Vertically-Aligned Carbon Nanotubes for Supercapacitor and the Effect of Surface Functionalization to its Performance

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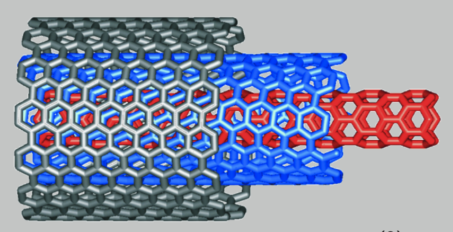
Background and introduction

- **Supercapacitors**
  They offer very promising alternatives compared to batteries and fuel cell to store and deliver energy.

Advantages	Disadvantages	Current applications
High power density (= how fast the energy can be supplied)	Lower energy density (= how long the energy can be supplied)	Hybrid Electric Vehicles (HEVs)
Longer cycle life (millions of cycles) = 2 to 3 times higher than conventional Li-ion batteries	Higher self-discharge rate	Diesel engine starting systems
Low toxicity materials	Lower cell voltage	Cordless power tools
Operation over a wide temperature range	Poor voltage regulation	Emergency and safety systems
Low cost per cycle	High initial cost	

- **Vertically-aligned carbon nanotubes**
  VANT are concentric tubes of graphite with nanometer-scale diameter
  - High surface area
  - High electronic conductivity
  - Relatively low costs, expected to decrease in the years to come
  - Usefulness of carbon-nanotubes for supercapacitors proven

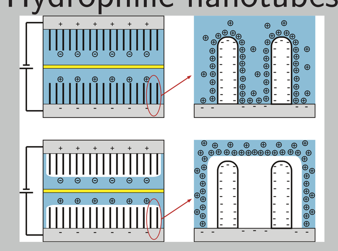


Balasubramanian, Small 2005 (2)
Multi-walled carbon nanotubes: around 20nm in diameter

Supercapacitors and energy storge

Electrochemical double layer phenomena: energy stored electrostatically.
To achieve higher gravimetric specific capacitance (storage capability):

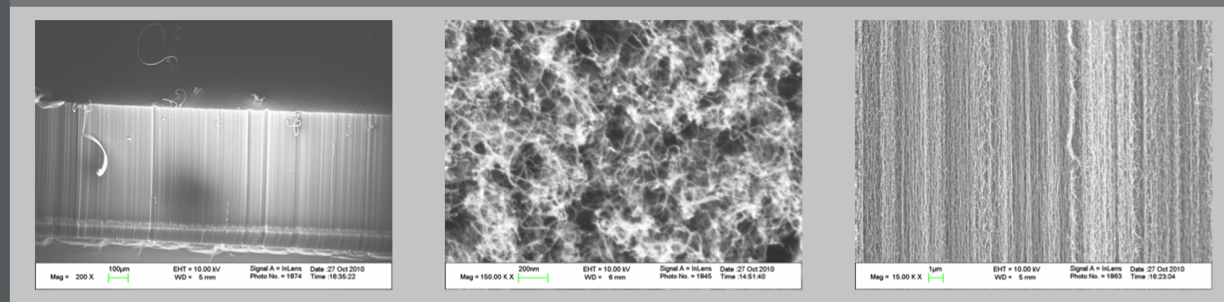
- **Electrodes**: larger surface area, lower resistance, lower density
- **Electrolyte**: higher dielectric constant, larger voltage window
- **Interface electrode - electrolyte**: better wetting



Material and methods

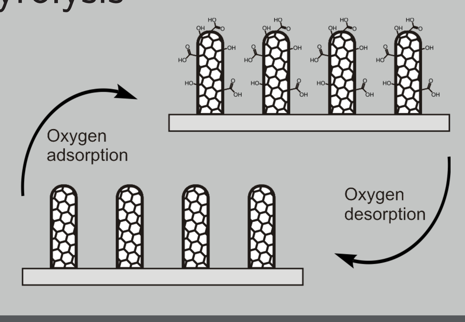
- Growth by thermal chemical vapor deposition: length comprised between 700 and 1000 μm
- Anchoring on copper tape (current collector)
- Electrochemical characterization: Cyclic voltammetry and Electrochemical impedance spectroscopy
- Lifetime assessment: Charge-discharge tests
- Imaging: Scanning Electron Microscopy
- Element characterization: Energy-dispersive X-ray spectroscopy

Vertically-aligned carbon nanotubes arrays



Densely-packed carbon nanotubes in vertical standing configuration
- Diameter: around 20nm
- Length: 700-1000 μm
- Density: 10^3 kg/m^3

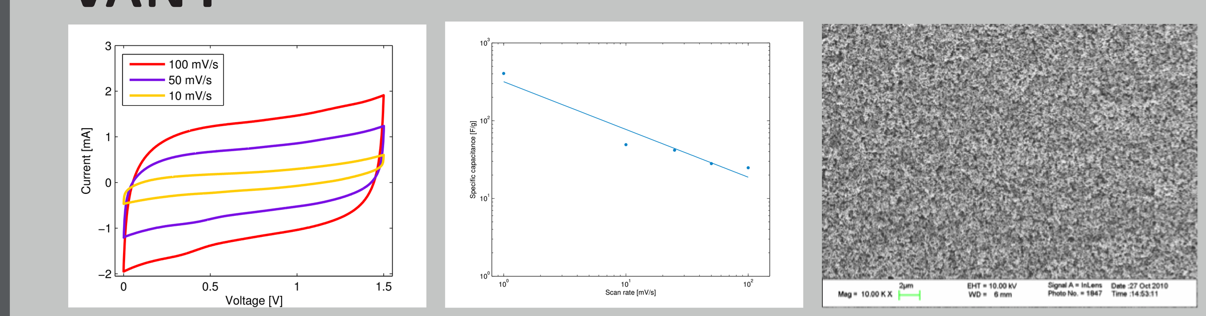
Functionalization using thermo-reduction process
- Oxygen adsorption: UV-ozone → allow site specific, quick and easy to use
- Oxygen desorption: vacuum pyrolysis



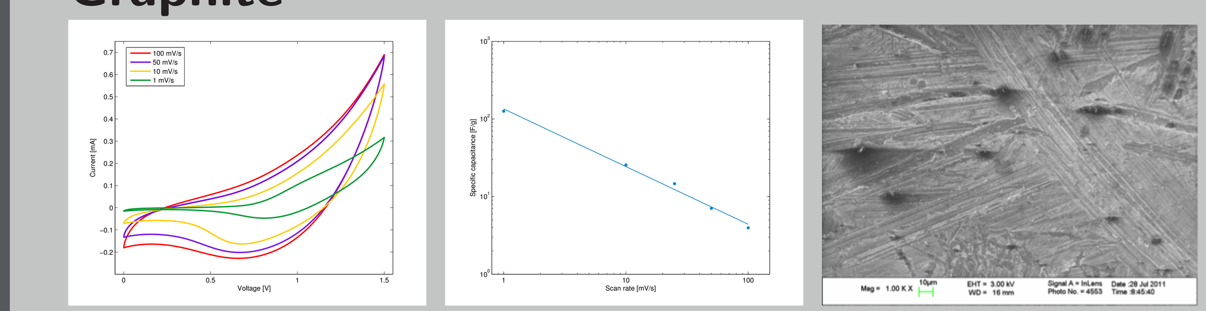
Comparison of VANT and graphite

- **VANT**: rectangular, featureless and symmetric over a large range of scan rates
- **Graphite**: narrow loops, oblique angle at 0.8V, elbow typical of a resistive electrode → cannot be used for the chosen voltage window 0-1.5V
- Specific capacitance in function of scan rate follows a power law : $\mathbf{SC} \simeq \alpha \frac{\mathbf{dV}}{\mathbf{dt}}^{\beta}$
  - graphite-based electrode: α = 130 and β = -3/4
  - VANT-based electrode: α = 310 and β = -3/5

VANT



Graphite

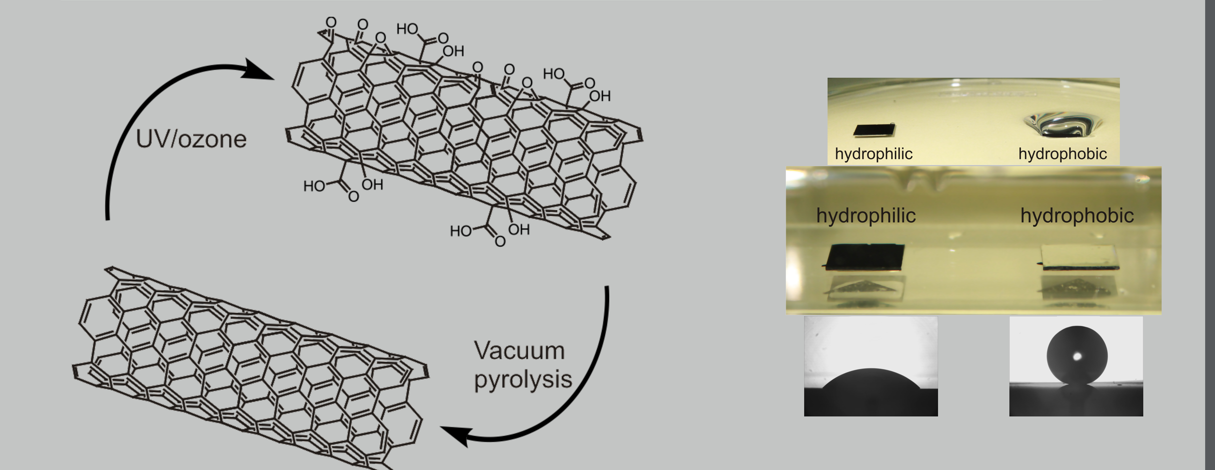


VANT
- Electrodes made of VANT, in a solution of 1M Et_4NBF_4-PC for different scan rates
- Log-log plot of relationship between the specific capacitance and the scan rate
- SEM image

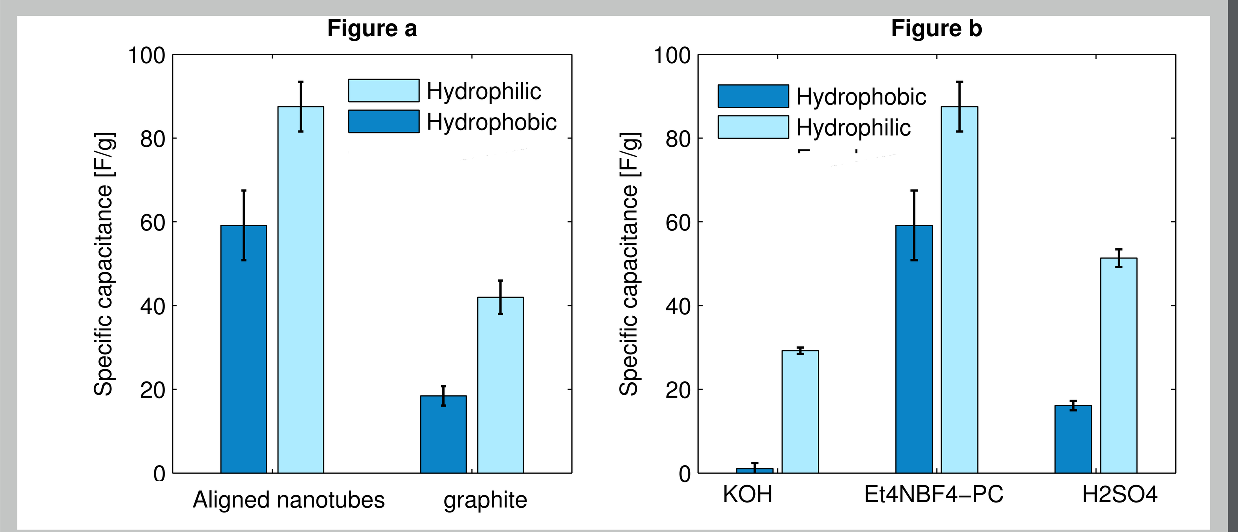
Graphite
- Electrodes made of graphite, in a solution of 1M Et_4NBF_4-PC. The shape is nearly independent of the scan rates when the scan rate is >25mV/s.
- Log-log plot of the relationship between the specific capacitance and the scan rate
- SEM image

Functionalization and electrolytes

		Polar protic		Polar aprotic
		1M H_2SO_4	6M KOH	1M Et_4NBF_4
Specific capacitance [F/g]	Hydrophobic	16	1	59
	Hydrophilic	51	29	89

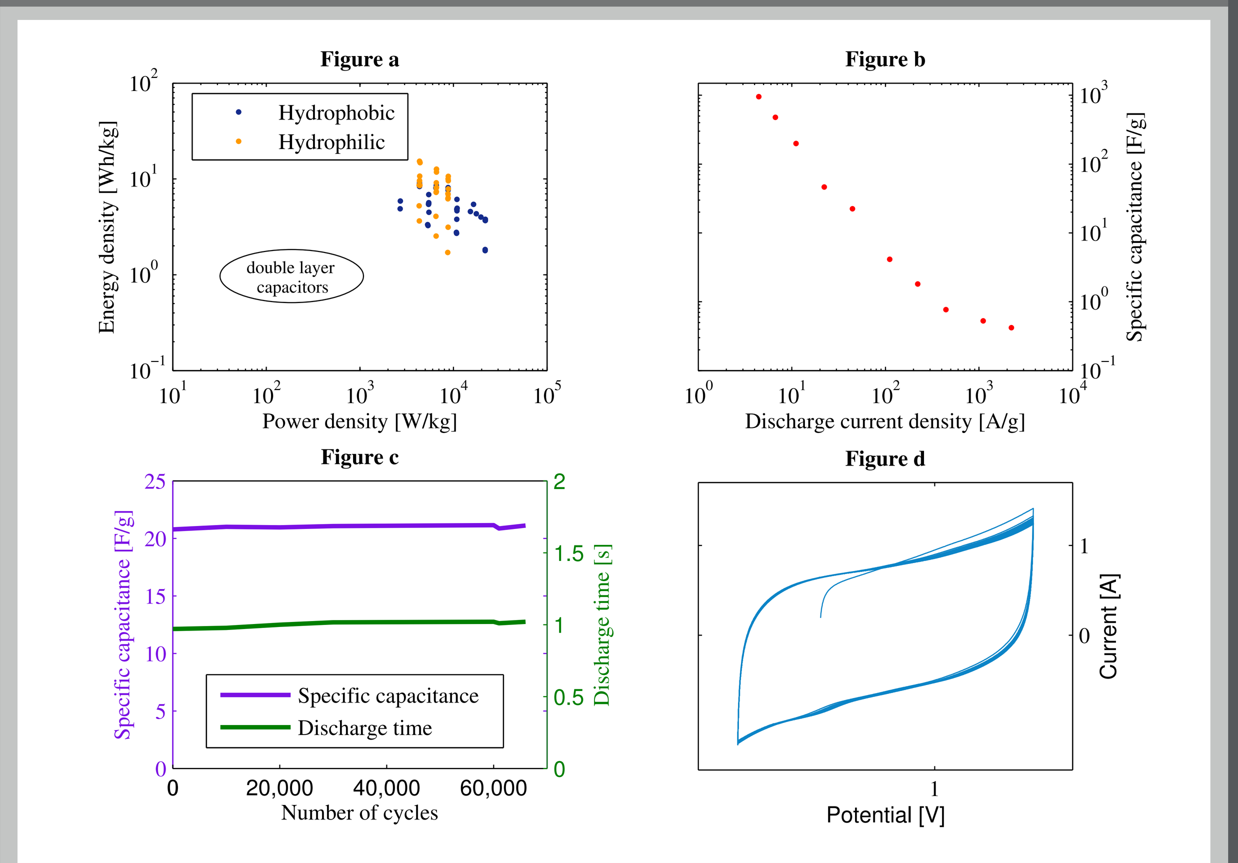


UV/ozone and vacuum pyrolysis treatments are used to vary the wetting properties of MWNT arrays. Oxygen adsorption occurs during UV/ozone treatment and oxygen desorption take places during vacuum pyrolysis treatment. (1)



Surface functionalization (a) Specific capacitance of the VANT array electrodes in 1M Et_4NBF_4-PC is higher by a factor 2 to 3 than that of the graphite, in both cases of hydrophilic and hydrophobic, at 25 mV/s. (b) Specific capacitance of the vertically-aligned CNT array electrodes in both aqueous (6M KOH-1M H_2SO_4) and non-aqueous (1M Et_4NBF_4-PC) solution, measured at 25 mV/s. Surface functionalization allows an increase of 60% to 150%.

Energy density, power density and lifetime



Electrochemical performance. (a) Ragone plot

Hydrophilic electrode	Hydrophobic electrode
Max E_D = 21 Wh/kg at P_D = 1.1 Wh/kg	Max P_D = 22 kW/kg at E_D = 2 Wh/kg

(b) Specific capacitance vs current density. Maximum specific capacitance: ~1 kF/g at a discharge current density of 4 A/g. Power law for I_D <10^3 A/g
(c) Specific capacitance in function of cycles, in Et_4NBF_4-PC. >130,000 cycles, 100mV/s
(d) No loss in storage capability nor degradation of the electrode. Voltammogram after 130,000 cycles

Conclusion

- Performance 3 times higher than graphite electrodes
- Increase in specific capacitance with hydrophilization and good choice of electrolyte
- Cheap system: every part of the system is non-expensive (copper, carbon nanotubes, propylene filter...) → commercially-attractive
- Non Lithium-based:
  - Lithium causes great damage to endangered ecosystems (3)
  - Li production could only sustain portable electronics, not also transportation → need to find alternatives for hybrid cars
  - Li is reactive and dangerous
- Entirely carbon-based electrodes
- Small ecological print compared to Li-based batteries
- More stable than Li-based batteries
- Long lifetime: >130,000 cycles achieved

References

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2. K. Balasubramanian and M. Burghard, "Chemically Functionalized Carbon Nanotubes", SMALL 2005, 1, (2), p. 180 192
3. Meridian International Research, Report: The trouble with lithium2

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