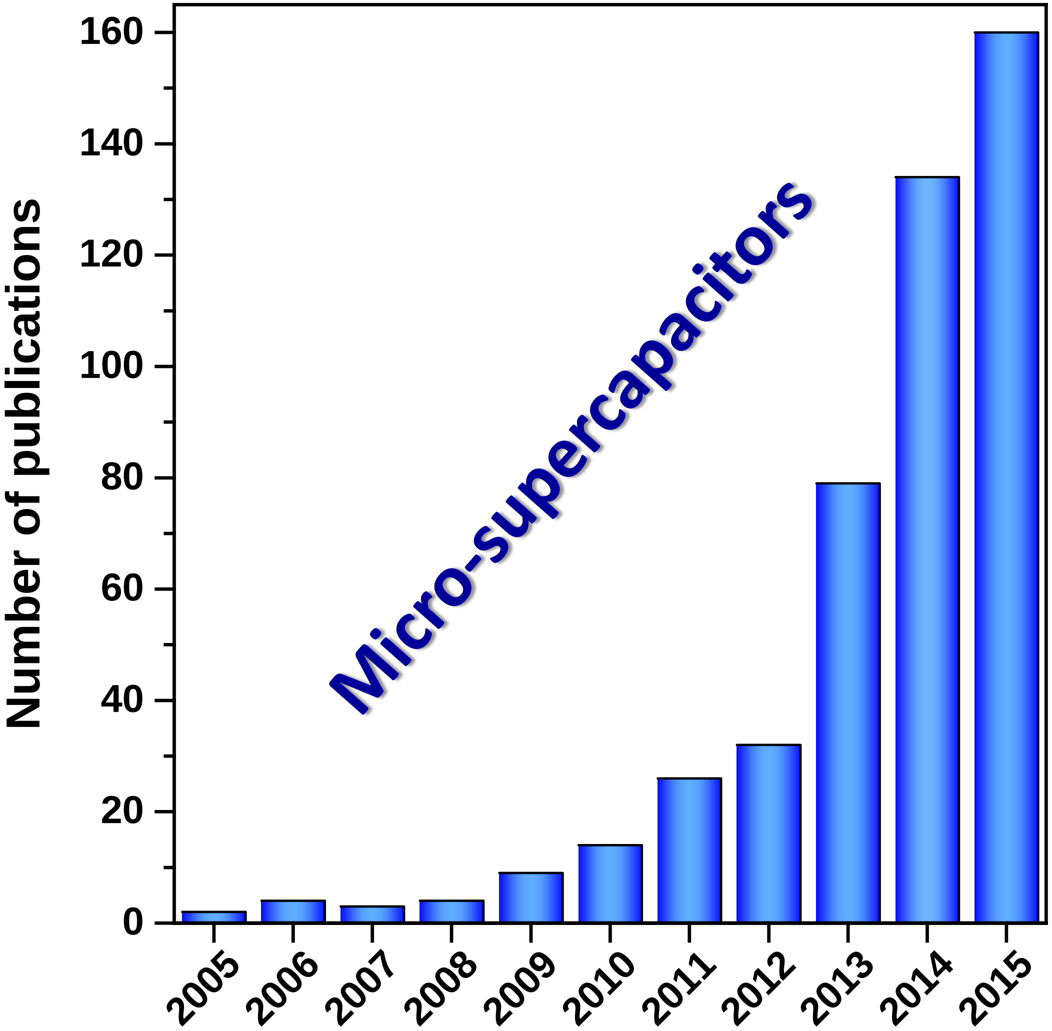
Technological Problem

Micro-batteries

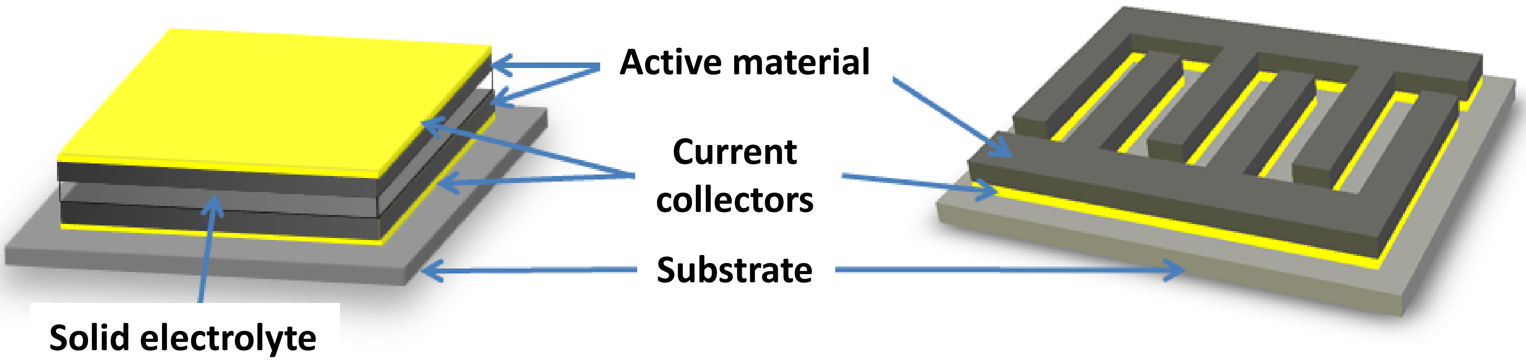
- ***Limited Lifetime***
  (→ restriction on the autonomy of the whole micro-system)
- ***Low power density***

→ **Energy storage in micro-supercapacitors**

An emerging and increasing field of research

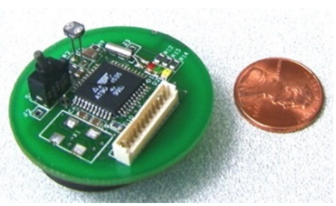


What is a micro-supercapacitor ?



Stack configuration ***Planar configuration***

Electrical energy storage micro-device → Limited surface area available in the electronic circuit



Performances normalized to its footprint area on the chip

~~F/g~~ ~~F/cm^3~~ → F/cm^2

M. Brunet, D. Pech, **Techniques de l'Ingénieur** vol. RE210 (2010).

Energy performances of thin-film micro-supercapacitors

Energy performances

Areal energy still far for self-powered applications…

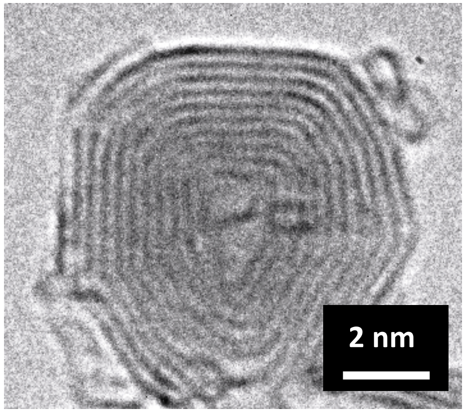
Typical capacitances ranging from µF to tens of mF/cm^2 :

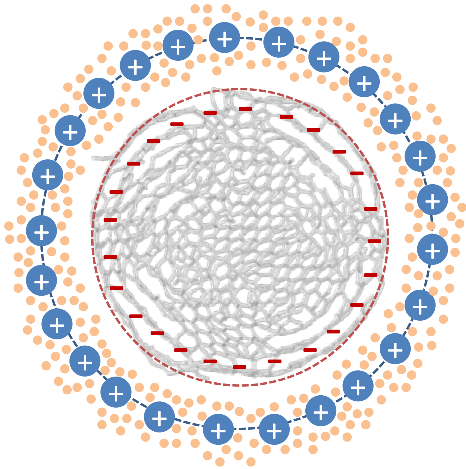
Orders of magnitude lower than the one of bulky electrodes !

Power performances
of thin-film micro-supercapacitors

OLC-based micro-supercapacitor

Onion-Like Carbon (OLC)



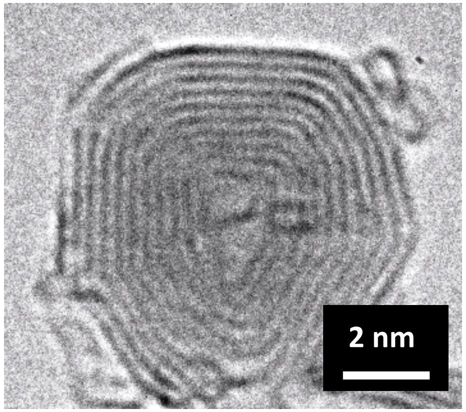


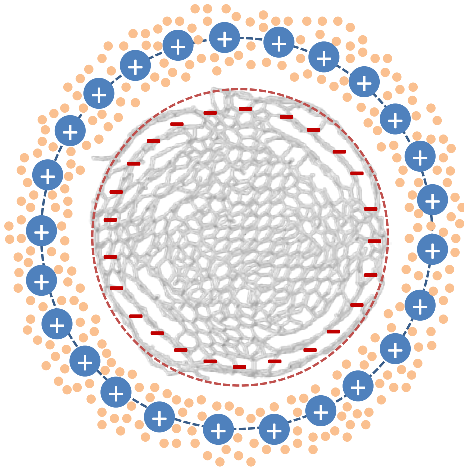
- From annealing of nanodiamonds at 1800°C under vacuum (Drexel University)
- Outer surface fully accessible to ions adsorption/desorption
- High surface area (520 m^2/g) – Good electronic conductivity (σ_e ~ 4 S/cm)

D. Pech *et al.*, **Nature Nanotechnology** vol. 5 p. 651 (2010).

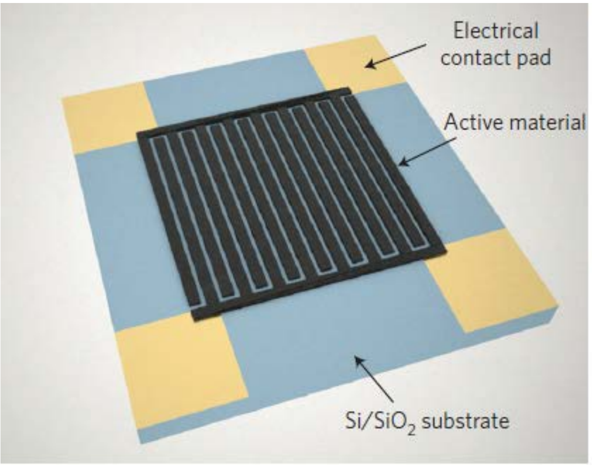
OLC-based micro-supercapacitor

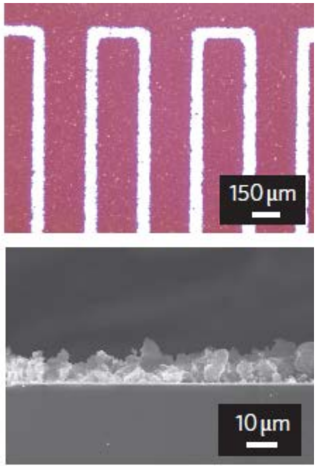
Onion-Like Carbon (OLC)





→ **Interdigitated micro-device using electrophoretic deposition**

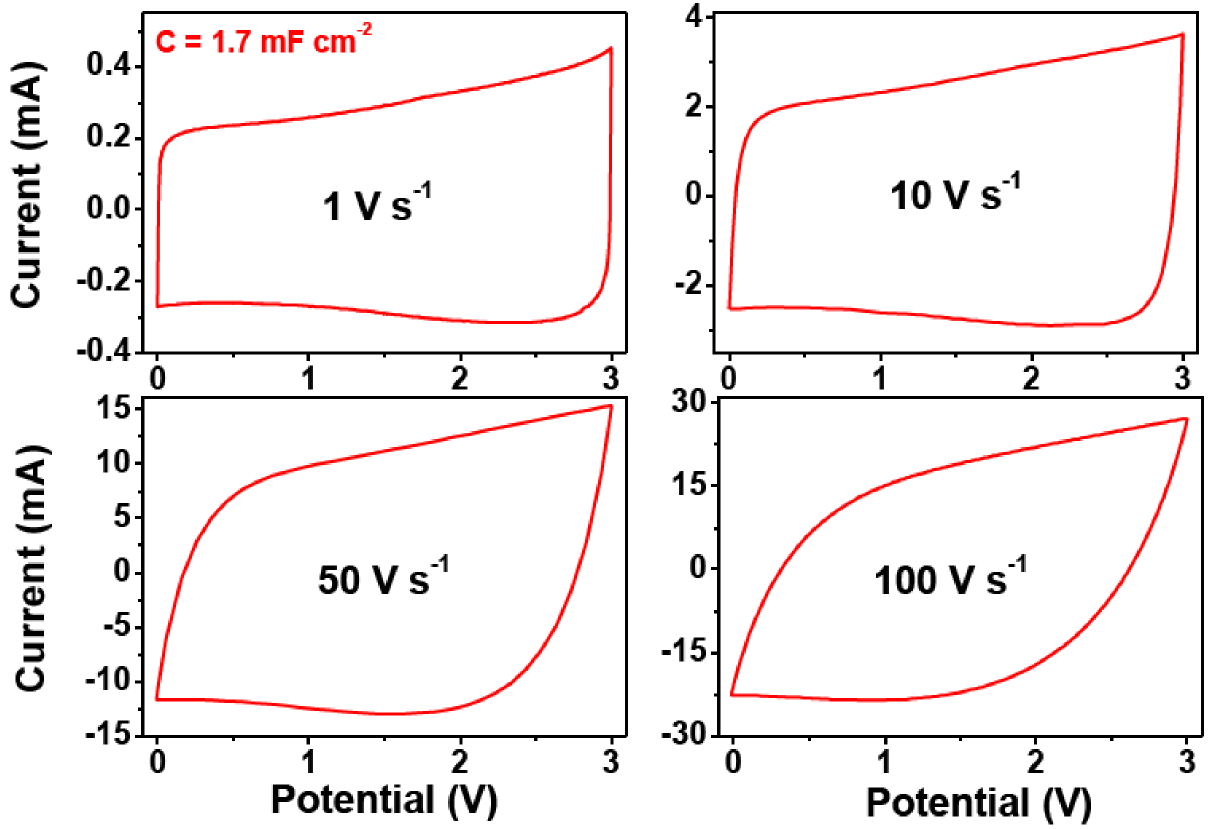




D. Pech *et al.*, **Nature Nanotechnology** vol. 5 p. 651 (2010).

… showing an ultrahigh power performance

(in 1M Et_4NBF_4 / propylene carbonate)

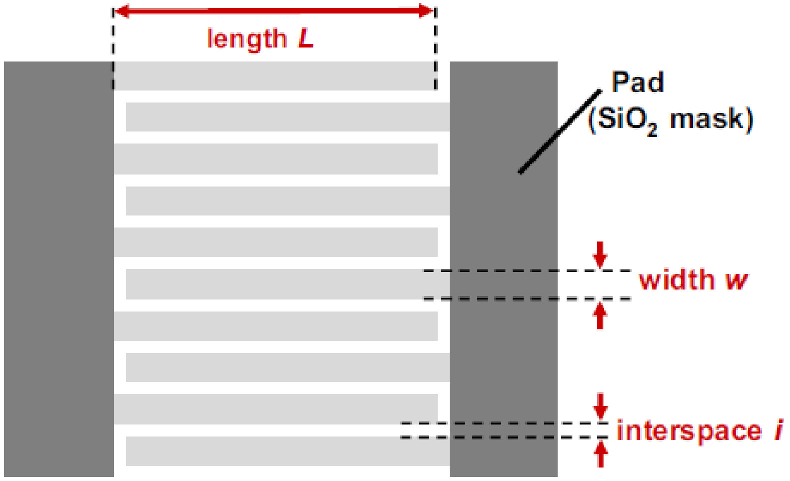


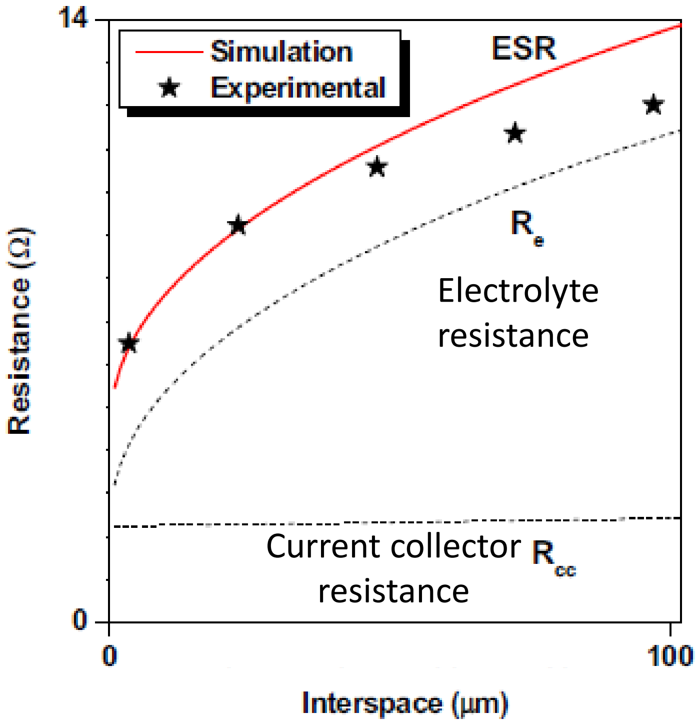
Capacitive behaviour @ ultrahigh voltage scan rate

D. Pech *et al.*, **Nature Nanotechnology** vol. 5 p. 651 (2010). (> 900 citations !)

Our first explanations…

- The use of innovative active material (OLC)
- The absence of organic binder using electrophoretic deposition
- Reduction of the interspace → low ESR (Equivalent Serie Resistance)



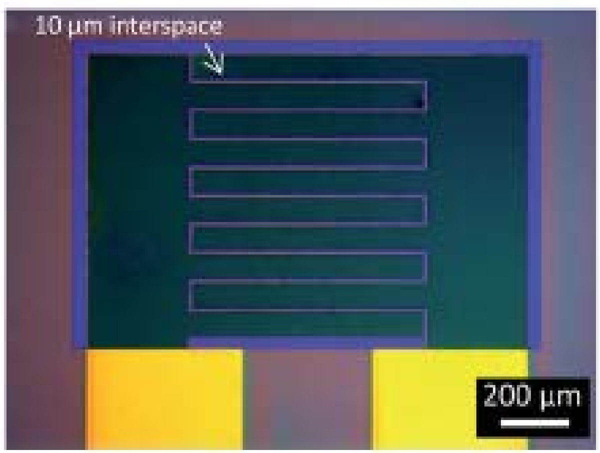


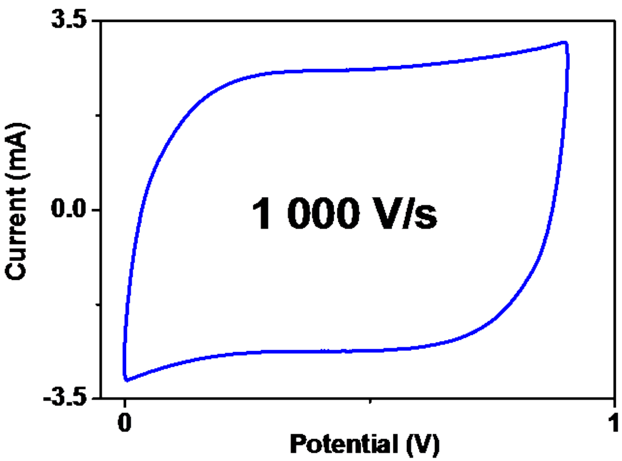
D. Pech *et al.*, **Journal of Power Sources** vol. 230 p. 230 (2013).

But similar behaviour obtained in numerous paper !

- with different active materials (OLC, graphene, Si nanowire, metal nitride…)
- with different geometrical configurations

Example : CNT-based micro-supercapacitor





High-power application : AC line-filtering in AC-DC converters

T.M. Dinh *et al.*, **Journal of Materials Chemistry A** vol. 2 p. 7170 (2014).

So why are they so powerful ????

ENERGY / POWER

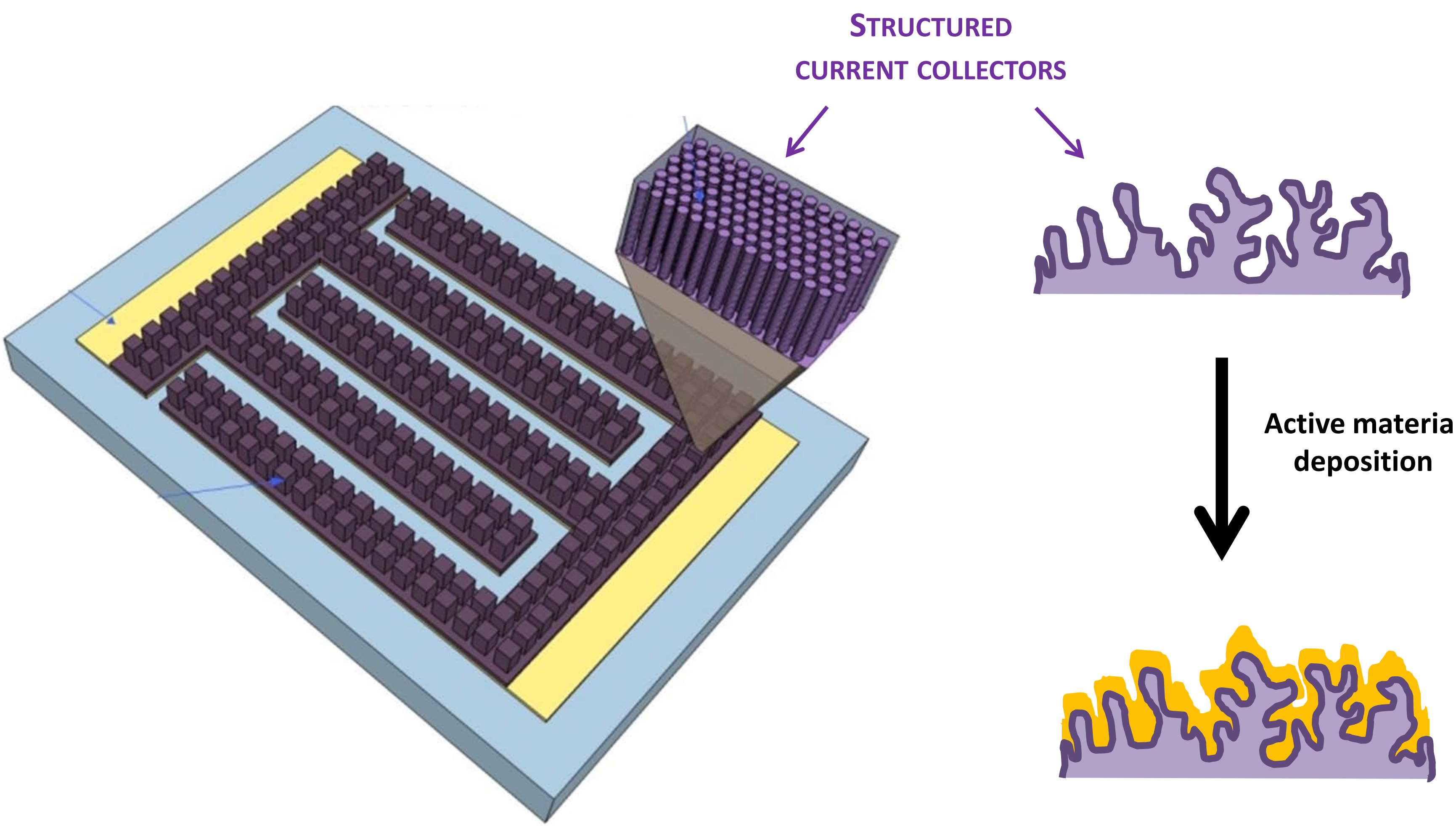
- Scan rate ability
- Phase angle close to -90° } depend on τ = **RC** time constant

Low C → Low τ → High Power

The high power characteristics of the state-of-the-art thin-film micro-supercapacitors are indicative of their poor energetic performances

How to increase the areal energy of micro-supercapacitors ?

Electrode structuration

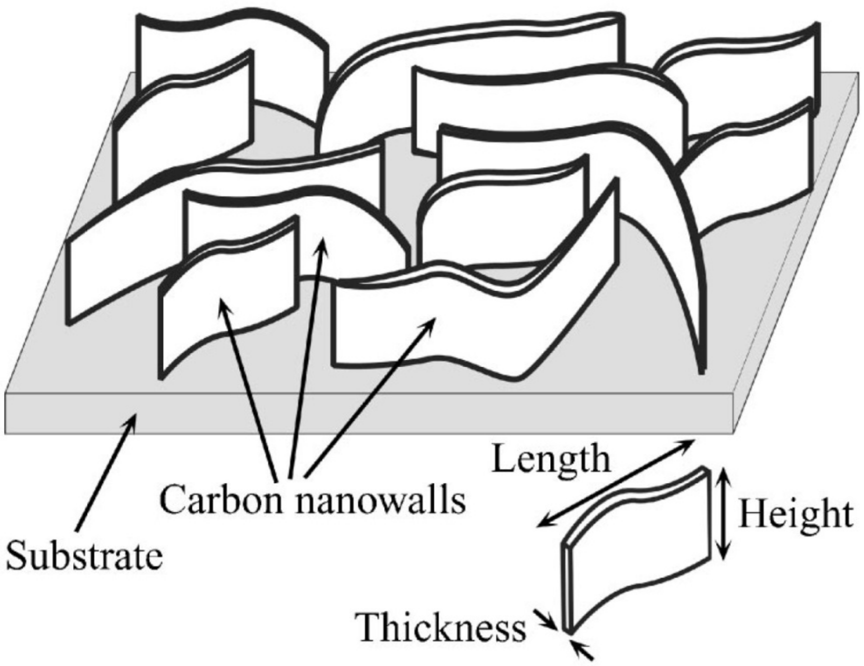


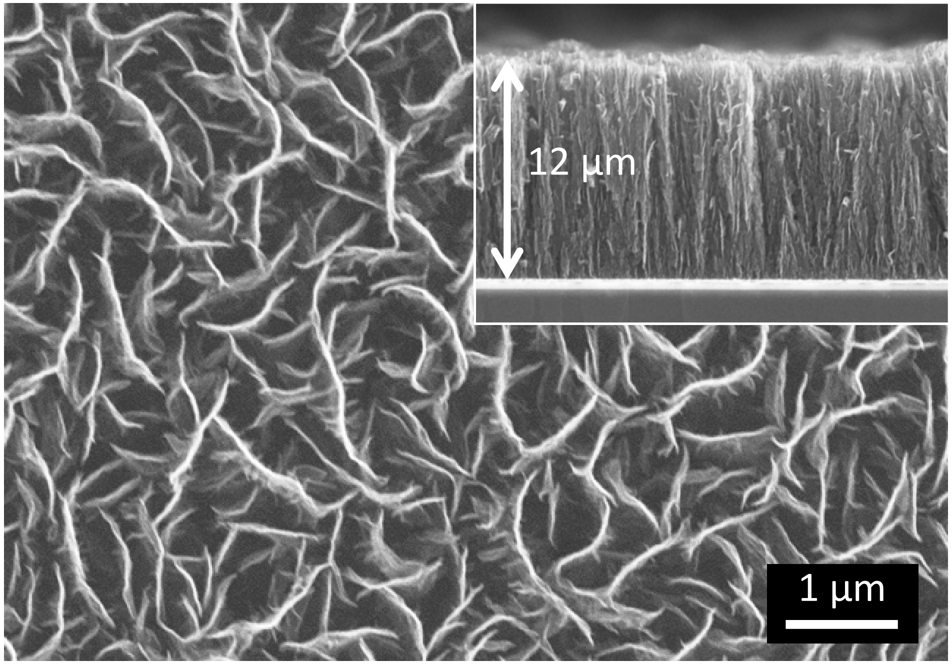
3D: a way to increase the quantity of active material per surface area

Deposition of RuO_2 on Carbon Nanowalls

Carbon Nanowalls : a nanostructured material

Vertically oriented graphene sheets





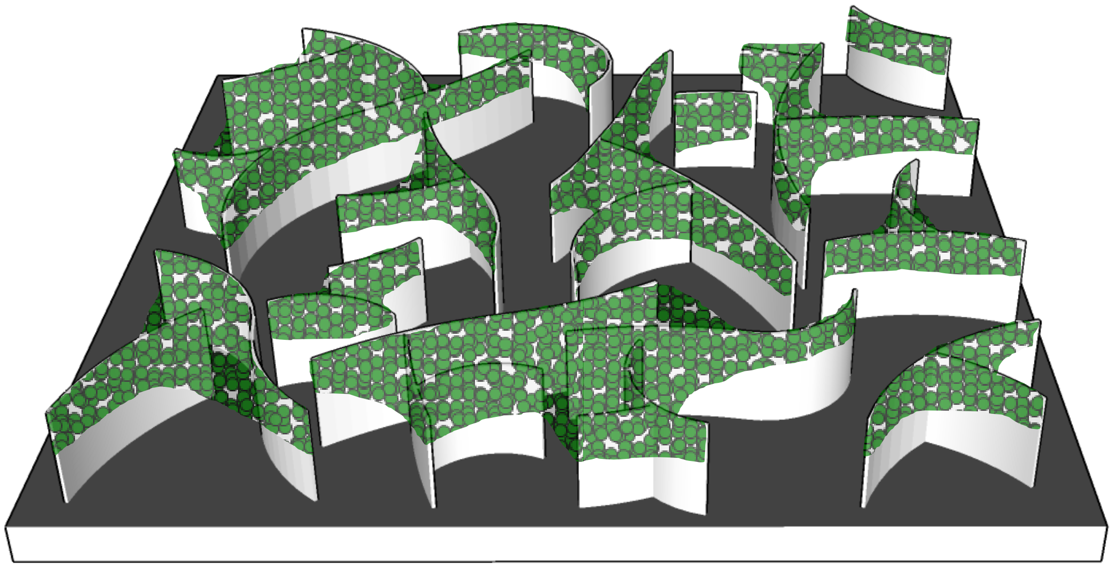
Collaboration with INFLPR (Romania)

with interesting properties

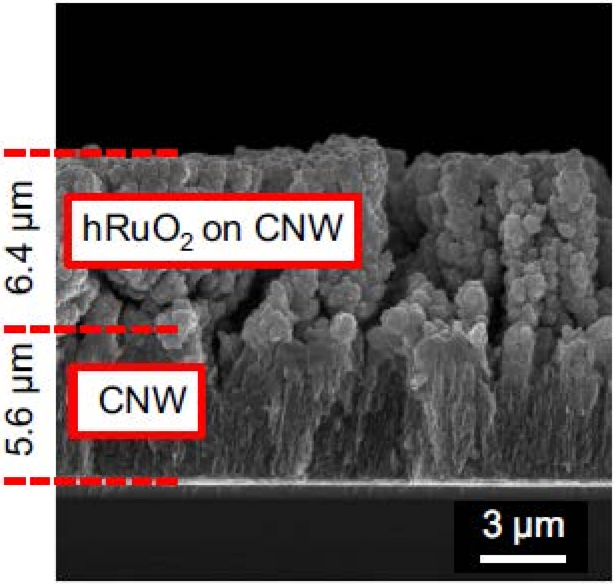
- Large surface area (100 – 1500 m^2/g)
- Good electronic conductivity (40 – 60 S/cm)
- Excellent chemical stability
- Very good mechanical strength / High flexibility

RuO_2 electrodeposition

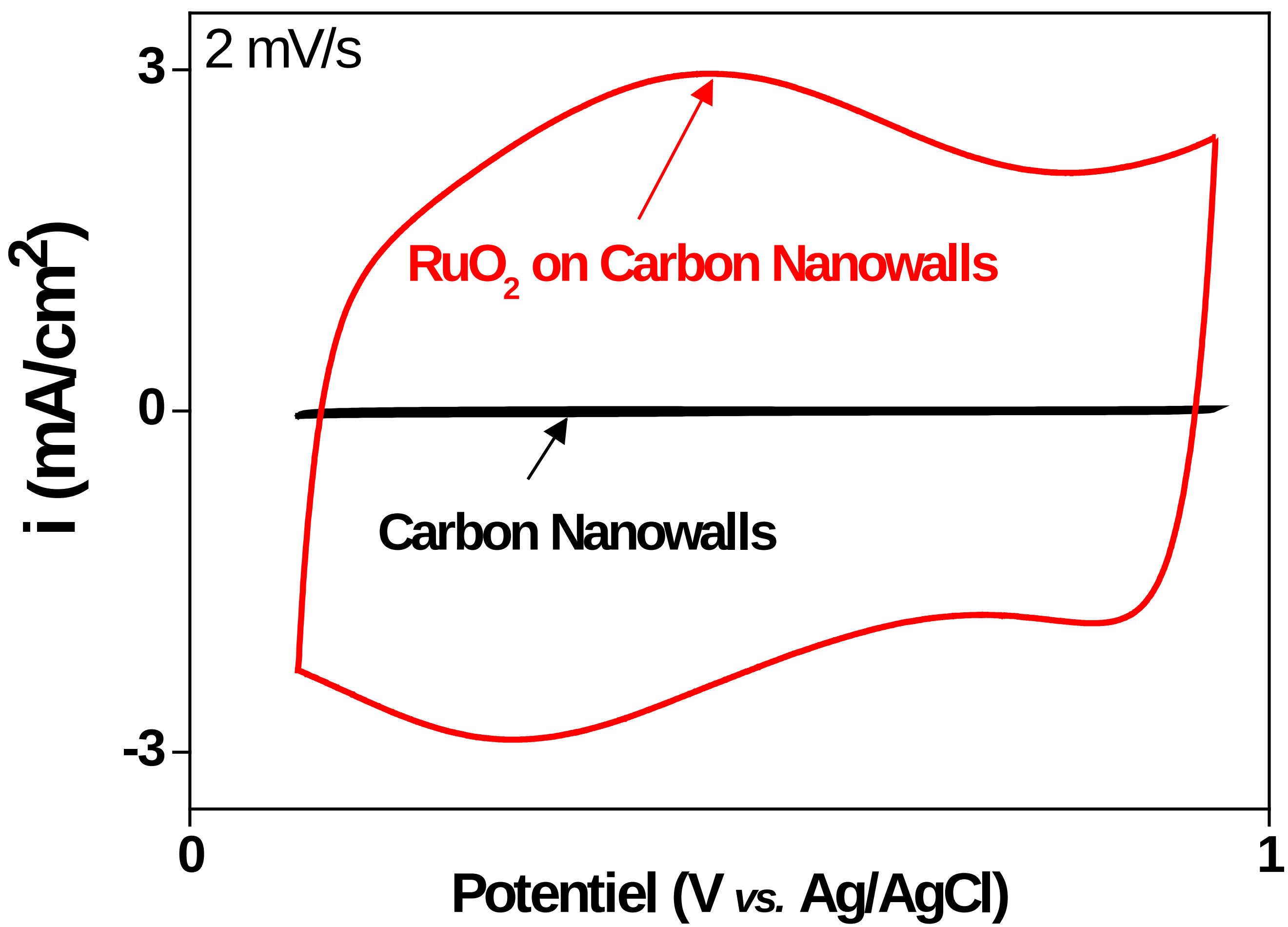
RuO_2/carbon nanowalls:
thick, in-depth coverage and porous.



● $hRuO_2$ particles

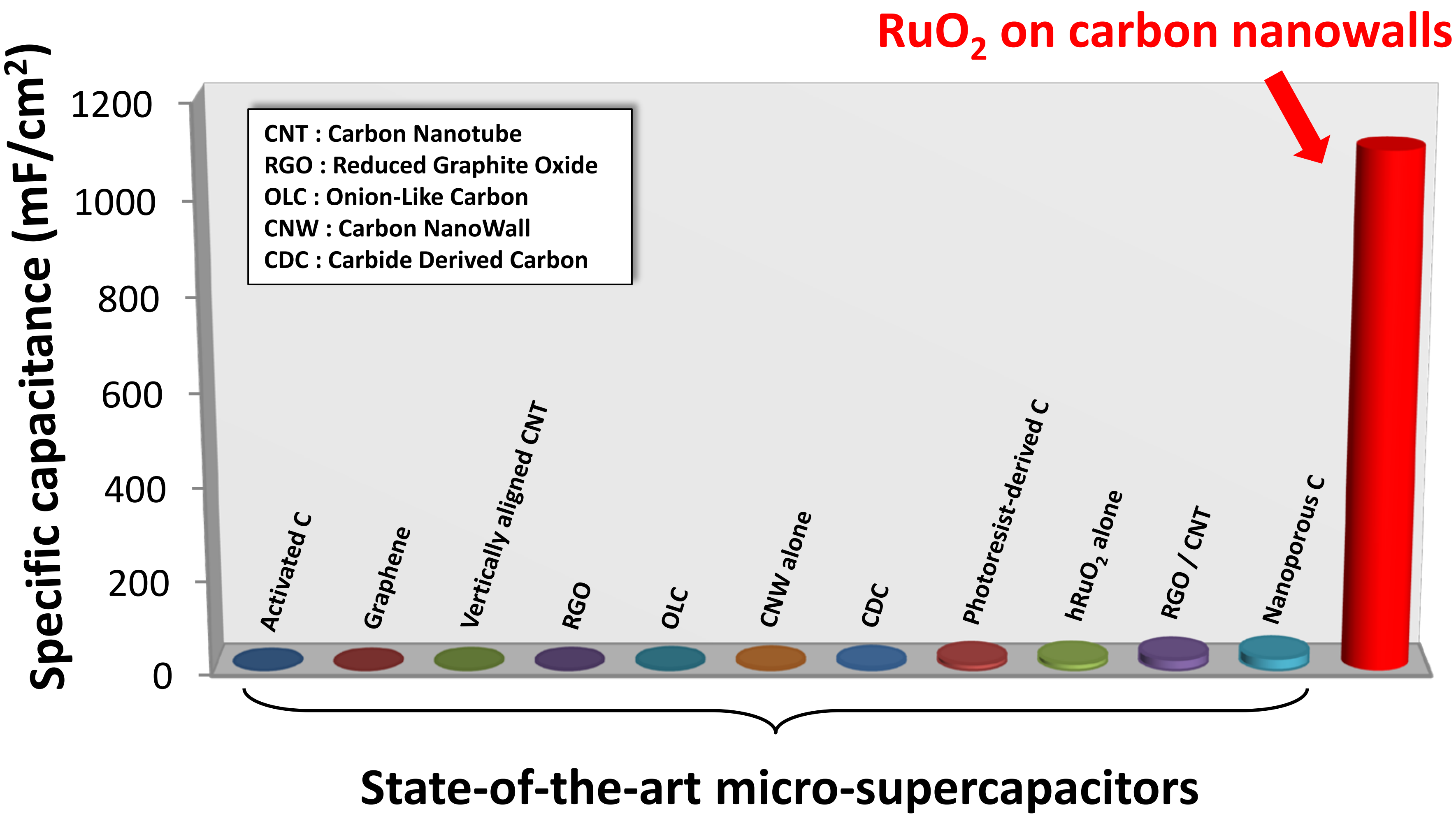


Characterization of the electrode



→ **Great increase of capacitance**

Highest value reported



T.M. Dinh *et al.*, **Nano Energy** vol. 10 p. 288 (2014).

Deposition of RuO_2 on Porous Gold

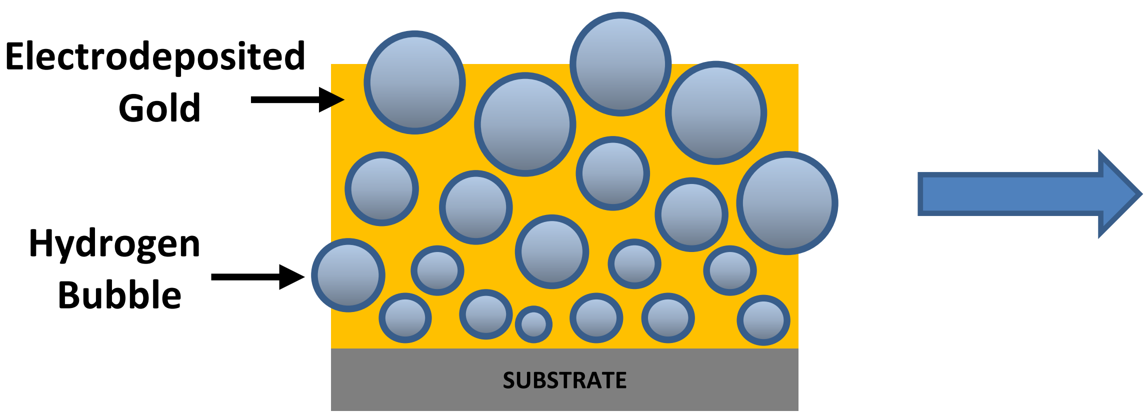
Hydrogen bubble dynamic template

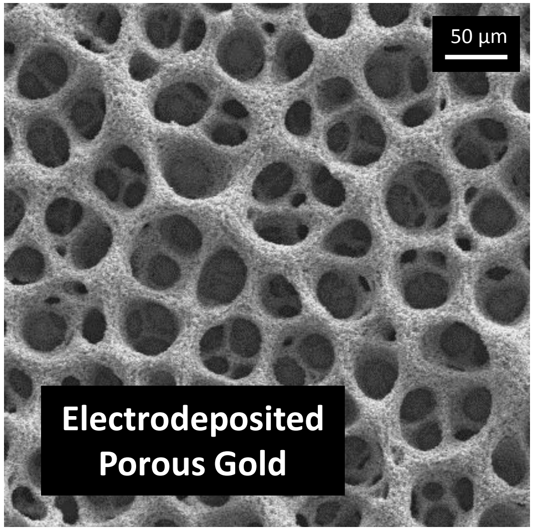
<u>Cathodic overpotential</u> (from -1.5 to -3.5 V vs. ECS):

$$Au^{3+} + 3e^{-} \rightarrow Au \quad \textbf{AND} \quad 2H^{+} + 2e^{-} \rightarrow \frac{1}{2} H_2$$

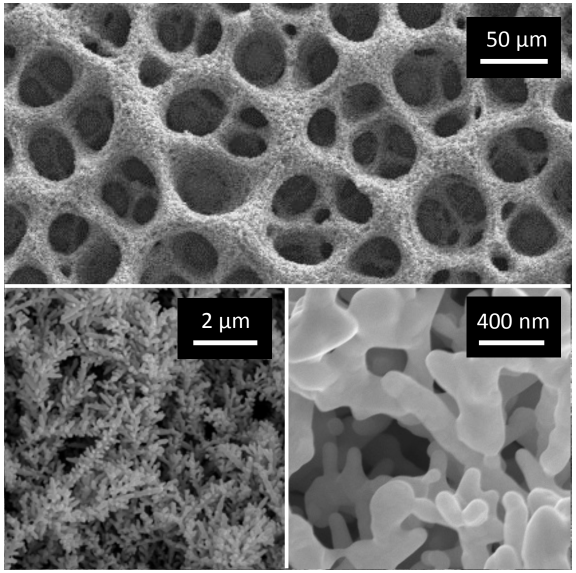
Simultaneous reactions

$HAuCl_4.3H_20$ in H_2SO_4



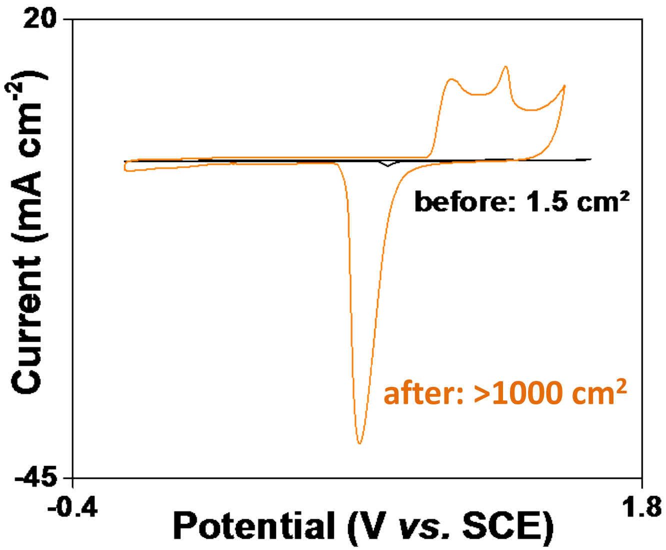


Different levels of pores



Honeycomb network

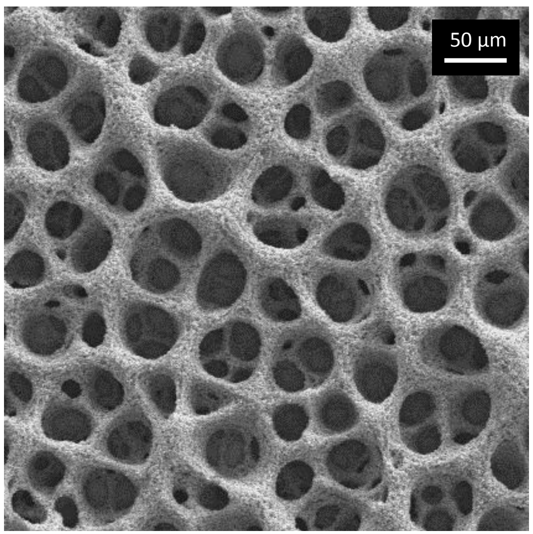
- Open porosity (20-40 µm)
- Dendrites (50-200 nm)
- Thickness = 80 - 100 µm



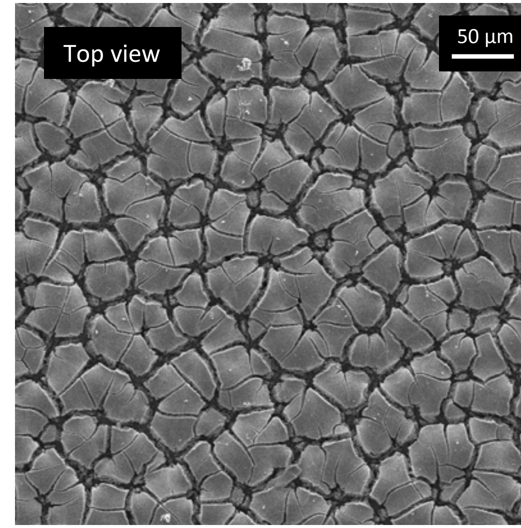
Extended surface area of Au with respect to the geometrical surface area.

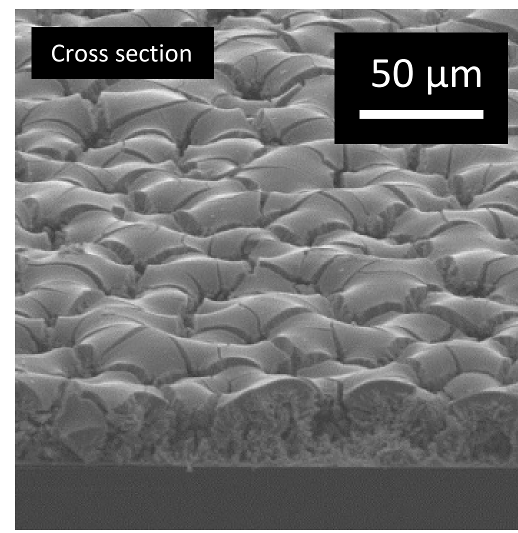
and we deposit the RuO_2…

Porous Gold substrate

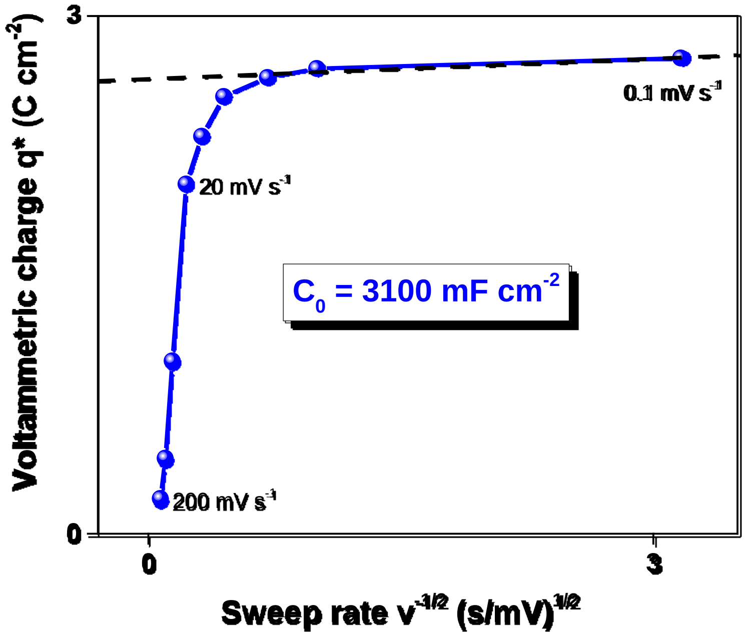


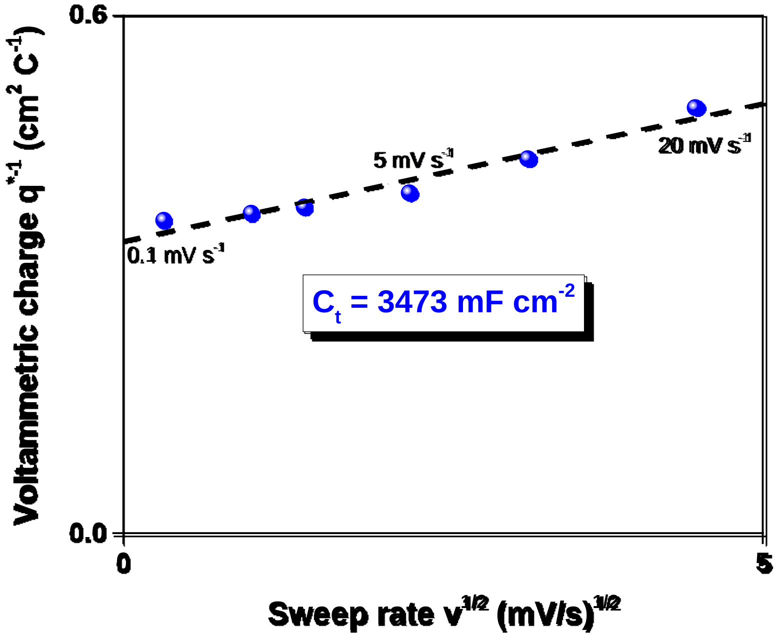
hRuO_2 electrodeposition

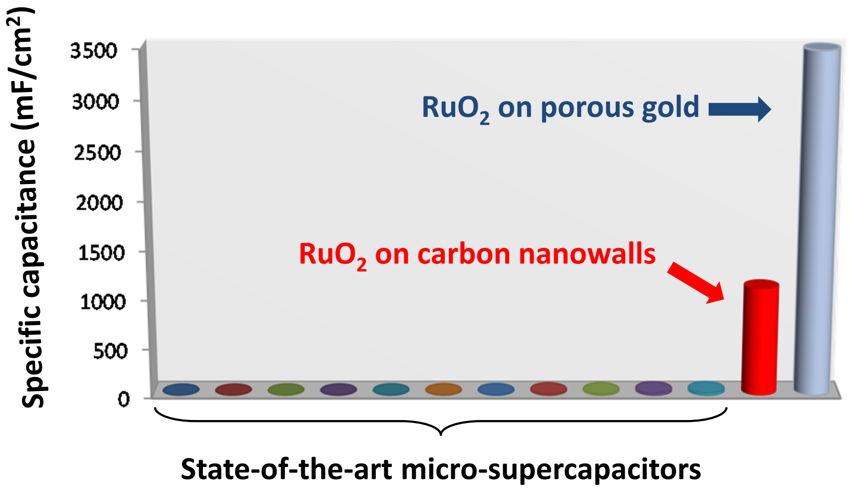




How much capacitance ?



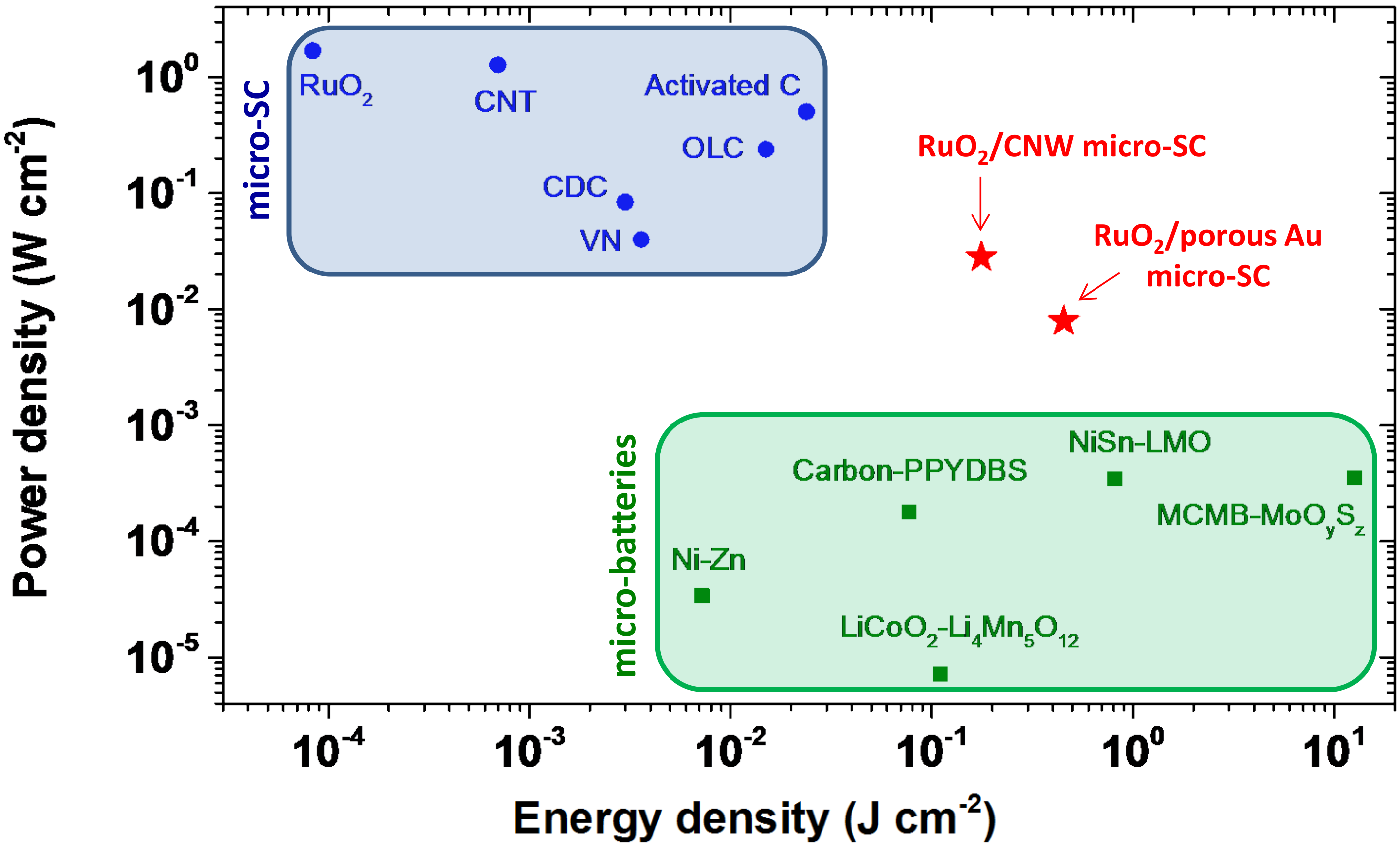




A. Ferris *et al.*, **Advanced Materials** vol. 27 p. 6625 (2015).

3D micro-supercapacitor performances

(All-solid-state)



Conclusions

- **Per-area performance critical**
- **Absence of standardized approaches**
- **Areal energy still far for self-powered applications**
- **Importance to always specify the power metrics with the time constant τ and the capacitance value C**
- **Need of a 3D paradigm shift for high-performance micro-supercapacitors**

LAAS

INRS
Université d'avant-garde

INSTITUT CARNOT
CIRIMAT


Ty Mai DINH


Anaïs FERRIS


Daniel GUAY


Sébastien GARBARINO


Patrice SIMON


Pierre-Louis TABERNA

Drexel
UNIVERSITY

INFLPR


Yury GOGOTSI


Vadym MOCHALIN


Sorin Vizireanu


Gheorge Dinescu


Leona C. Nistor

Questions ?